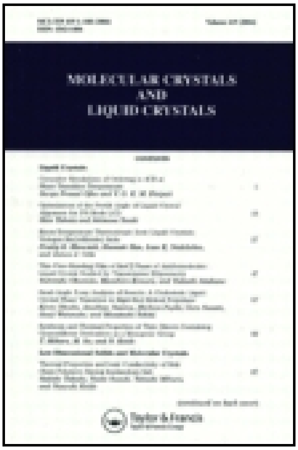

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# The Effect of Methyl Group Position in Branched Alkyl Chains on the Phenolic End of 4,4′-Disubstituted Phenylbenzoates on Mesomorphic Properties and Some Optically Active Analogs as Ferroelectric Liquid Crystals

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

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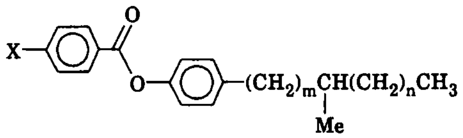
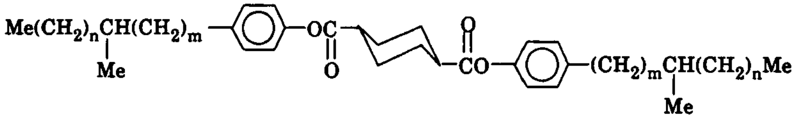
(*Received August 3, 1988; in final form January 10, 1989*)

A select number of homologs of the branched chain (BC) $C_5$ ester series:



in which $m = 0\text{-}3$ and $n = 0\text{-}2$, and $X = R$, RO, and $C_9CO_2$ have been synthesized to study the effect of branching and the position of the branching methyl group on mesomorphic properties. This effect was also determined for the BC cyclohexane diesters:



to test the generality of any trends observed in a different structural series. Mesomorphic properties of the esters were determined by hot-stage polarizing microscopy. Nematic, $S_A$, $S_C$, and $S_{(B?)}$ phases

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†Presented in part at the 12th International Liquid Crystal Conference, Friberg, August, 1988.
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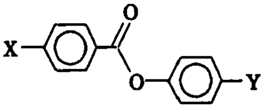
in various combinations were observed. Both clearing and melting temperatures for the BC phenylbenzoates, when X = RO and $C_9CO_2$ were always lower than for the analogous straight chain (SC) esters containing the same number of carbon atoms, as were in the backbone of the BC.

Comparisons of the effect of the BC on the mesomorphic properties of these esters are made with the effect observed in a variety of other thioesters, substituted phenylbenzoates, and the analogous biphenyl compounds. Often $S_C$ phases are enhanced at the expense of the $S_A$ phase, and N phases seem most preferred when the methyl group is in the 2-position on the chain of the phenol/thiol. Clearing temperatures are always lower than in the analogous SC compounds and melting temperatures are usually lower. However, enough discrepancies occur to make the melting trend a less general one. The effect of location of the methyl group on transition temperatures in $C_5$ BC phenylbenzoates is similar to that observed previously for the $C_4$ BC esters, i.e. they tend to increase as the methyl group is moved further from the benzene ring. This trend, however, does not always occur in other systems such as the thioesters.

Mesophase ranges were good among the BC phenylbenzoates with X = RO and room temperature $S_A$–$S_C$ combinations were found in this series when *m* = *n* = 2. Therefore, several homologs were prepared with an optical isomer of this chain to determine their usefulness in mixtures as ferroelectric materials.

## INTRODUCTION

In our earlier studies on the effect of methyl group location within the terminal chain in the esters *1* and *2*

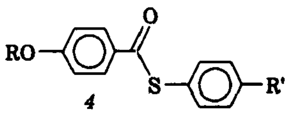


*1* $X = R, Y = OR'$ with $R' = C_4H_9$, CH(Me)Et and $CH_2CHMe_2$

*2* $X = RO, Y = R'$ with $R' = C_3H_7$, $C_4H_9$, CH(Me)Et or Pr, $CH_2CH(Me)_2$, $CH_2CH(Me)Et$ and $(CH_2)_2CHMe_2$

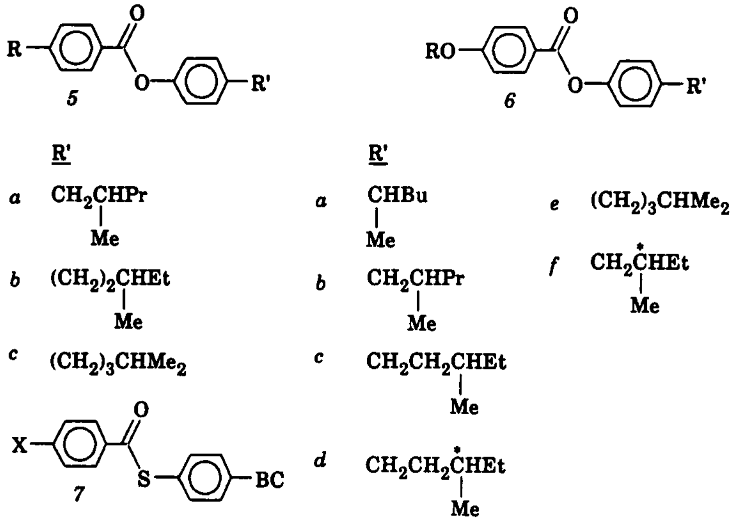
*3* $X = RCO_2, Y = R'$

on mesomorphic properties, the greater the distance between the methyl group and the benzene ring, the better these properties were, as shown by higher clearing temperatures and more and/or wider phase ranges.[1–3] No mesophases were observed in the 1-methyl branched chain (BC) esters except in the ester *2* when R = $C_8$ and R′ = CH(Me)Pr which shows a low temperature monotropic smectic A ($S_A$) phase. Only nematic (N) and a few $S_A$ phases were observed in the other BC esters. These are usually monotropic, making it difficult to compare phase lengths and limiting the types of phases on which the effect of methyl branching could be studied. Smectic polymorphism generally increases in longer chain homologs and the use of a longer BC would allow us to study the effect of an additional position for the methyl group. Although the analogous straight chain (SC) phenylbenzoates show more smectic phases when both chains are longer, these also are often monotropic.[3–5] However, the SC thiobenzoates *4*



*4*

show more smectic phases at shorter chain lengths, many of which are enantiotropic.[6] Thus, these thioesters would be better for studying the effect of methyl branching on mesomorphic properties. Since studies were already started in the esters, we were interested in studying the effect of branching in both series so a comparison could be made. Synthetically, the same intermediate can be used to prepare both the BC phenols and thiols, but the length of the BC is limited by the availability of the required BC alcohols or acids. Thus, we chose to prepare the esters *5* and *6* with a $C_5$ BC backbone (BB) and the thioesters *7* with the same BC backbones ($C_4$ and $C_5$).



*5*

R'

*a* $CH_2CH(Me)Pr$

*b* $(CH_2)_2CH(Me)Et$

*c* $(CH_2)_3CHMe_2$

*6*

R'

*a* $CH(Me)Bu$

*b* $CH_2CH(Me)Pr$

*c* $CH_2CH_2CH(Me)Et$

*d* $CH_2CH_2\overset{*}{C}H(Me)Et$

*e* $(CH_2)_3CHMe_2$

*f* $CH_2\overset{*}{C}H(Me)Et$

*7*

Mesomorphic properties of the phenylbenzoates are discussed in this paper, whereas those for the thioesters are presented in another paper.[7]

The BC dialkyl esters *5* were not expected to show good mesomorphic properties since the SC esters are often liquids at room temperature with either no mesophases or very low temperature monotropic N phases.[4,5,8] Branching was expected to lower the transition temperatures and decrease the mesophase lengths. Thus, most of our work concentrated on studying the alkoxy-alkyl (RO-R′) series *6*. We chose to concentrate on studying only a few longer R chain lengths, $C_8$–$C_{12}$ since past experience has taught us that these are the ones that will most adequately represent the trends in mesomorphic properties in the phenylbenzoates.

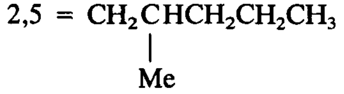
Branched chain esters are also of interest in the study of chiral mesophases and, in particular, ferroelectric $S_C$ phases for use in liquid crystal displays. Since many of the 3,5 esters *6c* had a near room temperature $S_C$ phase below a $S_A$ and/or a N phase, an optical isomer of these esters *6d* was prepared. A few of the BC dialkyl esters were synthesized both for comparison purposes and to see if any of these would be useful in obtaining room temperature liquid crystalline mixtures. The previously reported 2,4 esters *6f*[9] were also prepared for these mixture studies. Since the SC acyloxy esters *3* is another series with $S_C$ phases,[10] the BC analogs (Y = BC) were also included for studying as possible components for ferroelectric mixtures. A few di BC esters *6* with R and R′ = BC were prepared to determine what effect two BCs would have on mesomorphic properties and if the effect was a sum of that of both BCs.

As a test of whether the trends observed in the phenylbenzoates were general or series specific, the BC cyclohexane diesters *8* were synthesized.

*8*

These diesters have a totally different structure from that of the esters and thioesters in that the molecule is a symmetrical one with a longer core containing two functional groups and branched terminal chains. Additionally, the SC compounds have wider range enantiotropic mesophases at higher temperatures[11,12] making this series a good one for studying branching effects.

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



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

2 indicates the position of the methyl group; an asterisk (*) indicates the BC is *chiral*
5 indicates the number of carbon atoms in the backbone chain.
BC = branched chain
SC = straight chain; a single number indicates the chain length (e.g. 5)
BB = backbone.

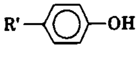
## SYNTHESIS

All the BC esters were synthesized by esterification of either the acid or acid chloride with the appropriate BC phenol by methods described earlier.[13] Purification was by recrystallization from absolute ethanol and, if necessary, by flash chromatography on silica gel until only one spot was observed by TLC. Although several methods are available for the preparation of 4-BC phenols, we chose to prepare our phenols by fusion of the 4-alkylbenzenesulfonates with potassium hydroxide since the sulfonates could also be used to prepare the thiols.[11,14] These sulfonates were prepared from the BC alkylbenzenes by sulfonation with sulfuric acid using the method previously described for the synthesis of 4-*n*-decylphenol,[14] and purified by recrystallization from water except for the 4,5 BC ester *6e* which was recrystallized from water-ethanol. The phenols were purified by vacuum distillation; yields and boiling points are given in Table I.

The 5 BC alkylbenzenes, except for the 1,5 one, were prepared by a Friedel-Crafts acylation of benzene with the BC acid chloride to give the ketones (purified yields = 64.5–93.7%) followed by either a Wolff-Kishner (Huang Minlen modification) reaction[15] or by catalytic reduction using 5% Pd-C in either ethanol[16] or

TABLE I

Purified Yields and Boiling Points for



| R' | Purified Yield (%) | bp (°C)/mm |
|---|---|---|
| 1.5 | 35.5 | 92/0.5 |
| 2*,4 | 75.7 | 95/1.0 |
| 2,5 | 29.5 | 120/1.0 |
| 3,5 | 72.9 | 105/0.4 |
| 3*,5 | 84.1 | 118/1.8 |
| 4.5 | 35.9 | 112/0.6 |

tetrahydrofuran using a few drops of acid.† Purified yields were a little higher for the catalytic (84.0–94.2%) than for the Wolff-Kishner (66.0–80.9%) reduction. Catalytic reduction was also used to prepare the optically active alkylbenzene to minimize racemization. Both the BC alkylbenzenes, and the precursor ketones have been previously prepared using other methods (see for example Reference 17). The 1,5 BC alkylbenzene was prepared from acetophenone (purified yield—98.7%) using the method reported earlier for synthesizing the 1,4 BC alkylbenzene.[2] The acid chlorides were obtained by treating the BC acid with either oxalyl or thionyl chloride, with higher yields being obtained using the latter (78.2–84.6%). The optically active phenol with R' = (+) $CH_2CH(Me)Et$ was prepared in the same manner as the 5 BC phenols using commercially available (+)-2-methylbutylbenzene.

The optically active acid, 2-methylpentanoic acid, was synthesized from (−)2-methylbutanol via a Grignard reaction as previously reported.[18,19] Although we were able to prepare the bromide from this alcohol via the tosylate in the presence of lithium bromide,‡ the yield (overall = 24.9%) was lower than that obtained using phosphorous tribromide (81.0%).[21] Another method was used to prepare some of the racemic bromides in which carbon tetrabromide is used in the presence of triphenylphosphine.[22] Although a large excess of triphenylphosphine is usually used, we found that the bromides could be prepared in high yields using a 1:1 ratio. Distilled (*in vacuo*) yields were high (~90%) but the bromides showed trace amounts of an aromatic material in their NMR spectra. These were, however, used successfully to prepare pure intermediates. The BC alkoxybenzoic acids were synthesized by alkylation of 4-hydroxybenzoic acid methyl ester with the BC bromides as described earlier.[23] Pure material was difficult to obtain by alkylating 4-hydroxybenzoic acid.

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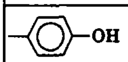
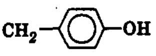
†As reported earlier, this reduction does not go in THF without addition of an acid.

‡More recently, we have obtained high yields using the method of Ghirardelli.[20] These results will be published later.

TABLE II

Optical Rotations for $\mathrm{Et\overset{*}{C}H(Me)CH_2X}$

| X | $[\alpha]^D(^\circ C)^a$ | lit. $[\alpha]^D(^\circ C)$/Ref. |
|---|---|---|
| Br | 2.8 | 3.9 (20)/24 |
| $CO_2H$ | 5.0 | 4.7 (20)/24 |
| COCl | 9.4 | 7.67 (25)/25 |
| COPh | -- | 17.39 (25)/25 |
| $CH_2Ph$ | -- | 10.7 (25)/26 |
|  | 10.1 | -- |
|  | 14.5 | |

a. Determined at 23.5° in $CHCl_3$.

Optical rotations for most of the intermediates prepared are given in Table II along with literature values for comparison. Optical purities were not determined as our primary goal was to first determine if the optically active esters would have the desired ferroelectric properties.

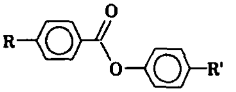
The purity of all liquid intermediates was checked by GLC and NMR was used to confirm all structures. NMR data for the SC phenylbenzoates[27] and the aromatic SC intermediates[11,14,16] are available in the literature. Data for the analogous BC compounds were identical except for the aliphatic proton region which varied with the specific BC being studied.

## MESOMORPHIC PROPERTIES

Transition temperatures for the BC esters prepared were determined by hot stage polarizing microscopy and are presented in Tables III through VII. Abbreviations used for the mesophases are given in the Experimental Section. Transition temperatures were all below 65° for the BC phenylbenzoates. Nematic, $S_A$, $S_C$, and an unconfirmed smectic phase were observed. Textures of the first three phases, as well as the chiral ones, were typical of textures previously reported for these phases. The texture for the S phase consisted of tightly wound spirals which became more mosaic on standing. Areas which had been a Schlieren texture in the $S_C$ phase were mosaic in this phase. It is possible this phase is a $S_B$ phase, as this one

TABLE III

Transition Temperatures (°C) for



| R | R' | C$^{a}$ | S | $S_A$ | N | I |
|---|---|---|---|---|---|---|
| 8 | 5 | 12.9 | | | 23.8-24.1 | 28.2-30.1 |
| 10 | 5 | 14.0 | (31.3-31.6)$^{b,c}$ | --- | (33.1-33.3) | 38.0-39.3 |
| 10 | 6 | 29.7 | | (30.8-31.0)$^{b}$ | | 45.3-47.7 |
| 8 | 2,5 | ~1.6 | | | (1.4-1.9)$^{b}$ | 11.1-12.3 |
| 10 | 2,5 | $\sim 3.9\ C_2 \xrightarrow{\sim 17.7} C_1$ | | (2.4-2.7) | (11.5-12.1) | 22.7-23.3 ($C_2$)<br>38.5-39.1 ($C_1$) |
| 8 | 3,5 | -2.0 | | (1.6-2.7) | | 17.2-21.6 |
| 8 | 4,5 | 7.3 | | | | 21.9-24.5 |

a. Crystallization temperature obtained using a cooling rate of 2°/min.

b. Observance of this phase depends on the crystallization temperature.

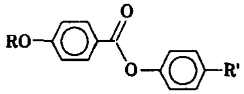
c. This phase showed a mosaic texture and is probably a $S_B$ phase but moving the cover slip to try to obtain a homeotropic texture caused crystallization.

has been reported to occur in the SC esters. However, in these BC esters, it occurred too close to the crystallization temperature to move the cover slip to try to obtain a homeotropic texture good enough for conoscopic studies to confirm this identification. Some of the BC esters which had a $S_C$ phase but no S phase crystallized in a spiral texture which was similar to that observed for the S phase, but these supercooled enough to differentiate them from the S phase.

In making comparisons of the properties of the BC with those for the SC esters the question arises as to which chain length to use for the SC compound; the one with the same number of carbon atoms as in the BB of the BC ester (R′ = 5), or the one with the same total number of carbon atoms as in the BC (R′ = 6). A comparison of the available melting temperatures for the SC esters of the type *6* with R′ = 3-6 shows too much variation in melting temperatures to select a good standard. A plot of clearing temperatures for the SC esters gives essentially parallel curves of the same shape for all four series (Figure 1). These curves show an odd–even alternation both within each series where R is varied and between each other where R′ is varied with the odd R′ and the even R (on an oxygen atom) having the higher temperatures when R′ = 3-5. Thus, choosing a chain length for R′ that has the same total number of carbon atoms as in the BC, as was done in our earlier studies with the 4BC esters, is not necessarily a better choice than using a chain length with the same number of carbon atoms as in the BB. Additionally, the curves for R′ = 5 and 6 are nearly superimpossible, so that either of these could be used as a standard. We chose to use R′ = 5 since more data are available for this series in both the esters and thioesters.

The dialkyl BC esters *5* showed surprisingly good mesomorphic properties with both N and $S_A$ phases being observed (Table III), although these were all low

TABLE IV - Transition Temperatures (°C) for



| R | R' | C[a] | S | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|
| 8 | 1,4 | 29.4 | | | | | 36.7-38.5[b] |
| 12 | 1,5 | 4.9 | | | (12.2-15.2) | - - - | 24.9-28.0 |
| 8 | 2,5 | 23.5 | | | 28.3-28.5 | 30.1-30.2 | 47.0-47.1 |
| 9 | | 18.7 | | | (32.3-33.0) | 38.9-41.6 | 43.4-44.2 |
| 10 | | 18.1 | | (18.7) | 39.7-40.2 | 43.8-44.0 | 49.8-50.0 |
| 12 | | 18.3 | | (22.0-22.3) | 36.2-39.7 | 50.7-50.8 | 52.0-52.1 |
| 8 | 3,5 | 14.7 | | 27.0-27.5 | 32.1-32.6 | - - | 48.8-49.1 |
| 9 | | 18.8 | | (37.7-38.7) | 41.8-43.4 | - - | 50.6-51.9 |
| 10 | | 15.6 | | 40.3-40.7 | 43.6-44.1 | - - | 53.8-54.1 |
| 12 | | 20.1 | (26.1-26.4) | 40.7-40.9 | 47.1-47.9 | - - | 56.8-57.5 |
| 3 | 4,5 | 19.5 | | | | (39.7-40.0)[c] | 39.1-41.5 |
| 8 | | 28.6 | | | 43.8-44.6 | 49.4-49.6 | 52.7-52.8 |
| 9 | | 19.1 | | (32.4-32.7) | (49.2-51.7) | - - | 51.7-52.9 |
| 10 | | 22.2 | | (40.2-40.8) | 49.4-50.0 | - - | 55.2-56.2 |
| 12 | | 24.2 | (27.9-28.0) | (45.8-47.7) | 51.0-52.2 | - - | 59.1-59.9 |
| 2,5 | 3,5 | < -20[d] | | | | | 7.3-9.6 |
| | 4,5 | < -20[d] | | | | | 13.1-17.4 |
| 3,5 | 3,5 | -9.2[d] | | | | | 12.3-16.0 |
| | 4,5 | -0.30 ($C_1$)[e] | | | | | 13.4-15.0($C_1$)<br>20.2-22.2($C_2$) |
| 4,5 | 3,5 | 0.9 | | | | (2.3-2.9) | 23.4-25.1 |
| | 4,5 | 20.7 | | | | | 34.4-35.8 |

a. Crystallization temperature obtained using a cooling rate of 2°/min.

b. This compound was prepared twice using phenol prepared by two different methods to be sure these data were correct.

c. Although this temperature range is within that for the melting temperature, we feel that this phase is monotropic at a temperature slightly below the melting temperature. No nematic texture was observed during C→I.

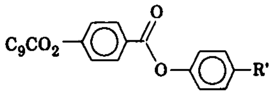
d. Crystallization did not occur by -20° (the limit of our equipment) but occurred on standing at RT overnight.

e. Crystallization was very slow. However, movement of the slide to non-crystalline areas did not reveal any low temperature mesophases.

temperature monotropic phases. Interestingly, mesophases seem to be less favored as the methyl group is moved further along the chain away from the benzene ring; a trend opposite to that observed in the RO–BC series. Also, the S phase observed in the SC ester is replaced by a $S_A$ phase in the BC ester. Melting temperatures were lower than those in the SC compound except for R = 10 and R' = 2,5 BC; a compound which shows two crystal forms with two different melting temperatures.

A comparison of both melting (Figure 2) and clearing (Figure 3) temperatures for the BC esters with X = RO, *6* with those for the analogous 5 and 6 SC esters with R > 7 indicates that these temperatures are always lower for the BC compounds than for the SC ones. Generally, in homologous series plots of melting

TABLE V - Transition Temperatures (°C) for

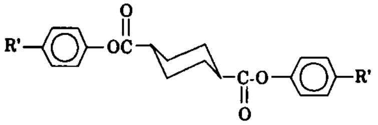


| R' | C[a] | $S_B$ | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|
| $C_5H_{11}$ | 21.3 | (46.7) | (51.7) | 59.4 | 61.0 | 67.4[b] |
| 1,4 | 5.6 | | | (6.7-7.6) | --- | 41.5-44.3 |
| 2,5 | -0.8 | | (18.0) | (24.0) | --- | 40.0-40.4 |
| 3,5 | 22.2 | | (41.5) | (44.6-44.8) | --- | 43.7-45.3 |
| 4,5 | 24.4 | | (41.4) | (44.7) | (49.0-49.1) | 48.2-49.7 |

a. Crystallization temperature obtained using a cooling rate of 2°/min.

b. Data from Ref. 10.

TABLE VI - Transition Temperatures (°C) for

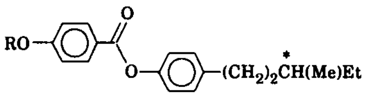


| R' | C[a] | $S_A$ | N | I |
|---|---|---|---|---|
| 1,4 | 62.7 ($C_2$)<br>63.3 ($C_1$) | | | 68.7-72.1 ($C_2$)<br>70.2-71.1 ($C_1$) |
| 2,5 | 89.6 $C_1$[b] | | 91.0-92.0 | 110.2-110.3 |
| 3,5 | 134.5 | | | 135.3-136.7 |
| 4,5 | 110.3 | 112.8-114.2 | 115.6-116.0 | 123.4-123.6 |

a. Crystallization temperature obtained using a cooling rate of 2°/min.

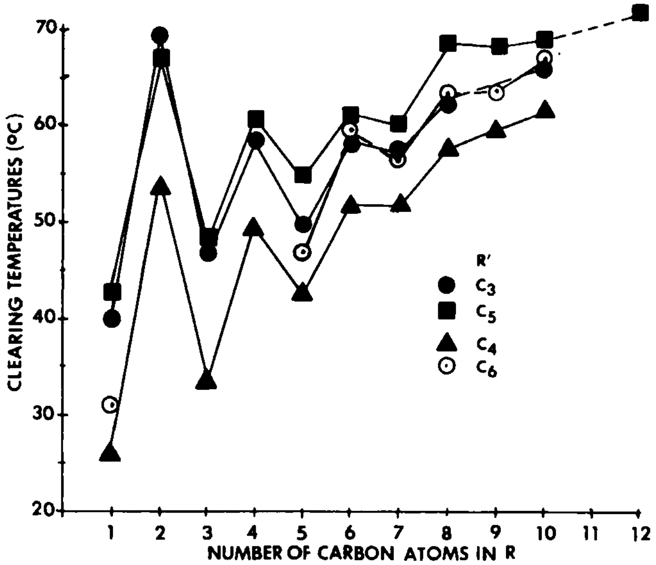
b. On further cooling $C_1 \rightarrow C_2$ at 77.3°; reheating $C_2$ gives $C_1$ at 86.5°.

TABLE VII - Transition Temperatures (°C) for

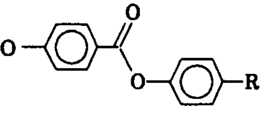


| R | $[\alpha]_D$[a] | C[b] | $S_C$* | $S_A$ | I |
|---|---|---|---|---|---|
| 3 | +9.2 | 42.3 | | | 48.7-49.8 |
| 4 | c | 35.8 | | | 40.2-40.6 |
| 8 | +8.2 | 15.6 | (32.0-32.4) | 34.6-35.8 | 48.8-49.2 |
| 10 | +8.4 | 24.2 | (40.7-40.8) | 41.4-42.0 | 44.6-44.8 |

a. In $CHCl_3$ at 23°.
b. Crystallization temperature obtained at a cooling rate of 2°/min.
c. Not enough material was isolated to determine rotation.



1. Clearing temperatures for RO



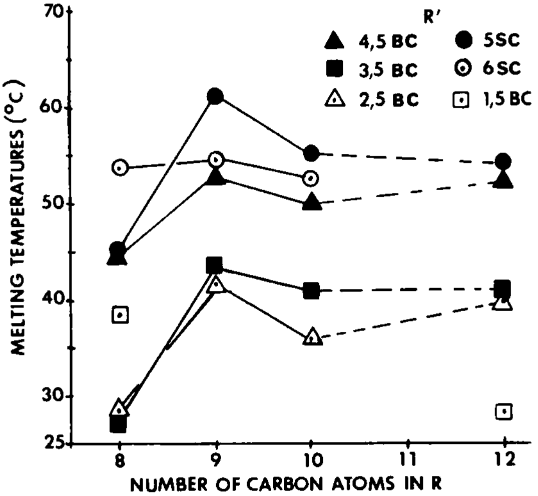
R', with R'=SC.

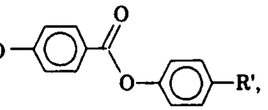
temperatures in the phenylbenzoates, large variations occur at short- to mid-chain lengths in the phenylbenzoates, but these disappear at longer CLs (>7), and trends become more regular. Although there does seem to be some trend of melting temperatures increasing as the methyl group is moved further from the benzene ring when R > 8, the similar melting temperature for the 2,5 and 3,5 series at R = 8 and the higher temperature for the 1,5 ester at 8 illustrates that this trend is not consistent in melting temperatures for these BC esters. A comparison of the clearing temperatures (Figure 3), however, does show a consistent trend of this type.

A comparison of the types of mesophases observed for the BC with those for the SC esters shows the following trends for series *6*:

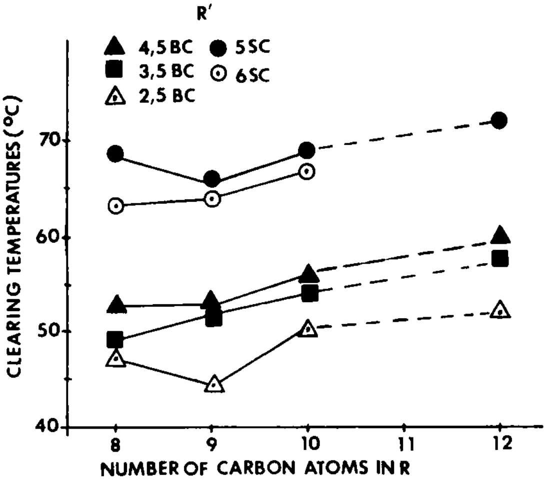
| Ester | Mesophases |
|---|---|
| 5 SC | $S_A$,N |
| 1,5 BC | ($S_A$) |
| 2,5 BC | $S_C$,N |
| 3,5 BC | S,$S_C$,$S_A$ |
| 4,5 BC | S,$S_C$,$S_A$,N |

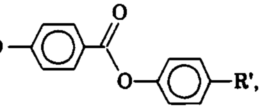
The N phase is the most favored in the 2,5 series where it occurs above a $S_A$ phase as it does in the 5 SC series. This phase is obviously not preferred as the methyl group is moved away from the benzene ring as it disappears in the 3,5 series and



2. Comparison of melting temperatures for RO

R',
with R' = SC and 5 BC.

occurs with a reduced phase range in only one homolog in the 4,5 esters. The $S_C$ phase is definitely more favored in all three BC series being at its best in the 3,5 esters while a $S_A$ phase disappears in this series but occurs often in the 2,5 and 4,5 esters. Only the $S_A$ phase is observed in both the 1,4 and 1,5 series. The S phase appears in the BC esters as a short range monotropic phase in the 3 and 4,5 series illustrating that higher ordered mesophases can occur in these BC esters. Inter-



3. Comparison of clearing temperatures for RO

R',
with R' = SC and 5 BC.

estingly, the most number of mesophases were observed in the 4,5 series; two more than seen even in the SC series.

All these mesophases occur within a temperature range of 10–60°. Two enantiotropic $S_C$ phases were found at or near room temperature (R = $C_8$, R′ = 2, and 3,5 chains). The 3,5 one also occurs below a $S_A$ phase making it the best candidate for a ferroelectric liquid crystal mixture. Many of the other esters have $S_A$–$S_C$ combinations often with the $S_C$ phase supercooling below room temperature which would also be useful in mixtures. Even those with a N phase could be helpful in aligning the mixture in a cell. Mesomorphic properties, along with optical rotations for the optically active 3,5 series, are given in Table VII. Mixture studies on these esters, along with the BC thioesters, are being done at Hughes Laboratories and will be reported in later papers.

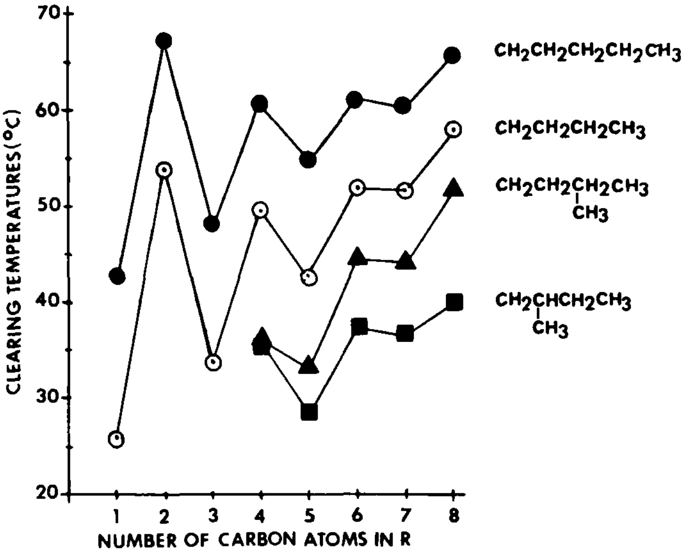
Mesomorphic properties for the BC esters with X = $C_9CO_2$ are presented in Table V. Both melting and clearing temperatures were lowered by branching. These increased as the distance between the methyl group and the benzene ring increased, except that the melting temperature for the 1,5 ester is higher than that for the 2,5 one. Only monotropic phases were observed, but these occurred in all four series including the 1,5 one. The $S_C$ phase was enhanced at the expense of the N and $S_A$ phases with the N phase occurring only in the 4,5 series. The $S_B$ phase observed in the SC series was not seen in these esters giving fewer phases in the BC than in the SC series. The chiral analog of R′ = 3,5 could be useful in ferroelectric mixtures having both low temperature $S_A$ and $S_C$ phases. Of the di BC esters, only one showed a mesophase *6* [R = $Me_2CH(CH_2)_3$ and R′ = $(CH_2)_2CH(Me)Et$]; a very low temperature monotropic N phase.

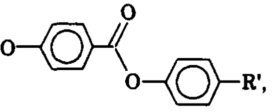
Unlike the SC dialkyl cyclohexane diesters, the BC esters *8* showed very poor mesomorphic properties (Table VI). In contrast with the phenylbenzoates, these were poorer for the 3,5 than for the 2,4 and 4,5 ester showing no mesophases at all. On heating the 3,5 ester, a DSC scan showed an intense peak at ~134° (ΔH = 22.9 Kcal/mole) corresponding to the melting temperature observed by microscopy and a weaker peak at ~69° (ΔH = 14.2 Kcal/mole) suggesting a crystal-to-crystal change. On cooling, this second peak occurred at ~67°. Clearing temperatures were always lower for the BC esters than for the 5 SC one, but melting temperatures were only lower when R′ = 1 and 2,5 BC. Only short range N and $S_A$ phases were observed.

## DISCUSSION

Clearing temperature depression occurred in all the 5 BC esters *6* suggesting a general trend for the effect of a methyl branched chain on mesomorphic properties. Thus, it was of interest to determine if this trend also applies to other types of esters. A comparison of the clearing temperatures for the 4 BC esters[2] with those for the 4 and 5 esters shows lower temperatures whether the SC ester is 4 or 5 (Figure 4). This is also true when the BC is on the acidic rather than the phenolic end.[1,3]

Thus, among the known esters with the BC attached directly to the ring, there



4. A Comparison of clearing temperatures for RO—


when R' = 4 BC with 4 and 5 SC.

are no examples in which the clearing temperature is higher than that for the analogous SC ester having the same length BB. Comparisons in other systems containing two benzene rings connected by a central group shows this same lowering trend (Table VIII). Even if one of the benzene rings is replaced with a cyclohexane ring or a biphenyl ring system (Table IX), this lowering continues. Thus, lowering of the clearing temperature in compounds containing a methyl branched terminal chain attached directly to an aromatic ring appears to be a reliable trend. It also occurs in the phenylbenzoates when the BC is part of an alkoxy group. Lowering of the melting temperatures was found to predominate in other series as well as in the 5 BC esters, but there are enough exceptions to make this trend a less reliable one (Tables VIII and IX) for predicting melting temperatures. This has been shown to be true for the SC esters as well as many other compounds.

The amount of lowering of transition temperatures caused by a branched methyl chain and how much this depends on the location of the methyl group within the chain is of interest in designing new materials. A comparison of the differences in melting and clearing temperatures for both the 4 and 5 BC esters (Table X) shows a general trend of decreased lowering as the methyl group is moved further from the benzene ring except for the melting temperature for the 1,5 BC with R = 8. This decrease is less for the clearing than for the melting temperatures, except for the 2,4 and 4,5 series, as can best be seen by averaging the values in each series. The amount of temperature lowering also decreases as the alkoxy chain length (R) increases, but again this effect is smaller in the clearing temperatures. The largest decrease of this type occurs in the melting temperatures for the 3,5 BC series. Both the 1,4 and 1,5 BC series show much larger decreases in clearing temperatures than do the other series where the decrease is never >18.4°.

The differences in the lowering of transition temperatures with increasing alkoxy chain lengths suggest that longer alkoxy chains can better accommodate the bulky branching methyl group in the packing of these molecules. The decrease in the amount of lowering of the transition temperatures as the methyl group is moved farther from the benzene ring can be explained by steric hindrance to packing caused by interaction between the *ortho* ring protons and the methyl group as proposed for the 4 BC esters.[1] However, this does not explain the high melting temperature observed for the 1,5 BC ester with R = 8 or the fact that this trend does not occur in the 5 BC thioesters where the largest decrease in the clearing temperatures occurs in the 3,5 rather than the 2,5 series (Table XI). More studies are needed to determine if this is an exception or whether other influencing factors help determine this effect. There also seems to be less effect of alkoxy chain length on the lowering of melting temperatures with larger variations and with some homologs having higher temperatures in the thioesters. The effect of alkoxy chain length on melting temperature lowering is the greatest in the 3,5 BC series and affects the clearing temperatures as well. Average lowering of melting and clearing temperatures are similar and about the same as in the BC esters. Lowering of the few clearing temperatures reported for the BC cyclohexane diesters *6* also occur (Table XII). Again, the effect on melting temperatures varies.

In order to make these comparisons, several new esters were prepared to use as standards and errors were found in data for a number of reported esters. Transition temperatures for these esters are given in Table XIII or in the Experimental Section.

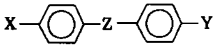
The effect of methyl branched chains on the types of mesophases occurring in various compounds is also presented in Tables VIII and IX. In the RO–R′ ester series 2 with R′ = 4 BC, data are available for chain lengths of R = $C_1$–$C_{10}$ when R′ = 4 SC and the 2,4 BC whereas for the other two BC series, the maximum R′ length is $C_8$. This makes a difference in comparing mesophases in that smectic phases begin to appear at R′ = $C_8$. The N phase is lost in the 1,4 series and is less favored in the 2,4 and 3,4 than in the SC series. Although the $S_A$ phase occurs in the 2,4 series, it is less favored, and the $S_C$ phase disappears. Clearly longer chain homologs are needed for a better comparison. When the 2,4 BC is on the acid end, the N phase observed in the SC series is clearly less favored in the BC series. In the dialkoxy esters (RO–OR′) which shows more mesophases, the N phase is also less favored, but the $S_A$ and $S_C$ phases are retained without much change except for an enhancement of the $S_A$ phase at shorter chain lengths. When R′ = 4,6 BC, the N phase changes little while the $S_A$ and $S_C$ phases are retained but with the $S_A$ phase being enhanced at shorter R lengths but at longer ones in the SC series. Thus, it seems that the enhancement of the $S_C$ phase is dependent on the chain lengths of both terminal groups. This is not surprising since $S_C$ enhancement often occurs at longer chain lengths in SC homologous series as well. When this BC is moved to the acid end, i.e. R = 4,6 BC, the N phase is less favored as was true with a corresponding alkyl BC and the $S_A$ phase is replaced with a $S_C$ one. Thus, a general trend is not apparent for the effect of a BC on the types of mesophases observed in these esters.

Among the 5 BC RO–R′ esters *6*, the N phase is enhanced in the 2,5 series, less favored in the 4,5 one, and disappears in the 3,4 series, while the $S_C$ phase is enhanced in all three BC series with the $S_A$ phase being lost in the 2,5 one and more favored in the 3,5 and 4,5 series. A similar trend was observed in the analogous 5 BC thioesters *3*,[7] but the N and $S_A$ phases never disappeared entirely. Thus, the trends seem to be more consistent in this comparison. However, data are not available for the 5 BC series with the BC on the acid side or for the dialkoxy BC compounds to determine if these series differ from the RO–R′ series. Among the 5 BC cyclohexane diesters *8*, both the N and $S_A$ phases seem less favored and no $S_C$ phases were found. Smectic C phases were also not observed in the SC esters and perhaps BC alkoxy esters are needed to see this phase.

The temperature range over which mesophases occur in the 5 BC esters can be either longer or shorter than that observed in the 5 SC esters. When it is longer, it is usually due to a lower crystallization temperature which allows for the observation of more monotropic phases and/or of longer phase length. Supercooling

TABLE VIII

Effect of Methyl Branched Terminal Chains on Mesomorphic Properties for



| Z | X | Y | Mesophases[a] | | | | | Change in | | Data[b] Source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | S | $S_B$ | $S_C$ | $S_A$ | N | mp[a] | Clp | |
| $CO_2$ | R 10 | R′ 5 | x | | | | x | | | OD |
| | 8 and 10 | 2,5 | | | | | x | ↓ | ↓ | OD |
| | 8 | 3,5 | | | | x | | ↓ | ↓ | OD |
| | 8 | 4,5 | | | | x | | ↓ | | OD |
| $CO_2$ | RO 1-10 | R′ 4 | | | x | x | x | | | 1,2,OD |
| | 1-8 | 1,4 | | | | x | | NC | ↓ | 2 |
| | 1-10 | 2,4 | | | | x | ↓ | ↓(1) | ↓ | 2,9,28,OD |
| | 1-8 | 3,4 | | | | x | ↓ | ↓(3) | ↓ | 2 |
| | 8-10 | 5 | | | | x | x | | | 5,8,OD |
| | 8 and 12 | 1,5 | | | | | | ↓ | | OD |
| | 8-10 | 2,5 | | | ↑ | | x | ↓ | ↓ | OD |
| | | 3,5 | | | ↑ | ↑ | ↓ | ↓ | ↓ | OD |
| | | 4,5 | x | | ↑ | ↑ | ↓ | ↓ | ↓ | OD |
| | R 3 | OR′ 1-8 | | | | | x | | | OD |
| | 1,3 | | | | | | | ↓(4) | | 1,3 |
| | 2,3 | | | | | | ↓ | ↓(3) | ↓ | 1,3 |
| | 4 | OR′ 6,10 and 12 | | | | | x | | | 1,3 |
| | 2,4 | | | | | | ↓ | ↓ | ↓ | 29,30 |

Table VIII (cont'd-2)

| Z | X | | Y | | *Mesophases* [a] | | | | | *Change in* | | Data [b] Source |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | S | $S_B$ | $S_C$ | $S_A$ | N | mp [a] | Clp | |
| | RO | 8-12 | OR' | 4 | | x | x | x | x | | | 4 |
| | | | | 2,4 | | | x | x | ↓ | ↓ | ↓ | 31-33 |
| | | | | 6 | | x | x | x | x | | | 4 |
| | | | | 4,6 | x | | ↑ | ↓ | x | ↓ | ↓ | 32 |
| | | 6 | | 6,9 | | | | x | x | | | 4 |
| | | 4,6 | | 6,9 | | | ↑ | ↓ | ↓ | ↓(1) | ↓ | 34 |
| | | 8 | | 7-10 | | | x | x | x | | | 4 |
| | | 6,8 | | 7-10 | | | ↑ | | ↓ | ↓ | ↓ | 30 |
| | $C_9CO_2$ | | | 5 | | x | x | x | x | | | 10 |
| | | | | 1,5 | | | | ↓ | | ↓ | ↓ | OD |
| | | | | 2,5 | | | ↑ | ↓ | | ↓ | ↓ | OD |
| | | | | 3,5 | | | ↑ | ↓ | | ↓ | ↓ | OD |
| | | | | 4,5 | | | ↑ | ↓ | ↓ | ↓ | ↓ | OD |
| COS | RO | 6-10,12 | R' | 5 | x | x | x | x | x | | | 6 |
| | | | | 2,5 | x | | x | x | x | ↓(1) | ↓ | 7 |
| | | | | 3,5 | x | x | x | x | x | ↓(1) | ↓ | 7 |
| | | | | 4,5 | x | | x | x | x | ↓(1) | ↓ | 7 |
| CH=N | RO | 7-10 | R' | 4 | | | x | x | x | | | 18 |
| | | | | 2,4 | | x | ↑ | ↓ | ↑ | ↑ | ↓ | 35 |
| | | | | 5 | x | x | x | x | x | | | 18,36,OD |
| | | | | 3,5 | x | x | ↑ | ↓ | | ↓ | ↓ | 35 |

a. The observance of a mesophase is indicated by an x. In the BC compounds x also indicates no obvious increase or decrease; arrows indicate obvious differences. Numbers in parentheses indicate exceptions to trends in melting temperatures. No attempt is made to indicate BC esters that were optical isomers. NC indicates no obvious change in temperature.

b. OD indicates our data as reported in Tables III-IV, XVII, or the Experimental Section.

## TABLE IX

Effect of Methyl Branched Terminal Chains on Mesomorphic Properties

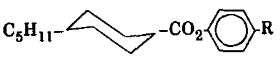
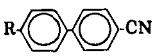
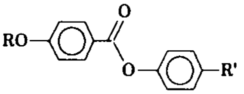
| Structure | R | Mesophases | | Change in | | Data Source |
|---|---|---|---|---|---|---|
| | | $S_A$ | N | mp | Clp | |
|  | 4 | x | x | | | 5 |
| | 2,4 | | ↓ | ↓ | ↓ | 5 |
|  | 4 | | x | | | 4 |
| | 2,4 | x | x | ↓ | ↓ | 4 |
| | 5 | | x | | | 4 |
| | 3,5 | x | x | ↓ | ↓ | 4 |
| | 6 | | x | | | 4 |
| | 4,6 | x | x | ↓ | ↓ | 4 |

TABLE X

Differences in Melting and Clearing Temperatures for



| R' | R | | Δmp (°C) (SC-BC) | Average Values | | Δclp (°C) (SC-BC) | Average Values |
|---|---|---|---|---|---|---|---|
| with R' = $C_4$ | | | | | | | |
| 1,4 | $C_8$ | | 24.7 | | | 52.5 | |
| 2,4 | $C_8$ | | 14.1 | | | 17.8 | |
| | $C_9$ | 12.1 | 6.4 | 7.5 | 0.7 | 14.5 | 16.5 |
| | $C_{10}$ | | 2.0 | | | 17.1 | |
| 3,4 | $C_8$ | | 11.3 | | 6.0 | | |
| with R' = $C_5$ | | | | | | | |
| 1,5 | $C_8$<br>$C_{12}$ | | 17.0<br>36.0 | | | 46.3 | |
| 2,5 | $C_8$<br>$C_9$<br>$C_{10}$ | 6.2 | 27.0<br>19.4<br>20.8 | 22.4 | 10 | 21.7<br>21.8<br>26.8 | 18.4 |
| 3,5 | $C_8$<br>$C_9$<br>$C_{10}$<br>$C_{12}$ | 17.9 | 28.0<br>17.6<br>15.8<br>10.1 | 17.9 | 5.2 | 19.7<br>14.1<br>15.0<br>14.5 | 15.8 |
| 4.5 | $C_8$<br>$C_9$<br>$C_{10}$<br>$C_{12}$ | 9.1 | 10.9<br>8.1<br>6.5<br>1.8 | 6.8 | 3.9 | 16.0<br>14.3<br>5.7<br>12.1 | 12.0 |

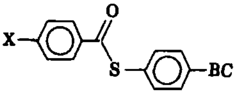
See Table VIII for literature sources of reported data.

seems to be much greater in many of the BC esters/thioesters than in the SC compounds giving lower crystallization temperatures than expected from the lowered melting temperatures.

The mesomorphic properties of the 5 BC esters are better than we anticipated, possibly because we studied longer alkoxy chain lengths than was done earlier. This makes them more appealing for use in ferroelectric materials than initially thought. The loss of the N phase with an increase in the S phases as the methyl group is moved away from the benzene ring suggests that the bulky methyl group is well tolerated in the packing of the molecules into smectic layers. That the N phase is strongest in the 2,5 BC series in both the esters and thioesters supports the idea that steric hindrance between the methyl group and the aromatic *ortho* protons makes smectic layer packing less favorable for smectic phases but still is acceptable for the end-to-end packing needed for nematic phases. This steric hindrance also seems to be more tolerated in smectic layered packing by tilting the molecules within the layers since the only smectic phase observed in the 2,5 BC esters series is the $S_C$ one. The $S_A$ phase reappears in the 3,5 and 4,5 BC series along with the more highly ordered phases at longer chain lengths. With these BCs there is less steric hindrance of the methyl group with the core which provides for better packing into smectic layers. However, the observance of only $S_A$ phases in the 1,5 series (X = RO, $C_9CO_2$) does not support this reasoning as the steric

TABLE XI

Differences in Melting and Clearing Temperatures for



as Compared to 5SC Thioesters

| X | BC | Δmp (°C) (SC-BC) | | Average Values | ΔClp (°C) (SC-BC) | | Average Values |
|---|---|---|---|---|---|---|---|
| $C_8$ | 2,5 | 2.4 | 4.7 | 3.3 | 2.8 | 17.8 | 15.5 |
| | 3,5 | | 4.4 | | | 13.6 | |
| | 4,5 | | 2.3 | | | 15.0 | |
| $C_6O$ | 2,5 | 3.1 | 25.5 | 18.9 | 0.7 | 16.6 | 16.6 |
| $C_7O$ | | | 18.1 | | | 17.7 | |
| $C_8O$ | | | 11.4 | | | 17.0 | |
| $C_9O$ | | | -6.0 | | | 16.8 | |
| $C_{10}O$ | | | 16.2 | | | 15.7 | |
| $C_{12}O$ | | | 22.4 | | | 15.9 | |
| $C_3O$ | 3.5 | 11.1 | 27.3 | 18.5 | 17.2 | 29.3 | 17.6 |
| $C_7O$ | | | 13.9 | | | 20.0 | |
| $C_8O$ | | | 22.7 | | | 18.2 | |
| $C_9O$ | | | 11.2 | | | 16.1 | |
| $C_{10}O$ | | | 22.1 | | | 14.2 | |
| $C_{11}O$ | | | 16.0 | | | 13.5 | |
| $C_{12}O$ | | | 16.2 | | | 12.1 | |
| $C_6O$ | 4,5 | | 5.8 | 10.7 | 2.4 | 13.3 | 13.2 |
| $C_7O$ | | | 1.7 | | | 15.6 | |
| $C_8O$ | | | 14.3 | | | 14.7 | |
| $C_9O$ | | | 18 | | | 12.5 | |
| $C_{10}O$ | | | 13.6 | | | 12.2 | |
| $C_{12}O$ | | | -4.1 | | | 10.9 | |
| $C_9CO_2$ | 2,5 | | 20.7 | | | 4.6 | 2.2 |
| | 3,5 | | -0.7 | | | 4.8 | |
| | 4,5 | | -6.2 | | | 0.1 | |

Data for the SC thioesters are from Ref. 6 except for X = $C_3$ which are from Ref. 5.

TABLE XII

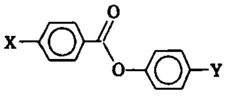
Differences in the Melting and Clearing Temperatures for

as Compared with the $C_5$ SC Diester

| BC | mp diff (°C) SC-BC | Clp diff (°C) SC-BC |
|---|---|---|
| 1,5 | 25.3 | - - |
| 2,5 | 3.3 | 43.3 |
| 3,5 | -41.4 | - - |
| 4,5 | -18.9 | 30 |

TABLE XIII

Transition Temperatures (°C) for



| X | Y | C[a] | Reference | $S_B$ | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|---|
| $C_8$ | $C_5$ | 12.9 | | | | | (23.8-24.1) | 28.2-30.1 |
| $C_{10}$ | $C_6$ | 29.7 | 8 | | | (30.8-31.0) | --- | 45.0-47.8 |
| $C_9O$ | $C_4$ | 40.7 | | | | 55.5-55.9 | 56.0-56.2 | 57.1-57.2[b] |
| $C_{10}O$ | $C_4$ | 34.8 | | | | 43.7-44.3 | --- | 60.4-61.2 |
| | $C_5$ | 37.4 | | | | (55.2-56.5) | 68.6-68.9 | 68.9-69.1[c] |
| | $C_6$[d] | 35, 36.9 | 8 | | | 56.6-57.5 | --- | 65.9-66.9 |
| $C_{14}O$ | $C_8$ | 53.4 | 8 | (59.7-60.1) | (64.2-64.5) | 69.9-70.3 | --- | 74.3-76.6 |
| $C_3$ | $OC_3$ | 41.4 | 3 | | | | (42.9-43.1) | 60.8-61.2 |
| $C_5$ | $OC_9$ | 36.3 | | | | | 45.9-48.2 | 58.3-58.4 |
| $C_9$ | $OC_{18}$ | 68.6 | 3 | | | | | 73.4-74.6 |

a. Crystallization temperature obtained using a cooling rate of 2°/min.

b. Different temperatures for this ester were reported in ref. 5.

c. Two crystal forms were observed.

d. Previously reported in ref. 5.

hindrance would be the greatest for this BC. Also, in the BC thioesters, the $S_A$ and $S_B$ phases occur in the 2,4 and 2,5 series so that if the influencing factor is steric hindrance, it would have to be less important in the thioesters than in the esters.

## EXPERIMENTAL

The 4-alkoxybenzoic acids were obtained from Frinton Laboratories or prepared by the method described in Reference 23. The 4-alkylbenzoic acids were synthesized using the method described in References 16 and 37, and the acyloxybenzoic acid as given in Reference 10. The following optically active starting materials were obtained from commercial sources: (−)-2-methylbutanol (EKC,$[\alpha]^{D}_{23}$ = 7.0° in $CHCl_3$ and (+)2-methylbutyl-benzene (Aldrich $[\alpha]^{D}_{23}$ neat = +10.7°).

All compounds were checked for purity and identification by TLC (Anal-Tech, silica gel GHLF uniplates, $CHCl_3$, UV), IR (Pye Unicam 3-200), GLC (when applicable, Varian model 3700, 3% SP-200 on 80/100 Supelcoport 6′ × 1/8″ SS column), and NMR (Varian EM360, $CCl_4$, internal TMS). Optical rotations were determined in $CHCl_3$ using a Polyscience SR6 instrument.

Transition temperatures (°C) were obtained 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 described in Reference 38. Abbreviations used for phases are C = crystal, M = mesophase, S = smectic, $S_B$ = smectic B, $S_C$ = smectic C (* indicates chiral), $S_A$ = smectic A, N = nematic, and I = isotropic liquid. Monotropic phases are indicated in tables by parentheses. The observance of these phases depended on the crystallization temperature and therefore some were not always observed. Samples were cooled at 2°/min until they crystallized (as indicated by C) so no monotropic phases before this temperature were missed. Phases were identified by typical textures observed by parallel alignment to the plate and by conoscopic studies for homeotropic alignment. DSC scans were obtained using a Perkin-Elmer DSC-2 instrument interfaced to a Digital Equipment Corporation PDP-11U-3 minicomputer.

### (+)-3-Methylpentanoylbenzene

To a stirred suspension of 78.0 g (0.58 mole) $AlCl_3$ in 250 ml anhyd benzene was added dropwise, a soln of 63.0 g (0.47 mole) of (+)-3-methylpentanoyl chloride in 50 ml benzene. The rxn mixture was refluxed 1.5 hr, cooled in an ice bath, and poured slowly into a mixture of 125 ml concd HCl and 200 ml ice. The organic layer was separated, washed with $H_2O$, 5% aq KOH and $H_2O$, dried, and filtered. The filtrate was rotovaped to give 88 g (quant) of the crude product. This material was distilled at 115° and 5.0 mm (lit b.p.[25] 118–120° at 10 mm) to give 77.2 g (93.7%) of the desired ketone [BC = 3*,5; TLC ($CHCl_3$)] showed one spot with $R_f$ = 0.63 ($R_f$ for heptanoylphenone = 0.64) and IR (film) 1675 (str C = 0) and 1600, 1580 $cm^{-1}$ (med Ar).

### (+)-3-Methylpentylbenzene

A soln of 67.1 g (0.38 mole) of the above ketone in 250 ml THF containing 10 drops of concd $H_2SO_4$ and 7.0 g of 5% Pd/C (Strem) was hydrogenated at 40–50° and 60 $lb/in^2$ for 1.75 hr. The catalyst was removed by vacuum filtration through Celite and the filtrate rotovaped to give a cloudy liquid. This material was dissolved in $Et_2O$, washed with 2 × 40 ml $H_2O$, dried, filtered, and the filtrate rotovaped to give 63.0 g (>quant) of the crude alkylbenzene. Distillation of this material at 162° (90 mm) gave 58.1 g (94.2%) of the purified alkylbenzene: TLC ($CHCl_3$) $R_f$ = 0.93 ($R_f$ for ketone = 0.78); IR (film) showed no ketone at 1675 but a weak aromatic absorption at 1610 $cm^{-1}$.

### 3-Methylpentyl bromide

Triphenylphosphine (46.2 g, 0.176 mole) was added to a stirred soln of 3-methylpentanol (15.0 g, 0.147 mole) in 40 ml $Et_2O$ containing $CBr_3$ (58.6 ml, 0.176 mole) in an ice bath at a rate which maintained a mild reflux of the solvent. Periodic shaking by hand became necessary as increasing amounts of $\phi_3PO$ precipitated. After 1 hr, GLC of an aliquot showed no alcohol was present. The precipitate was removed from the rxn mixture by filtration and washed thoroughly with hexane. The filtrate was rotovaped carefully to avoid bumping as more solid precipitated and the remaining material passed rapidly through a 2 × 3″ column of silica gel (Aldrich 60–100 mesh, grade 635) with hexane to remove additional $\phi_3PO$. The first liter of eluant was distilled to remove solvent and then at 68° (29 mm) to collect 21.6 g (89.3%) of the bromide: IR (film) showed no OH absorption but one at 650 $cm^{-1}$ (str, C-Br) and NMR (see discussion in text) showed a small amount of aromatic protons. GLC (T = 70°) of the 4-isomer prepared in this manner but using a large excess of $\phi_3PO$ showed a major peak with $t_r = 1.88$ (74.2%) and a smaller peak with $t_r = 1.63$ (24.2%) for the bromide isolated after chromatography and also after distillation.

Literature sources for data used are given in Table VIII unless otherwise noted. Corrected data for some esters previously reported are as follows: Reference 6, Table I, p. 48 $R' = R = C_6$ read $R' = C_5$, $R' = C_6$; and for $R = C_{10}$ the $S_C$ phase is enantiotropic and as given in Table XIII. We rechecked the transition temperatures for two of the $R' = C_5$ anils for Table VIII: $R = C_8$ 45.8–46.7 (S), 55.4–55.5 ($S_B$), 73.1–73.3 ($S_A$), 87.5–87.8 (I), 5.1 (C), and $R = C_9$ 37.1–38.8 (S), 64.8 ($S_B$), 75.2–75.4 ($S_A$), 88.3–88.5 (I), 3.9 (C). Our data for ester *2* with $R = C_{10}$ and $R' = CH_2CH(Me)Et$ are 39.6–41.3 ($S_A$), 41.7–42.2 (Ch), 43.9–44.1 (I), and 32.7 (C).

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