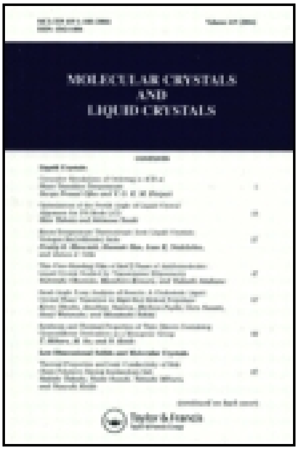

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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The Synthesis and Mesomorphic Properties of 4-Methyl-Pentyloxyphenylthio-4′-Substituted Benzoatest

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Version of record first published: 24 Sep 2006.

To cite this article: M. E. Neubert & I. G. Shenouda (1991): The Synthesis and Mesomorphic Properties of 4-Methyl-Pentyloxyphenylthio-4′-Substituted Benzoatest, Molecular Crystals and Liquid Crystals, 205:1, 29-45

To link to this article: http://dx.doi.org/10.1080/00268949108032076

Mol. Cryst. Liq. Cryst., 1991, Vol. 205, pp. 29–45
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Printed in the United States of America

The Synthesis and Mesomorphic Properties of 4-Methyl-Pentyloxyphenylthio-4′-Substituted Benzoates†

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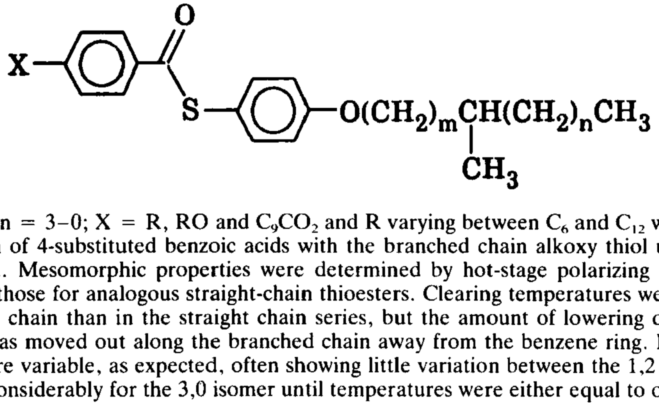
(Received August 14, 1990; in final form March 8, 1991)

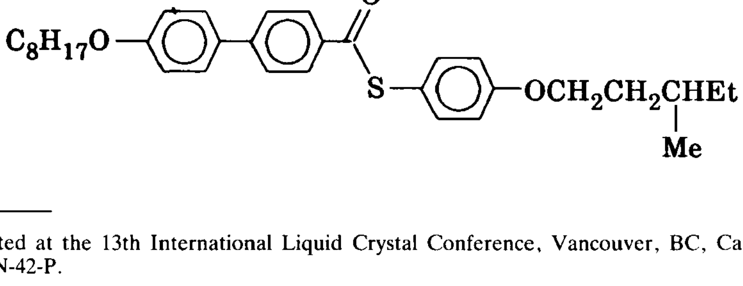
Three different series of branched chain alkoxy thioesters of the type



with m = 0–3, n = 3–0; X = R, RO and C_9CO_2 and R varying between C_6 and C_{12} were synthesized by esterification of 4-substituted benzoic acids with the branched chain alkoxy thiol using the carbodiimide method. Mesomorphic properties were determined by hot-stage polarizing microscopy and compared with those for analogous straight-chain thioesters. Clearing temperatures were always lower in the branched chain than in the straight chain series, but the amount of lowering decreased as the methyl group was moved out along the branched chain away from the benzene ring. Melting temperatures were more variable, as expected, often showing little variation between the 1,2 and 2,1 isomers but increasing considerably for the 3,0 isomer until temperatures were either equal to or slightly higher than those in the straight-chain compounds.

The smectic C phase was enhanced usually at the expense of the nematic phase. Nematic-smectic C combinations predominated with the smectic A phase occurring as a short phase range only in the RO–2,1 and X = R series. The most mesophases were usually observed in the 2,1 series; moving the methyl group further out along the chain tended to give restoration of the nematic phase as the predominant phase.

The biphenyl thioester



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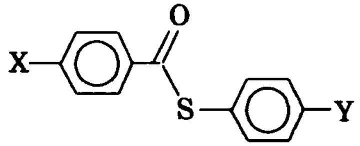
† Presented at the 13th International Liquid Crystal Conference, Vancouver, BC, Canada, July, 1990, #SYN-42-P.

was also synthesized and showed an enantiotropic sequence of S_C, S_A and N phases with a monotropic smectic G phase which supercooled considerably. Transition temperatures were all >100°.

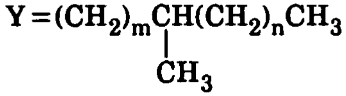
The thiols with $m > 0$ were prepared by alkylation of sodium 4-hydroxybenzene-sulfonate with the branched chain bromide, conversion to the sulfonyl chloride and reduction to the thiol. When $m = 0$, synthesis was by alkylation of 4-bromophenol with the branched chain bromide, treatment with cuprous thiobutane and cleavage of the butyl group with $NaNH_2$.

INTRODUCTION

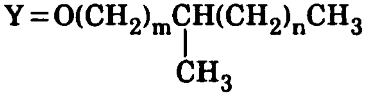
Our earlier studies of the effect of replacing a straight chain (SC) on the thiol end of the thioesters *1*



1 $X=RO$ $Y=C_5H_{11}$

2 $X=RO$

$Y=(CH_2)_m\underset{CH_3}{CH}(CH_2)_nCH_3$

3 $X=RO$ $Y=OR'$

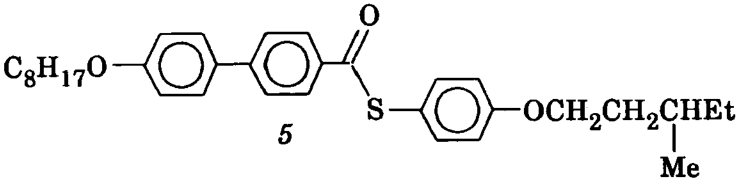
4a $X=RO$

$Y=O(CH_2)_m\underset{CH_3}{CH}(CH_2)_nCH_3$

b $X=R$

c $X=C_9CO_2$

with a methyl branched chain *2* indicated that a lowering of transition temperatures and an enhancement of the smectic C phase usually occurs.[1] Although the RO–R′ thioesters *1* have better mesomorphic properties than the corresponding esters (central group = COO) having more mesophases with wider ranges,[2] the SC dialkoxythioesters *3* show fewer mesophases with a nematic-smectic C combination predominating.[3] Clearing temperatures were higher in the dialkoxy thioesters, as is true with the esters. By combining the branched chain (BC) with an alkoxy group, both of which seem to enhance the smectic C phase but which have opposite effects on the clearing temperatures, it seemed that wider range smectic C phases would be observed in the BC dialkoxy thioesters *4a*. If this were true, then these thioesters might be useful as ferroelectric liquid crystal (FLC) display materials if one of the optical isomers were prepared.

Thus, we synthesized a few of the BC thioesters *4a* along with some thioesters with X = R, *4b*, and C_9CO_2, *4c*, to test the generality of the trends observed. The biphenyl thioester *5*

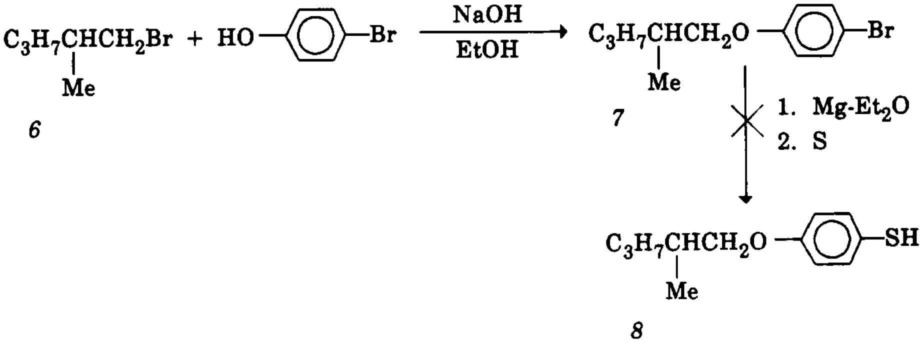


5

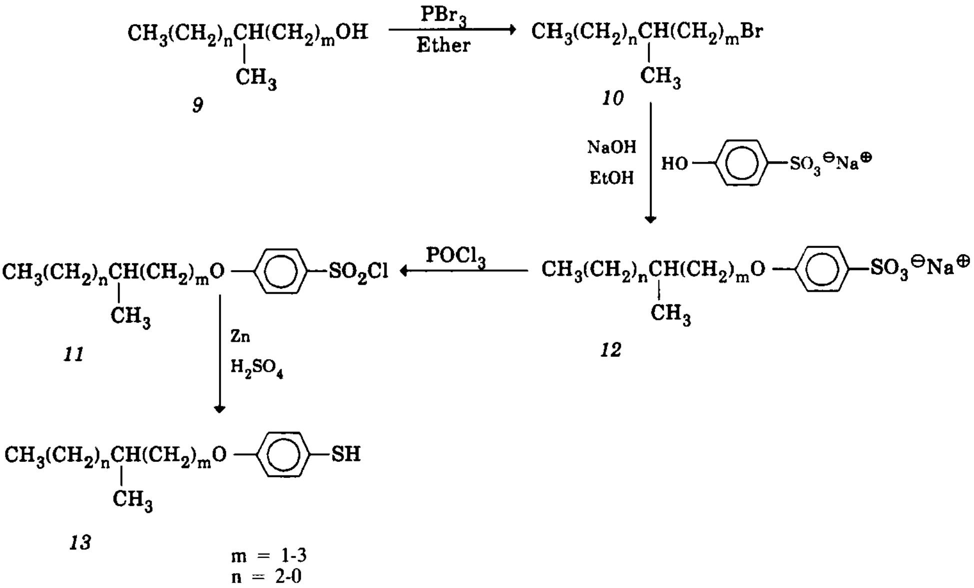
was also prepared to determine if it would have any interesting mesomorphic properties.

SYNTHESIS

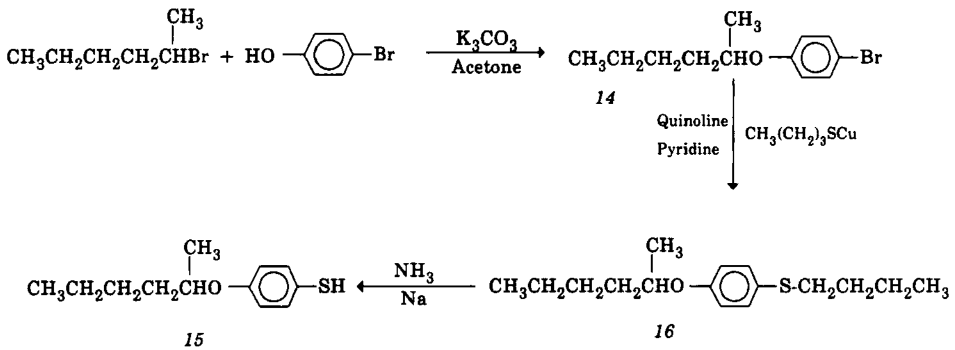
Several methods were investigated for the synthesis of the BC alkoxy thiols. In an attempt to prepare the 2-methyl BC thiol *8* using a Grignard reaction similar to that reported for the synthesis of methyl 2-thienyl sulfide (Scheme I).[4] However,



SCHEME I



SCHEME II



SCHEME III

in our hands,‡ no reaction occurred as indicated by the recovery of the starting bromide *7*. This thiol, along with the other two with m > 2, *13*, were successfully prepared using the procedure shown in Scheme II. This method was not used to prepare the thiol with m = 0 since decomposition of the sulfonyl chloride *11* (m = 0) occurred during distillation. Instead, this thiol *15* was synthesized using the reactions shown in Scheme III; a method developed earlier for the synthesis of 1,2-dimercaptobenzene.[6,7]

The thioesters *4* and *5* were prepared by esterification of the thiols with the appropriate acids using the carbodiimide method.[2] Details are provided in the experimental section which includes typical examples for synthesis of the intermediates. Structures were confirmed by IR and NMR.

MESOMORPHIC PROPERTIES

Transition temperatures for the phenylthiobenzoates *4* prepared were determined by hot-stage polarizing microscopy and are given in Table I. Abbreviations are defined in the experimental section. The effect of the location of the methyl group in the BC alkoxy group on the melting and clearing temperatures is illustrated in Figure 1. In all three X series, there are only small differences in the melting temperatures for the 1,2 and 2,1 series. This is also true for the 0,3 series when X = C_9CO_2 but not for the other two series. Interestingly, this temperature is higher when X = C_{10} than OC_{10} for the 0,3 series. Melting temperatures for all three series increase considerably when the methyl group is moved to the third carbon atom (3,0 series). Clearing temperatures gradually increase as the methyl group is moved out along the chain away from the benzene ring with the greatest increase occurring between the 0,3 and 1,2 series. Interestingly, the X = $C_{10}O$ series has higher clearing temperatures than when X = C_9CO_2 but lower melting temperatures.

A comparison of the types of mesophases observed in the BC thioesters with the SC series to which X = C_8O is given in Figure 2. Melting temperatures for

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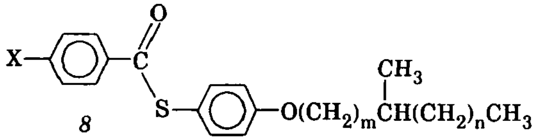
‡ The synthesis of 4-fluorinated alkoxy chain benzene thiols using this method has been reported.[5]

TABLE I

Transition temperatures (°C) for



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X	m	n	C[a]	S	S_C	S_A	N	I
C_8O	0	3	14.3	- - -	(25.0)	- - -	34.5	34.9
C_9O			15.9	- - -	(26.6)	- - -	(32.0)	40.5-40.9
$C_{10}O$			8.9-9.4	- - -	28.1-28.4	29.4-29.7	30.6-31.0	33.6-34.6
$C_{12}O$			16.0	- - -	36.6	38.5	- - -	41.1-41.3
C_{10}			-12.2	- - -	- - -	(-2.8)	(-1.9)	38.6-38.8
C_9CO_2			-12.8	- - -	(18.5)	- - -	(24.6)	51.2-51.9
C_8O	1	2	28.2	- - -	45.7-45.9	- - -	57.4	63.6
$C_{10}O$			28.0-28.0	- - -	39.6-40.0	62.5-63.0	63.8-64.6	65.5-65.7
C_{10}			13.8	- - -	- - -	(16.9)	- - -	27.1-27.4
C_9CO_2			26.6-27.0	- - -	(47.5)	- - -	52.4-52.5	53.1
C_6O	2	1	29.9	(29.9)	- - -	- - -	43.3-43.5	78.0-78.2
C_8O			35.2	- - -	50.2-50.7	55.4-55.7	55.8-55.9	77.7-78.0
C_9O			29.2	- - -	51.2-51.4	- - -	62.0-62.2	75.6
$C_{10}O$			30.3	- - -	44.9-45.1	- - -	67.7-67.8	77.2
C_{10}			10.2	- - -	(20.8)	(25.2-25.4)	30.8	40.6-41.0
C_9CO_2			35.2 35.2	- - -	(44.5)	- - -	52.3-54.5[b] 51.7	67.4-67.6
C_8O	3	0	49.0	- - -	(67.0)	- - -	77.0-77.2	88.4-88.5
$C_{10}O$			47.0	- - -	71.2-71.5	- - -	78.5-78.8	86.9-87.3
C_{10}			45.1	- - -	- - -	- - -	(55.6)	66.6-66.8
C_9CO_2			32.4	(37.0)	(59.5)	- - -	76.1-76.3	79.9

a. Abbreviations used are defined in the experimental section.

b. Two crystal forms which showed different melting temperatures were observed.

the BC series are all lower than those for the SC thioesters, except for the 3,0 series, but clearing temperatures are lower for all four BC series. Interestingly, the smectic C phase has its widest range when the methyl group is in the 2-position (1,2 isomer). The same comparison with X = C_{10} (Figure 3) shows that the BC enhances the formation of monotropic smectic phases, none of which exist in the SC thioester.§ This occurs at the expense of the nematic phase in the 0,3 and 1,2

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§ Caution is necessary in comparing only single compounds. Longer SC–R′ groups in these thioesters do show smectic phases.[3]

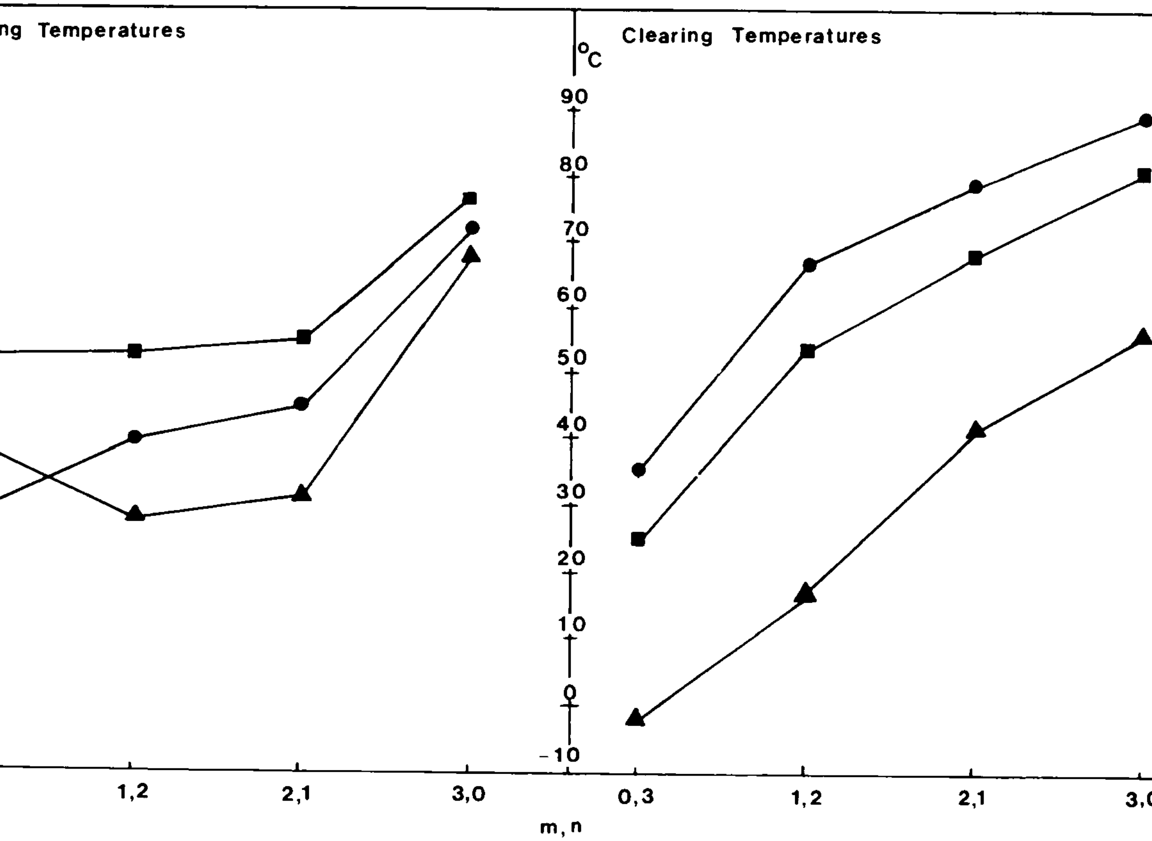
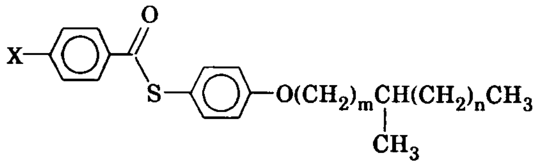


FIGURE 1 Comparison of the melting and clearing temperatures for



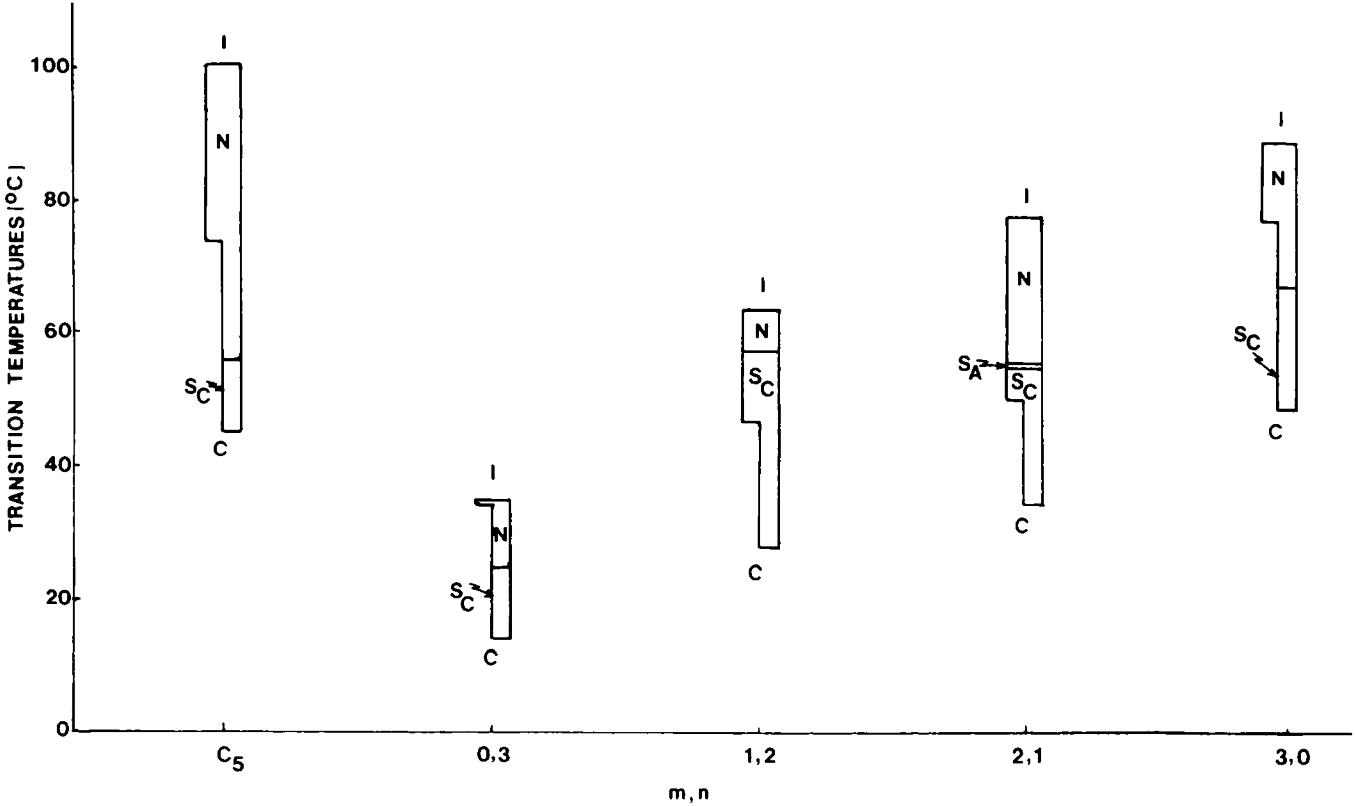
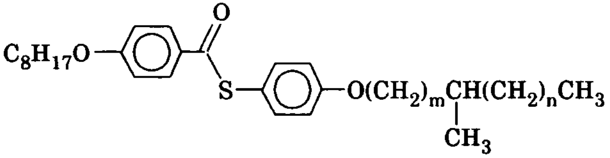


FIGURE 2 Comparison of the mesomorphic properties for



$C_8H_{17}O-C_6H_4-CO-S-C_6H_4-O(CH_2)_mCH(CH_3)(CH_2)_nCH_3$

with those for Y = $C_5H_{11}O$ (data from Reference 3).

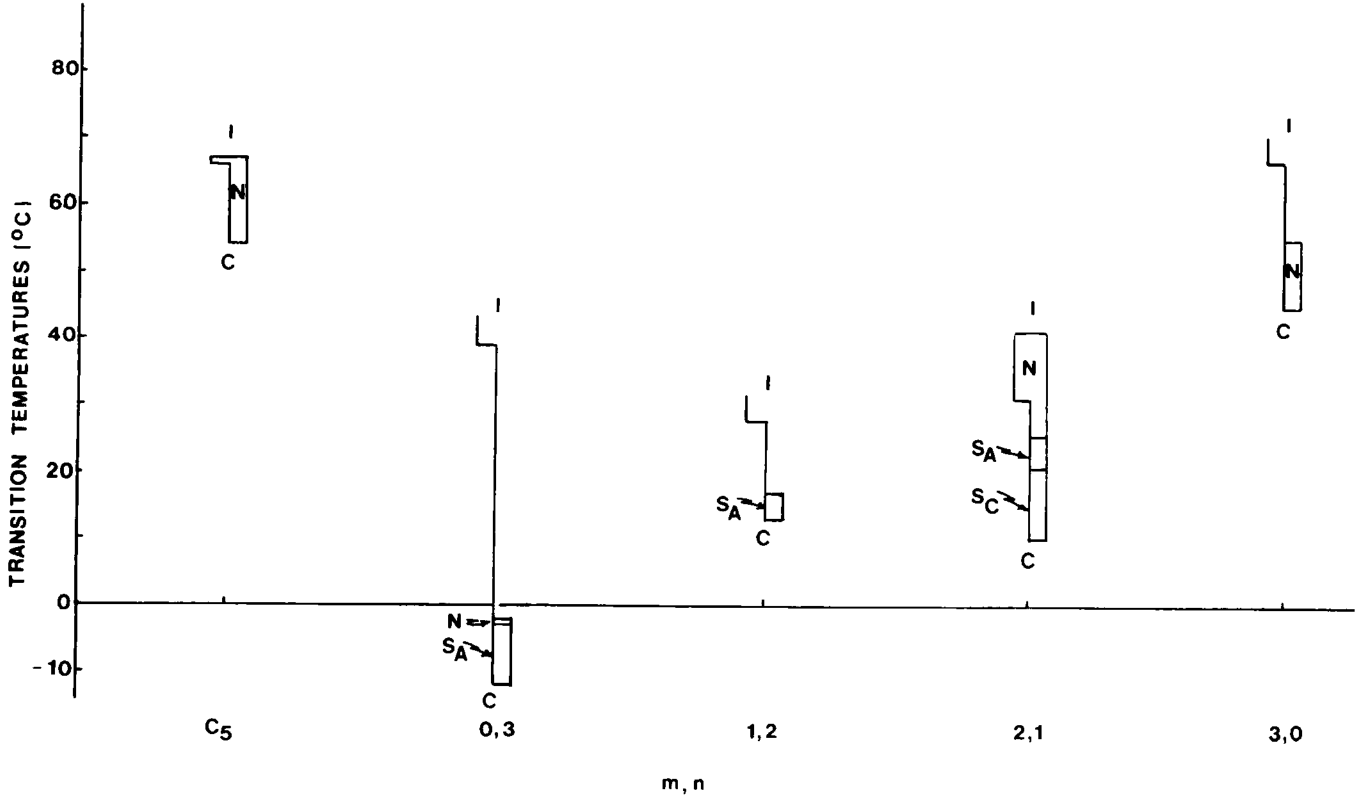
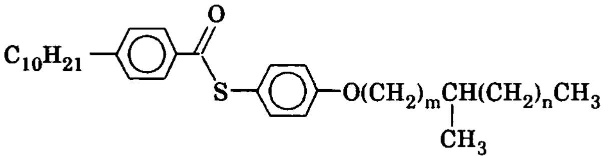


FIGURE 3 Comparison of the mesomorphic properties for



with those for Y = $C_5H_{11}O$.

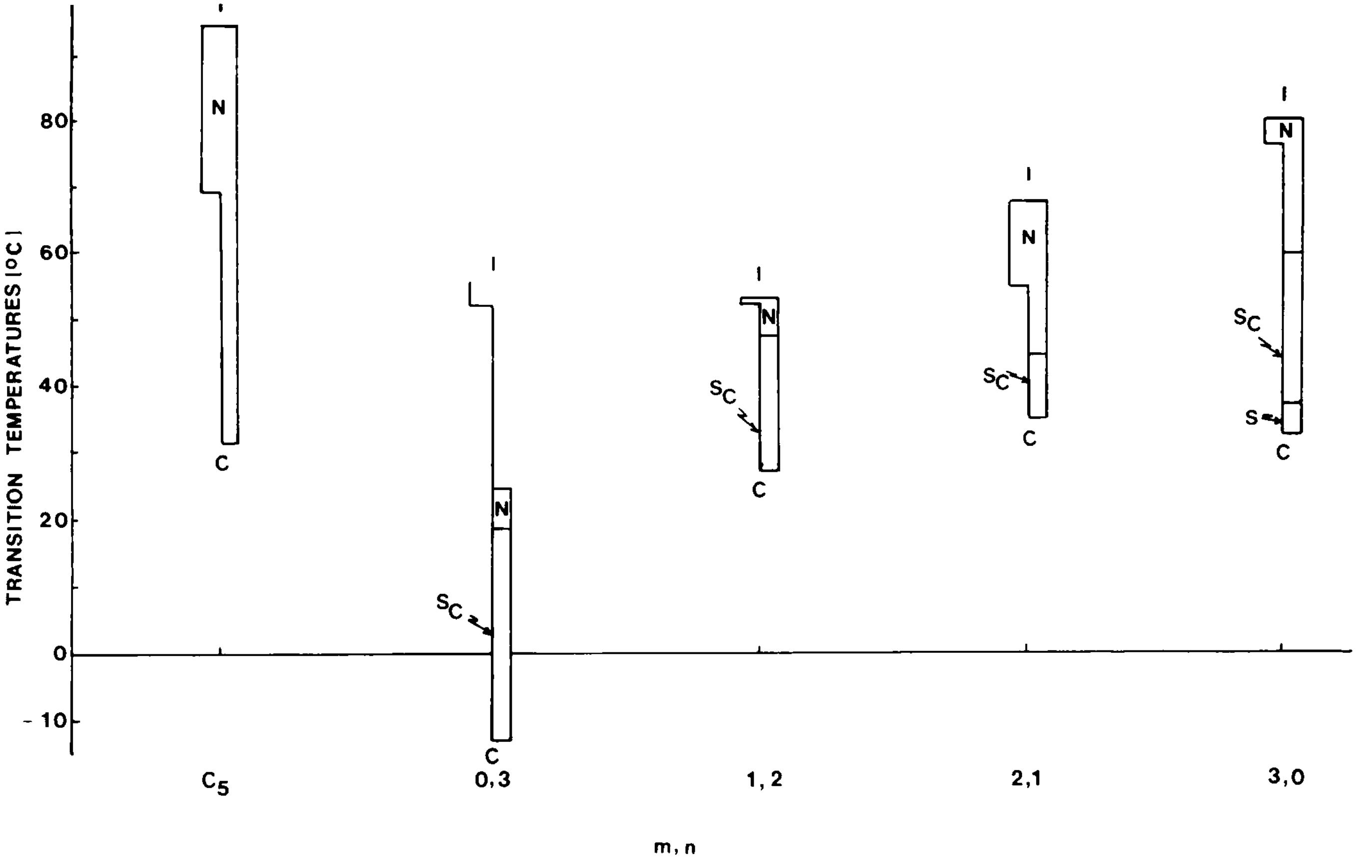
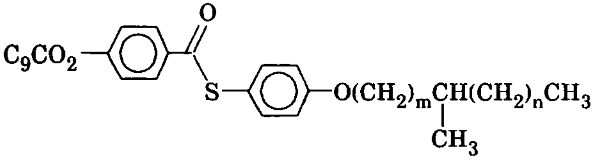


FIGURE 4 Comparison of the mesomorphic properties for



with those for Y = $C_5H_{11}O$.

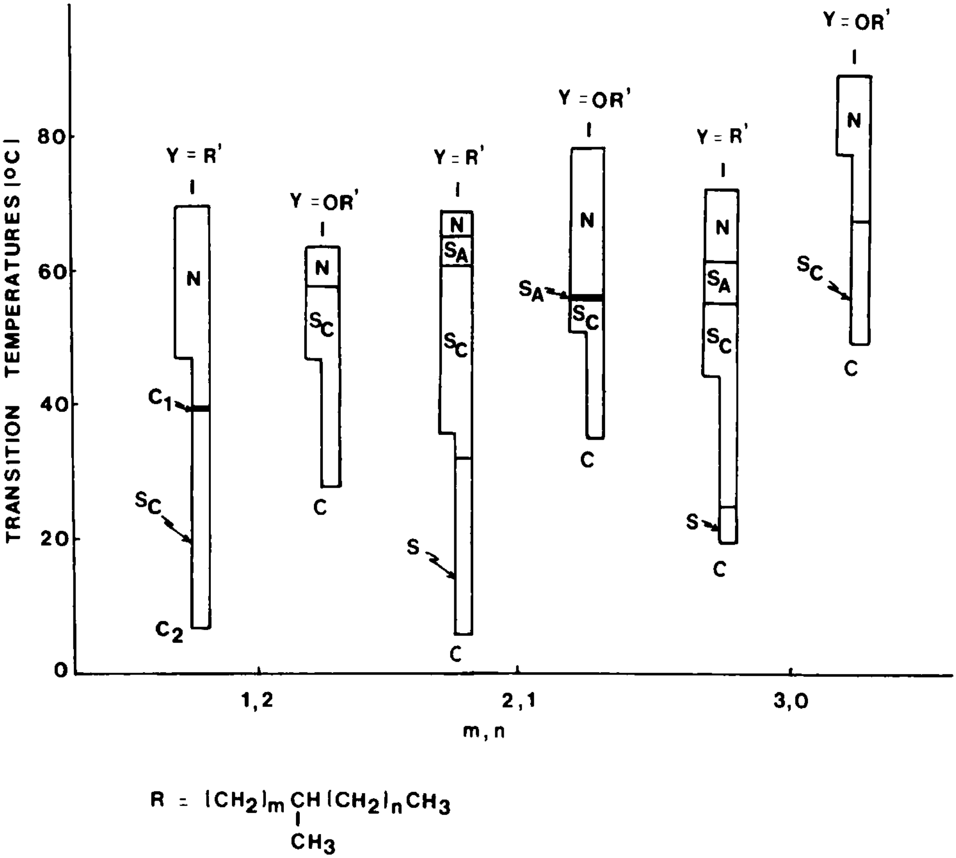
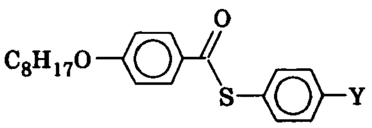


FIGURE 5 Comparison of the mesomorphic properties for



with those for Y = branched chain R′ (data from Reference 1) and branched chain OR′.

isomers but not in the 2,1 and 3,0 thioesters. In both these series with X = C_{10} and X = C_8O, the nematic phase becomes more favored as the methyl group is moved out along the BC, and the 2,1 thioesters have the most mesophases with N, S_A and S_C combinations. This is also true in the RO–R′ series *2* suggesting that the ether oxygen atom acts as part of the core rather than part of the flexible chain. Again melting temperatures for the BC series with X = C_{10} were lower than those for the SC series except for the 3,0 isomer with the clearing temperatures being lower for all four BC thioesters. When X = C_9CO_2, the N–S_C combination predominates in the BC series (Figure 4). No smectic A phases were observed, although an unidentified smectic phase was found below the S_C phase in the 3,0 series.

A comparison of the mesomorphic properties for the BC alkoxy with the BC alkyl thioesters with X = C_8O or C_9CO_2 (Figures 5 and 6) indicates there is little

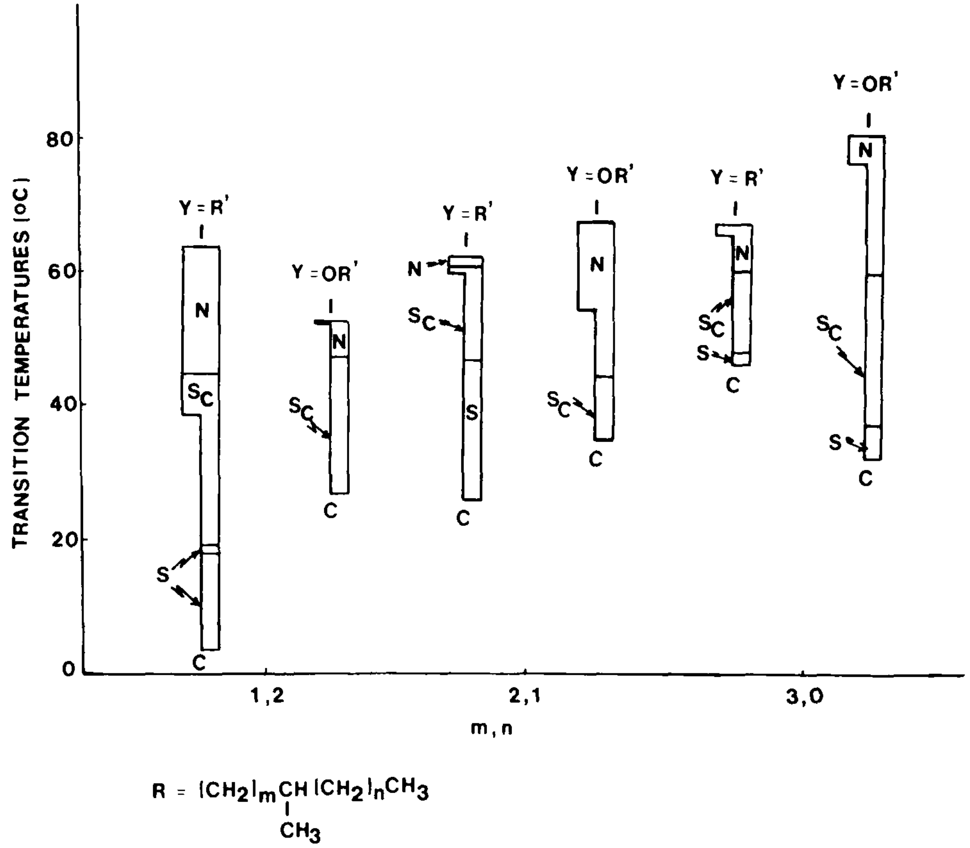
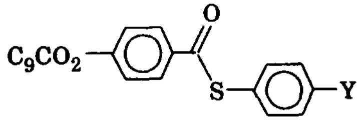


FIGURE 6 Comparison of the mesomorphic properties for



with those for Y = branched chain R′ (data from Reference 1) and branched chain OR′.

advantage in replacing the BC alkyl with a BC alkoxy group. In the series with the most mesophases having the broadest temperature ranges, the X = C_8O–2,1 thioester, only a short range S_A phase is observed sandwiched between the wider range N and S_C phases. The other isomers all show N–S_C combinations.

For both the X = C_8O and C_9CO_2 series, the clearing temperatures are higher when Y = OR′ than R′ except for the 1,2 isomers. Consideration of steric factors would predict that steric hindrance between the α-methyl group and the benzene ring ortho protons would be relieved by insertion of the oxygen atom between the chain and the ring resulting in higher rather than lower clearing temperatures. Consideration of dipole moments would give the same prediction. Thus, an explanation of this clearing point depression currently eludes us.

As expected, more mesophases with broad temperature ranges were observed for the biphenyl thioester *5* than for the phenylthiobenzoates *4*:

$$\begin{tikzcd}
C \arrow[rr, "135\text{-}136^\circ"] & & S_C \arrow[r, "195.9\text{-}196.1^\circ"] & S_A \arrow[r, "202.7^\circ"] & N \arrow[r, "209.8\text{-}210.2^\circ"] & I \\
& S_G \arrow[ul, "-13.0^\circ"] \arrow[ur, "115.8^\circ"'] & & & &
\end{tikzcd}$$

We were surprised to find that a compound with all its transition temperatures above 100° would have such a low crystallization temperature. The smectic G phase was identified by the presence of large colored mosaic platelets. However, x-ray crystallographic studies are needed to confirm this identification. A comparison of these data with those for the corresponding chiral ester (COO) reported earlier[8]:

$$C \xrightarrow{77.5^\circ} S_B \xrightarrow{101.5^\circ} S_C{*} \xrightarrow{154.2^\circ} S_A \xrightarrow{186.8^\circ} Ch \xrightarrow{187.4^\circ} I$$

suggests that the ester would be a better material for FLC displays but the thioester, if the optically active material were prepared, would be of more interest for the study of the highly ordered chiral smectic phases.

CONCLUSIONS

Replacing the BC alkyl group in the thioesters *2* with a BC alkoxy group *4* does not give more favorable smectic C range FLC materials. Clearing temperatures were always lower for the BC thioesters than for the SC analogs with the lowest temperature always occurring in the 0,3 series. Temperatures gradually increased as the methyl group was moved out along the BC away from the ring approaching that of the SC thioester in the 3,0 series but never becoming as large as those for the SC compounds. As expected, melting trends were more variable. Melting temperature lowering occurred in all isomers except the 3,0 series where the temperature either equaled or surpassed those for the SC thioesters. In the $X = C_{10}$ series, the melting temperature was higher in the 0,3 than in the 1,2 isomer.

The effect of methyl group location on the type of mesophases observed has some dependence on X. When both terminal chains are attached to the aromatic ring through an oxygen atom, a $N\text{-}S_C$ combination predominates. When X is an alkyl group more smectic A phases were observed as is true in the SC analogs. However, it is obvious that branching usually enhances the smectic C phase at the expense of the nematic phase. This latter phase gradually recovers with increasing methyl group distance until in the 3,0 series it approaches that observed in the SC series but never quite equals it in phase length and temperature. This illustrates that even a methyl group in the terminal chain this far removed from the benzene ring affects the mesomorphic properties. As was true in the BC alkyl series *2*, the 2,1 series is the most likely to show the $N\text{-}S_A\text{-}S_C$ sequence. In the three X series presented here, the R and RO-2,1 isomers would be the best choices. Fortunately, these are the ones for which an optical isomer is easiest to prepare. Although many of these branched alkoxy thioesters have a $N\text{-}S_C$ combination instead of the preferred $N\text{-}S_A\text{-}S_C$, the larger tilt angle in the S_C phase below the nematic phase could make these thioesters useful in FLC displays as well.

Our studies agree with some of the conclusions reached in the studies by Coates on the influence of alkyl chain branching on S_C^* formation.[9]

EXPERIMENTAL

The starting 4-alkyl and acyloxybenzoic acids were prepared by the methods described earlier,[10-12] and the 4-alkoxybenzoic acids were purchased from Frinton Laboratories. The alcohols; 2,3 and 4-methyl-1-pentanol (Aldrich Chemical Co.) were used as precursors to the corresponding bromides whereas 2-bromohexane was purchased from Lancaster Synthesis Ltd. The biphenyl acid was prepared by acidic hydrolysis of the nitrile, 8OCB (or M24), obtained from E.M. Merck Co.

Anhydrous Na_2SO_4 was used to dry all organic extracts unless otherwise noted. TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as detectors. All compounds were purified until they showed only one spot by TLC. Silica gel (60–100 mesh, regular column and 230–400 mesh, flash) was used for purification by chromatography. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus and are corrected. The elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

IR spectra were run on a Pye-Unicam 3-200 instrument and NMR spectra obtained in $CDCl_3$ (unless otherwise noted) using a Varian FT80 or a General Electric GN-300 instrument (GN) with TMS as the internal standard.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min as previously described.[13] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperatures and so no monotropic phases occurring below this temperature were missed. Monotropic phases obtained on cooling were immediately reheated to obtain the more accurate heating transition temperature. Abbreviations used are C = crystal, N = nematic, I = isotropic liquid crystals and G, C and A indicate identified smectic phases while S represents an unidentified smectic phase. Mesophases were identified by the observance of known textures under crossed polarizers.[14,15] Conoscopic studies were done to determine whether smectic phases were uniaxial or biaxial.

1-Bromo-2-methylpentane, *10* (m = 1, n = 2)

To a stirred ice-cold soln of 2-methylpentanol (50.0 g, 0.49 mole) in anhyd (dried over Linde #4A molecular sieves) Et_2O (200 ml) was added dropwise PBr_3 (66.3 g, 0.25 mole). The reaction mixture was refluxed for 3 hr, cooled to RT and poured onto crushed ice. The product was extracted into Et_2O, the Et_2O washed with H_2O, dried and filtered. The filtrate was rotovaped and the residue distilled at 35° (2 mm) to give 36.5 g (45.1%) of the bromide *10* (m = 1, n = 2): TLC (9:1 CH_2Cl_2–EtOAc) $R_f = 0.9$ (alcohol *9* $R_f = 0.6$) and NMR δ 3.32 (q, $J = 2.0$ Hz, 2, CH_2Br), 1.10–2.10 (m, 5, CH_2CH_2CH) and 0.97 (t, $J = 6.0$ Hz, 6, 2Me).

The other two bromides *10* were prepared in the same manner:
m = 2, n = 1: 62.7%, bp. 39–41° (10–15 mm) and NMR δ 3.40 (t, $J = 7.0$ Hz, 2, CH_2Br), 1.05–2.00 (m, 5, CH_2CHCH_2) and 0.75–1.05 (m, 6, 2Me).

m = 3, n = 0: 64.3%, bp. 54–60° (10–15 mm) and NMR δ 3.35 (t, J = 7.0 Hz, 2, CH_2Br), 1.10–2.10 (m, 5, $CHCH_2CH_2$), 0.93 (s, 3, Me) and 0.85 (s, 3, Me).

Sodium-4(2′-methylpentyloxy)benzenesulfonate, *12* (m = 1, n = 2)

A soln of NaOH (6.0 g, 0.15 mole) in 80% EtOH (180 ml) was added to a stirred soln of sodium-4-hydroxybenzenesulfonate (29.4 g, 0.126 mole) in 80% EtOH (360 ml). To this mixture was added dropwise 1-bromo-2-methylpentane (29.7 g, 0.18 mole). The reaction mixture was refluxed for 20 hr, a 50% aq soln of NaOH (16 ml) added dropwise and refluxing continued for 2 hr. A precipitate was collected by filtration from the cooled (RT) reaction mixture. The filtrate was concentrated to a small volume *in vacuo*, cooled in an ice bath and the resulting precipitate removed by filtration. This material was dried at 105° to give 19.0 g (53.9%) of the sulfonate salt *12* (m = 1, n = 2): mp > 300°, IR (Nujol), 1600 (str, Ar) and 1240, 1180 cm^{-1} (str, $SO_3^{\ominus}$); and NMR (D_2O) δ 7.60 (d, J = 8.0 Hz, 2, ArH ortho to S), 6.75 (d, J = 8.0 Hz, 2, ArH ortho to O), 4.20 (m, 2, OCH_2), 1.00–2.20 (m, 8, C_4H_8) and 0.87 (t, J = 6.0 Hz, 3, Me). The other two salts *12* were prepared in the same manner: m = 2, n = 1 (78.8%) and m = 3, n = 0 (74.6%).

4(2′-Methylpentyloxy)benzenesulfonyl chloride, *11* (m = 1, n = 2)

A mixture of the sulfonate salt *12* (21.0 g, 75 mmol) in $POCl_3$ (35.0 g, 0.23 mole) was refluxed for 2 hr, cooled to RT and diluted with H_2O (100 ml). The resulting oil was extracted into $CHCl_3$ and the $CHCl_3$ washed with H_2O, dried and filtered. The filtrate was rotovaped and an attempt made to distill the residue which gave some of the product at 190–193° (0.4 mm). However, continued heating caused decomposition so the distillation was terminated. The pot residue was purified by flash chromatography on silica gel using hexane-EtOAc (9:1) as the eluting solvent. The total yield of the sulfonyl chloride *11* (m = 1, n = 2) was 8.5 g (41.0%): IR (film) 1380 (SO_2Cl) and 1260 cm^{-1} (OR) and NMR δ 7.90 (d, J = 8.0 Hz, 2, ArH ortho to S), 7.00 (d, J = 8.0 Hz, 2, ArH ortho to O) 3.82 (2d, J = 6.0 Hz, 2, OCH_2), 1.70–2.10 (m, 1, CH), 1.07–1.55 (m, 4, CH_2CH_2), 1.07 (s, 3, $\underline{Me}CH$) and 0.98 (t, 3, Me).

The other two sulfonyl chlorides *11* were prepared in the same manner:
m = 2, n = 1: 48.0%, bp 185–190° (1.0–1.5 mm) and NMR δ BC aliphatic protons at 4.02 (t, J = 7.50 Hz, 2, OCH_2), 1.10–2.00 (m, 5, CH_2CHCH_2), 0.95 (s, 3, $CH\underline{Me}$) and 0.87 (s, 3, $CH_2\underline{Me}$).
m = 3, n = 0: 93.0%, b.p. 185–186° (0.3 mm) and NMR δ BC aliphatic protons at 4.03 (t, J = 7.0 Hz, 2, OCH_2), 1.55–2.00 (m, 2, $CH_2\underline{CH_2}CH_2$), 1.05–1.55 (m, 3, CH_2CH), 1.00 (s, 3, Me) and 0.92 (s, 3, Me).

4(2′-Methylpentyloxy)benzenethiol, *13* (m = 1, n = 2)

Zinc dust (12.0 g, 183.2 mmole) was added in small portions to a stirred cooled (0°) solution of the sulfonyl chloride *11* (8.0 g, 28.9 mmole) in concd H_2SO_4 (12 ml) and H_2O (75 ml) while maintaining the temperature at 0–5° with an ice bath. Stirring was continued for an additional 45 min at 0°, refluxed for 3 hr, cooled to

RT and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried and filtered. The filtrate was rotovaped and the remaining liquid distilled at 145–150° (0.9–1.1 mm) to give 4.9 g (80.0%) of the thiol *13* (m = 1, n = 2): IR (film) 2550 cm^{-1} (wk, br SH) and NMR: δ 7.15 (d, *J* = 8.0 Hz, 2, ArH ortho to SH), 6.70 (d, *J* = 8.0 Hz, 2, ArH ortho to O), 3.65 (2d, *J* = 6.0 Hz, 2, OCH_2), 3.25 (s, 1, SH), 1.60–2.00 (m, 1, CH), 1.05–1.60 (m, 4, CH_2CH_2), 1.02 (s, 3, $CH\underline{Me}$) and 0.93 (t, 3, $CH_2\underline{Me}$). Anal Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.62. Found: C, 68.66; H, 8.69.

The other two thiols *13* were prepared in the same manner:
m = 2, n = 1: 79.7%, bp 135–137° (1.4 mm) and NMR δ 3.90 (t, *J* = 6.0 Hz, 2, OCH_2).
m = 3, n = 0: 79.7%, bp 132–135° (0.5–0.7 mm) and NMR δ 3.85 (t, *J* = 6.5 Hz, 2, OCH_2).

1-Bromo-4-(1′-methylpentyloxy)benzene, *14*

To a stirred solution of 4-bromophenol (21.0 g, 0.12 mole) and NaOH (23.8 g, 0.60 mole) in H_2O (20 ml) and 95% EtOH (40 ml) was added dropwise 2-bromohexane (19.2 g, 0.12 mole). The reaction mixture was refluxed for 48 hr, the EtOH removed by distillation and replaced with H_2O, cooled to RT and extracted with Et_2O. The Et_2O was washed with H_2O, dried, filtered and the filtrate rotovaped to give the crude product. Distillation of this material at 110–114° (0.20–0.25 mm) gave 13.0 g (43.3%) of the bromide *14*: NMR δ 7.25 (d, *J* = 8.0 Hz, 2, ArH ortho to Br), 6.65 (d, *J* = 8.0 Hz, 2, ArH ortho to O), 4.00–4.40 (m, 1, $\underline{CH}Me$), 1.05–2.00 (m, 9, C_4H_9) and 0.90 (s, 3, $CH_2\underline{Me}$).

1-Butylthio-4-(1′-methylpentyloxy)benzene, *16*

A stirred mixture of the bromide *14* (13.0 g, 50.6 mmole) and cuprous *n*-butylmercaptide[6] (10.0 g, 65.8 mmole) in freshly distilled quinoline (51 ml) and pyridine (16 ml) was refluxed at 170° for 4 hr. The reaction mixture was cooled to 100°, poured into a mixture of crushed ice (300 g) and 36% HCl (100 ml) and stirred for 2 hr. The aqueous layer was decanted from the gummy residue and extracted with Et_2O. This extract was added to the gummy residue, stirred for 5 min, filtered and the insoluble material washed thoroughly with Et_2O. The filtrate was washed with 10% HCl and H_2O, dried (anhyd K_2CO_3), filtered and the filtrate rotovaped. Distillation of the residue at 150–154° (0.2–0.3 mm) gave 11.8 g (87.9%) of the thioether *16*: NMR δ 7.22 (d, *J* = 9.0 Hz, 2, ArH ortho to S), 6.72 (d, *J* = 9.0 Hz, 2, ArH ortho to O), 4.25 (m, 1, OCH), 2.75 (t, *J* = 7.0 Hz, 2, SCH_2), 1.05–2.00 (m, 13, C_6H_{13}) and 0.88 (d, *J* = 7.0 Hz, 6, 2 Me).

4(1′-Methylpentyloxy)benzenethiol, *15*

Small pieces of Na (1.07 g, 46.7 mmole) were added to a stirred solution of the thioether *16* (12.4 g, 46.7 mmole) in liq NH_3. Excess Na was added until the blue color remained for 15 min. Then NH_4Cl was *cautiously* added in small portions to destroy any excess Na and a stream of N_2 passed through the flask to flush out all the NH_3. The remaining solid was dissolved in H_2O, crushed ice added, the solution made basic with NaOH and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried, filtered and the filtrate rotovaped to give 8.27 g (84.4%) of the crude product. Distillation of this material at 117–120° (0.25–0.30 mm) gave a yield of 75.5% of the thiol *15*: IR (film) 2560 (wk, br SH) and 1600 cm^{-1} (str, Ar) and NMR δ 7.10 (d, J = 8.0 Hz, 2, ArH ortho to S), 6.60 (d, J = 8.0 Hz, 2, ArH ortho to O), 4.00–4.35 (m, 1, OCH), 3.20 (s, 1, SH), 1.10–1.80 (m, 9, C_4H_9) and 0.80 (t, 3, Me). Anal Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.62. Found: C, 68.47; H, 8.69.

4-Pentyloxybenzenethiol was prepared in the same manner for the synthesis of some SC thioesters. Yields were 52.9% (sulfonate salt), 95.5% (sulfonyl chloride) and thiol (92.9%). Additional information on this thiol can be found in Reference 3.

Synthesis of the Thioesters *4* and *5*

These thioesters were prepared using the carbodiimide method as previously reported.[2] Purification was by either classic or flash column chromatography on silica gel followed by recrystallization. Mixtures of EtOAc-hexane (ratio = 1:9 for m = 1–3 series and 1–5% for m = 0 series) were used for column elution. Methanol (m = 0), abs EtOH (m = 1, X = C_9CO_2 and m = 2, X = C_9O) or petroleum ether (30–60°) were used as recrystallization solvents. All esters showed only 1 spot on TLC. IR spectra showed a COS peak at 1670–1680 cm^{-1} and an additional CO_2R peak at 1760–1770 cm^{-1} when X = C_9CO_2. NMR spectra were used to confirm the structures of these compounds. They were identical to those previously reported for the SC thioesters[3,12] except for the BC aliphatic regions which were the same as those reported for the thiols and their precursors.

The biphenyl thioester *5* was chromatographed using 1:4 $CHCl_3$:petroleum ether (30–60) and recrystallized from abs EtOH. Its structure was confirmed by NMR: δ 7.98 (d, J = 8.0 Hz, 2, biphenyl H ortho to C=O), 7.50 (t, J = 7.0 Hz, 4, biphenyl H meta to C=O and OC_8), 7.33 (d, J = 9.0 Hz, 2, benzene H ortho to S), 6.90 (d, J = 8.0 Hz, 4, Ar ortho to OBC and OC_8), 3.95 (m, 4, $2ArOCH_2$), 1.10–2.00 (m, 17, C_6H_{12} and CH_2CHCH_2) and 0.90 (m, 9, 3 Me).

Two new SC thioesters with Y = OC_5 were prepared for use in comparisons with the BC thioesters. These had the following transition temperatures (°C):

X	C	N	I
C_{10}	54.6	65.5-65.7	66.9-67.0
C_9CO_2	31.6	69.3	94.3-94.4

Acknowledgements

This material is based on work supported in part by the National Science Foundation-Solid State Chemistry grant DMR88-1851. We also appreciate the work of C. Citano in preparing the 4′-octyloxybiphenylcarboxylic acid.

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