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# The Effect of Terminal Alkyl Chain Length on Mesomorphic Properties of 4-Alkoxyphenyl-4′-Alkylbenzoates

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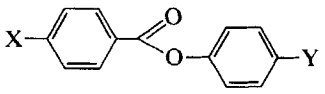
Esters in the homologous series 4-alkoxyphenyl 4′-alkylbenzoates, **1a**, have been synthesized with both straight and methyl-branched R-groups from $C_3$–$C_6$, plus *n*-$C_9$ and *n*-$C_{10}$ and with straight chain R′O-groups = $C_1$–$C_8$, $C_{10}$, $C_{12}$, $C_{14}$ and $C_{16}$. The mesophase transitions and properties were studied by hot-stage microscopy; DSC data were also determined for the R=$C_5$ series. Comparisons within the **1a** series and for some 4,4′-dialkylphenylbenzoates and 4-alkylphenyl 4′-alkoxybenzoates enable generalizations to be made regarding the liklihood of observing specific smectic mesophases as a function of structure.

## INTRODUCTION

Our initial interest in the 4,4′-disubstituted phenylbenzoates **1** was the



**1a**: X = R, Y = OR′

**1b**: X = R′O, Y = R

systematic study of the effect of methyl group substitution at various positions along a terminal alkyl chain attached directly to the aromatic ring on the mesomorphic properties of these compounds in comparison with the

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straight chain series.[1] The fact that the **1a** series seemed to possess only nematic properties up to chain lengths of R = $C_5$ and R'O = $C_8$ whereas both smectic A and nematic phases were observed in the **1b** series prompted us to further investigate the **1a** series as part of a continued interest in determining which structural features favor the formation of smectic phases.[2]

Of specific concern was to determine if this series would not form smectic phases or whether these phases had not been observed simply because the alkyl chains had not been made long enough. This required that the **1a** series be extended beyond R = $C_5$ and R' = $C_8$ and the mesomorphic properties determined. If this extended series did not show smectic phases, it would be useful to determine why this was so when the **1b** series shows smectic A phases (as well as nematics) at medium chain lengths.[1] Additionally, the increased stability of these compounds over the anils, azo and azoxybenzenes and stilbenes made it desirable to investigate these compounds as a potentially useful series of low melting liquid crystals in which the terminal substituents could be easily varied.

## RESULTS AND DISCUSSION

Only nematic phases were observed in series **1a** compounds with alkyl groups (R) from $C_3$ to $C_6$ and when the length of the alkoxy chain (R'O) was increased until mesophases no longer occurred (Table I). When the R group length was increased to $C_{10}$, both nematic (R'O = $C_1$ to $C_{10}$) as well as smectic A, C, and B(R'O $\simeq$ $C_5$ to $C_1$ ) mesophases were observed, although the temperature ranges are short (Table II). This is in contrast to the occurrence of only nematic and smectic A behavior for series **1b** (longest chain lengths were R' = $C_{10}$, R = $C_9$,[3a] and R' = $C_8$, R = $C_{10}$).[4] During the present study, the **1a** series with R = $C_9$, R'O = $C_1$ to $C_{10}$ was reported[3a] to have only nematic and smectic C phases; this data suggests similarly to series such as the alkoxybenzoic acids.[3b] We confirmed these observations but have also observed smectic A and B phases as well as smectic C phases for **1a** with with R = $C_9$, R'O = $C_{12}$–$C_{18}$ (Table III).

The plots of transition temperatures versus chain length for R = $C_5$ given in Figure 1 are characteristic for **1a** series with R $\leq$ $C_6$. The *melting* transition plot shows a minimum at R'O = $C_6$; melting of compounds with longer R'O— occurs at increasingly higher temperatures and for R'O > $C_{12}$, "crosses" the nematic-isotropic transition after which mesophase properties disappear. All **1a** compounds without branched chains have a similar minimum, although they do not always show a plot as "linear" as in Figure 1 for short R'O— chain lengths:

| R | R'O at minimum |
|---|---|
| $n$-$C_3$ | $C_5$ |
| $n$-$C_4$ | $C_6$ |
| $n$-$C_5$ | $C_6$ |
| $n$-$C_6$ | $C_4$ |
| $n$-$C_9$ | $C_5$ |
| $n$-$C_{10}$ | $C_6$ |

The minimum occurs at longer R'O— chain lengths for branches R— chains:

| R | R'O at minimum |
|---|---|
| $i$-$C_3$ | $C_{10}$ |
| $i$-$C_4$ | $C_7$ |
| $s$-$C_4$ | $C_7$ |

Such melting behavior for homologous series consisting of both a rigid (aromatic rings and "resonance-locked" central group) as well as a flexible (aliphatic chains) part should not be regarded as either unusual or unexplainable. Comparison of these data with melting curves for telomer series of varying degrees of flexibility[5,6] provide useful correlations. All aromatic

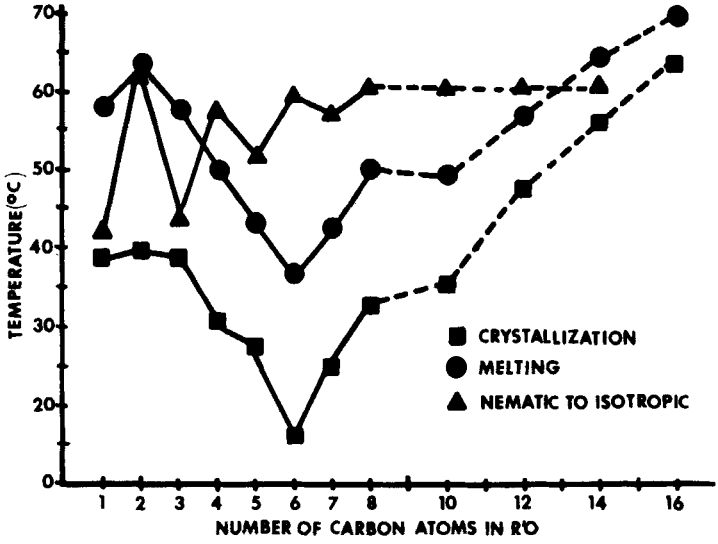



FIGURE 1 Transition temperature versus alkoxy chain length for

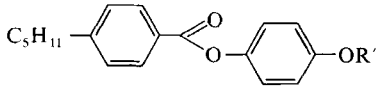
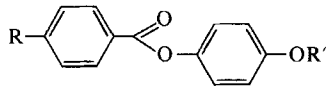


TABLE I

Transition temperatures (°C) for



| R | R′ | $C_1^a$ | $C_2^b$ | N | I |
|---|---|---|---|---|---|
| *n*-$C_3$ | $C_1$ | 38.7 | — | (40.4)[c] | 56.8–58.0 |
| *n*-$C_3$ | $C_2$ | 58.2 | — | (68.5) | 75.0–76.1 |
| *n*-$C_3$ | $C_3$ | 50.6 | — | (42.9) | 63.7–65.1 |
| *n*-$C_3$ | $C_4$ | 34.2 | — | (58.7–59.2) | 70.3–72.3 |
| *n*-$C_3$ | $C_5$ | 21.6 | — | 44.9–45.5 | 49.9 |
| *n*-$C_3$ | $C_6$ | 26.1 | — | 50.8–52.3 | 58.5–59.1 |
| *n*-$C_3$ | $C_7$ | 27.5 | — | 45.5–46.3 | 53.2 |
| *n*-$C_3$ | $C_8$ | 31.8 | — | 50.2–51.7 | 58.8–59.4 |
| *n*-$C_3$ | $C_{10}$ | 37.8 | 42.6–43.7 | 50.5–50.9 | 57.4–57.5 |
| *n*-$C_3$ | $C_{12}$ | 48.4 | — | 54.0–54.6 | 58.1 |
| *n*-$C_3$ | $C_{14}$ | 59.2 | 55.9 | (57.3)[d] | 60.9–62.9 |
| *n*-$C_3$ | $C_{16}$ | 63.1 | 65.2 | — | 66.8–68.5 |
| *i*-$C_3$ | $C_1$ | 67.6 | 88.9 | — | 96.4–98.0 |
| *i*-$C_3$ | $C_2$ | 79.3 | — | — | 105.2–106.6 |
| *i*-$C_3$ | $C_3$ | 54.4 | 82.2 | — | 84.9–90.9 |
| *i*-$C_3$ | $C_4$ | 40.0 | — | — | 79.3–81.2 |
| *i*-$C_3$ | $C_5$ | 40.1 | — | — | 69.2–70.9 |
| *i*-$C_3$ | $C_6$ | 45.5 | — | — | 53.0–54.0 |
| *i*-$C_3$ | $C_7$ | 33.3 | — | — | 51.7–54.3 |
| *i*-$C_3$ | $C_8$ | 27.5 | — | — | 47.8–50.3 |
| *i*-$C_3$ | $C_{10}$ | 34.7 | — | — | 47.0–48.3 |
| *i*-$C_3$ | $C_{12}$ | 40.0 | — | — | 50.0–54.2 |
| *i*-$C_3$ | $C_{14}$ | 45.9 | — | — | 54.3–57.9 |
| *i*-$C_3$ | $C_{16}$ | 52.5 | 57.8 | — | 60.4–64.8 |
| *n*-$C_4$ | $C_1$ | 34.8 | — | [e] | 61.7–62.6 |
| *n*-$C_4$ | $C_2$ | 38.3 | — | (51.0) | 58.0–59.7 |
| *n*-$C_4$ | $C_3$ | 33.8 | — | [e] | 64.7–65.8 |
| *n*-$C_4$ | $C_4$ | 39.8 | — | (45.3) | 46.5–47.3 |
| *n*-$C_4$ | $C_5$ | 28.6 | — | (39.2) | 39.1–40.0 |
| *n*-$C_4$ | $C_6$ | 4.9 | — | 28.9–31.6 | 48.4 |
| *n*-$C_4$ | $C_7$ | 28.2 | — | 35.7–37.1 | 46.0 |
| *n*-$C_4$ | $C_8$ | 24.8 | — | 41.8–43.6 | 51.2 |
| *n*-$C_4$ | $C_{10}$ | 37.3 | — | 44.3–45.7 | 51.2 |
| *n*-$C_4$ | $C_{12}$ | 50.0 | — | (52.0) | 54.4–55.1 |
| *n*-$C_4$ | $C_{14}$ | 55.6 | — | — | 61.8–62.6 |
| *n*-$C_4$ | $C_{16}$ | 64.9 | — | — | 67.3–68.0 |
| *s*-$C_4$ | $C_1$ | 51.4 | — | — | 81.7–85.0 |
| *s*-$C_4$ | $C_2$ | 52.5 | — | — | 81.0–85.0 |
| *s*-$C_4$ | $C_3$ | 51.1 | — | — | 79.5–82.7 |
| *s*-$C_4$ | $C_4$ | 36.6 | — | — | 56.9–58.3 |
| *s*-$C_4$ | $C_5$ | 31.1 | — | — | 46.0–50.6 |
| *s*-$C_4$ | $C_6$ | 17.9 | — | — | 44.9–46.8 |

TABLE I (continued)

| R | R′ | $C_1$[a] | $C_2$[b] | N | I |
|---|---|---|---|---|---|
| *s*-$C_4$ | $C_7$ | 7.8 | — | — | 27.7–30.2 |
| *s*-$C_4$ | $C_8$ | 17.5 | — | — | 33.0–34.3 |
| *s*-$C_4$ | $C_{10}$ | 29.7 | — | — | 38.1–40.8 |
| *s*-$C_4$ | $C_{12}$ | 40.7 | — | — | 47.5–48.3 |
| *s*-$C_4$ | $C_{14}$ | 44.7 | 48.5 | — | 54.5–55.3 |
| *s*-$C_4$ | $C_{16}$ | 55.6 | — | — | 60.5–61.4 |
| *i*-$C_4$ | $C_1$ | 47.4 | — | [e] | 67.6–69.0 |
| *i*-$C_4$ | $C_2$ | 49.0 | — | [e] | 78.9–79.7 |
| *i*-$C_4$ | $C_3$ | 28.1 | — | [e] | 65.2–67.5 |
| *i*-$C_4$ | $C_4$ | 3.4 | — | 40.1–42.1 | 43.7 |
| *i*-$C_4$ | $C_5$ | 6.9 | — | (36.7) | 38.8–40.0 |
| *i*-$C_4$ | $C_6$ | 27.0 | — | (44.0) | 48.0–49.9 |
| *i*-$C_4$ | $C_7$ | 18.6 | — | 38.3–39.5 | 39.7 |
| *i*-$C_4$ | $C_8$ | 30.8 | — | 41.2–43.2 | 44.4 |
| *i*-$C_4$ | $C_{10}$ | 31.9 | — | 39.4–40.4 | 43.8 |
| *i*-$C_4$ | $C_{12}$ | 42.0 | — | (44.9) | 53.4–54.1 |
| *i*-$C_4$ | $C_{14}$ | 50.4 | — | [e] | 60.4–61.1 |
| *i*-$C_4$ | $C_{16}$ | 58.4 | — | — | 65.6–66.6 |
| *n*-$C_5$ | $C_1$ | 38.6 | — | (42.2) | 57.0–57.9 |
| *n*-$C_5$ | $C_2$ | 39.6 | — | 61.2–63.0 | 63.4 |
| *n*-$C_5$ | $C_3$ | 38.6 | — | (44.0) | 56.0–57.3 |
| *n*-$C_5$ | $C_4$ | 30.5 | — | 48.4–49.6 | 57.7 |
| *n*-$C_5$ | $C_5$ | 27.5 | — | 42.0–42.8 | 51.8 |
| *n*-$C_5$ | $C_6$ | 15.9 | — | 34.2–36.4 | 59.9 |
| *n*-$C_5$ | $C_7$ | 25.1 | — | 40.5–42.2 | 57.4 |
| *n*-$C_5$ | $C_8$ | 32.7 | — | 49.0–49.8 | 60.6 |
| *n*-$C_5$ | $C_{10}$ | 35.3 | — | 48.1–49.0 | 60.3 |
| *n*-$C_5$ | $C_{12}$ | 47.7 | — | 56.0–56.5 | 60.6 |
| *n*-$C_5$ | $C_{14}$ | 56.1 | — | (60.9) | 63.5–64.6 |
| *n*-$C_5$ | $C_{16}$ | 63.9 | — | [e] | 68.5–69.9 |
| *n*-$C_6$ | $C_1$ | 31.1 | — | [e] | 63.2–65.2 |
| *n*-$C_6$ | $C_2$ | 32.9 | 52.0 | (51.8) | 55.7–56.4 |
| *n*-$C_6$ | $C_3$ | 36.2 | — | (33.2)[d] | 57.3–59.8 |
| *n*-$C_6$ | $C_4$ | 25.4 | 24.1 | 39.7–40.2 | 49.4 |
| *n*-$C_6$ | $C_5$ | 30.8 | 28.8 | 41.6–42.5 | 45.0 |
| *n*-$C_6$ | $C_6$ | 30.0 | — | 45.4–46.3 | 53.2 |
| *n*-$C_6$ | $C_7$ | 34.9 | 33.3 | 48.4–49.1 | 51.5 |
| *n*-$C_6$ | $C_8$ | 29.9 | — | 44.4–45.3 | 56.7 |
| *n*-$C_6$ | $C_{10}$ | 37.0 | — | 44.5–45.5 | 57.3 |
| *n*-$C_6$ | $C_{12}$ | 45.5 | — | 54.8–55.6 | 58.3 |
| *n*-$C_6$ | $C_{14}$ | 54.7 | — | (58.2) | 62.2–63.5 |
| *n*-$C_6$ | $C_{16}$ | 62.5 | — | [e] | 67.8–69.1 |

[a] $C_1$ = crystallization temperature on cooling at 2°/min.

[b] $C_2$ = crystal-to-crystal transition on heating $C_1$; not all such transitions were recorded.

[c] Parentheses indicate monotropic transition.

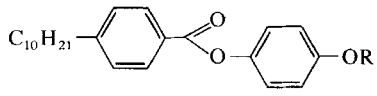
[d] Transition observed only on cooling at 10°/min.

[e] No mesophases were observed on cooling either at 2 or 10°/min.

[f] The R=$C_6$, R′=$C_1$-$C_{10}$ series has also been reported in Ref. 3a.

TABLE II

Transition temperatures for



| R′ | C[a] | $S_B$ | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|
| $C_1$ | (42.1) | | | | (43.1)[b,c] | 62.4–64.3[d] 52.3–53.5[e] |
| $C_2$ | (56.3) | | | | (58.5) | 61.5–62.2 |
| $C_3$ | (40.2) | | | | (45.0) | 60.2–61.3[d] 53.6[e] |
| $C_4$ | (31.6)[f] (34.9) | | | | 45.9–46.1 48.0–48.9 | 55.7 |
| $C_5$ | (31.5) | | | (42.4) | 52.2–52.5 | 52.51[g] |
| $C_6$ | (30.4) | (33.5–33.6) | | 43.5–44.1 | 47.7 | 59.0 |
| $C_7$ | (39.5) | (38.2)[h] | (40.0–40.6) | (51.7) | 51.5–52.8 | 58.6–58.7 |
| $C_8$ | (40.4) | (40.3 40.5)[h] | (52.4) | 55.1–55.2[i] | 55.9 | 62.5 |
| $C_{10}$ | (45.2) | (45.9)[c,h] | (60.2–60.5) | 61.3–61.4[i] | 62.1 | 64.5 |
| $C_{12}$ | (46.9) | (51.0) | (64.1) | 64.3–64.5 | | 65.6–65.7 |
| $C_{14}$ | (55.2) | (57.8–58.1) | 63.7–65.2 | | | 66.4–66.7 |
| $C_{16}$ | (62.5) | (64.1–64.2) | 67.1–67.2 | | | 68.9–69.6 |
| $C_{18}$ | (67.7) | | | | | 73.9–74.4 |

[a] C = crystallization temperature obtained on cooling 2°/min.

[b] ( ) indicates monotropic transition.

[c] A heating transition temperature could not be obtained for this phase before crystallization occurred.

[d] Temperature obtained on heating from fresh crystals.

[e] Temperature obtained on heating crystals formed on cooling the isotropic liquid.

[f] Two crystal forms were observed on cooling which gave the nematic phase on heating at two different temperatures.

[g] This phase has an extremely narrow range.

[h] Observed only when cooled 10°/min. and then immediately reheated.

[i] Enantiotropic only if heated 0.2°/min.

(rigid) systems are higher melting, and their curves rise steeply as aromatic increments are added. All-aliphatic (flexible) systems have much lower melting points and a gradual rise with added increments. The present ester system is more like the aromatic telomer system for very short R— and R′O— chains, but since the increments are added-$CH_2$-groups, melting points decrease to a minimum with "change-over" to an aliphatic-like telomer system, then rise gradually with additional increments.

It is also reasonable that branched R— chain series have their melting minima for somewhat longer R′O— chains since the branched groups are more rigid than straight chains. The minima in the melting point curves for the **1b** series occur with greater regularity at R′O — = $C_5$, *including* branched chain homologs:[4]

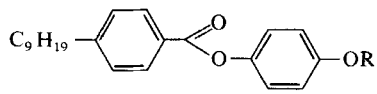
| R | R′O at minimum |
|---|---|
| $C_3$ | $C_5$ |
| $C_4$ | $C_5$ |
| $C_5$ | $C_5$ |
| $C_{10}$ | $C_6$ |
| $CH(CH_3)CH_2CH_3$ | $C_5$ |
| $CH_2CH(CH_3)_2$ | $C_5$ |
| $CH_2CH(CH_3)_2$ | $C_5$ |
| $CH(CH_3)CH_2CH_2CH_3$ | $C_8$ |
| $CH_2CH_2(CH_3)CH_2CH_3$ | $C_5$ |
| $CH_2CH_2CH(CH_3)_2$ | $C_4$ |

Thus branching variations of the alkyl (R—) group on the phenol moiety (in the **1b** series) is of less consequence than on the carboxylate moiety (i.e., the **1a** series) toward disturbing intermolecular forces and resulting in lower melting temperatures.

Examples of typical plots of the nematic-to-istotropic transition temperatures versus alkoxy chain lengths for $R \leq C_6$ are given in Figure 2 ($R = C_3, C_6$). All such plots showed an in-phase odd-even alternating effect diminishing with increasing alkoxy chain length. There seems to be little

TABLE III

Transition temperatures for




| R | C[a] | $S_B$ | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|
| $C_1$[b] | | | | | (46)[c] | 53 |
| $C_2$ | | | | | 54 | 61 |
| $C_3$ | | | | | (48) | 54 |
| $C_4$ | | | | | 45 | 59 |
| $C_5$ | | | | | 40 | 56 |
| $C_6$ | | | (34) | | 43 | 62 |
| $C_7$ | | | (41) | | 46 | 61 |
| $C_8$ | | | (48) | | 53 | 64 |
| $C_9$ | | | (52) | | 54[b] | 63 |
| $C_{10}$ | | | (56)[b] | | 57[b] | 66[b] |
| | (41.6) | | (57.9) | | 58.3–58.7 | 65.8 |
| $C_{12}$ | (46.7) | (47.5) | 61.4–62.1 | 63.0–63.1 | 63.7–63.8 | 66.4–66.5 |
| $C_{14}$ | (54.5) | (55.7) | 63.0–63.7 | 65.4 | | 66.8 |
| $C_{16}$ | (61.6) | (61.8–61.3)[d] | (66.1–66.4) | (66.8–67.6) | | 69.1–69.4 |
| $C_{18}$ | (68.6) | | | | | 63.4–74.6 |

[a] C = crystallization temperature obtained on cooling 2°/min.

[b] Values for $C_1$–$C_{10}$ obtained from Ref. 3a.

[c] ( ) indicates monotropic transition.

[d] A heating transition temperature could not be obtained for this phase before crystallization occurred.

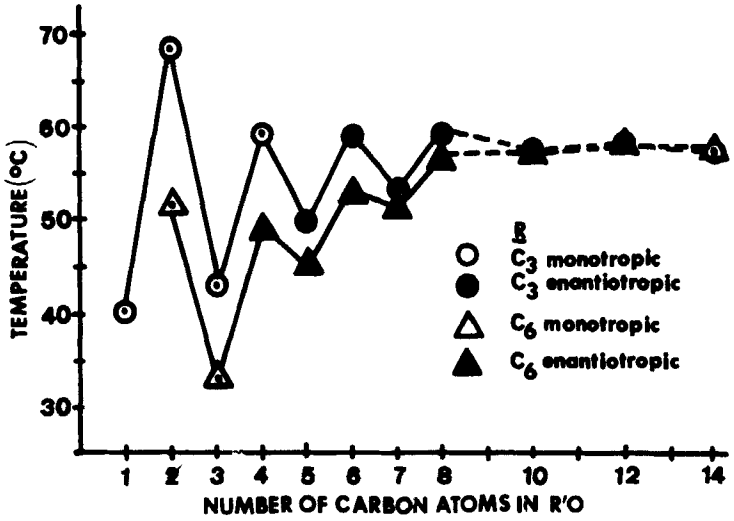
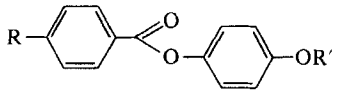



FIGURE 2 Nematic-to-isotropic transition temperatures versus alkoxy chain length for




effect on increasing the alkyl chain length of R for either the nematic-isotropic or the melting transitions, however. Branched chain R groups lower both of these transition temperatures without changing these trends.

Higher transition temperatures were expected for the **1b** series relative to the **1a** series since "through-resonance" conjugation of the R'O— and acyl group should increase the polarizability of the system, therefore providing stronger London forces. This expectation was born out both for the nematic-isotropic transition (Figure 3; data from Ref. 3a and 4) and for the melting temperatures (Figure 4) of straight chain derivatives; usually the greatest difference was observed for the melting transition of comparable members of each series. Owing to large and somewhat irregular excursions for the melting transitions of successive members of the **1b** series, a simple statement cannot be made about the nematic range of these two series; thus some **1a** have a wider nematic range than the comparable **1b** (Ex., $R = C_5$, $R'O = C_6$) despite the generally higher thermal stability for the nematic phase of the **1b** series. The effect of a branched chain R— group on the overall "rigidity" in the **1a** series, as mentioned above, is even sufficient to overturn the expectation of higher melting temperatures in the **1b** series (Figure 5). Such branching does *not*, however, raise the nematic-isotropic transition in the **1a** series relative to the **1b** series.

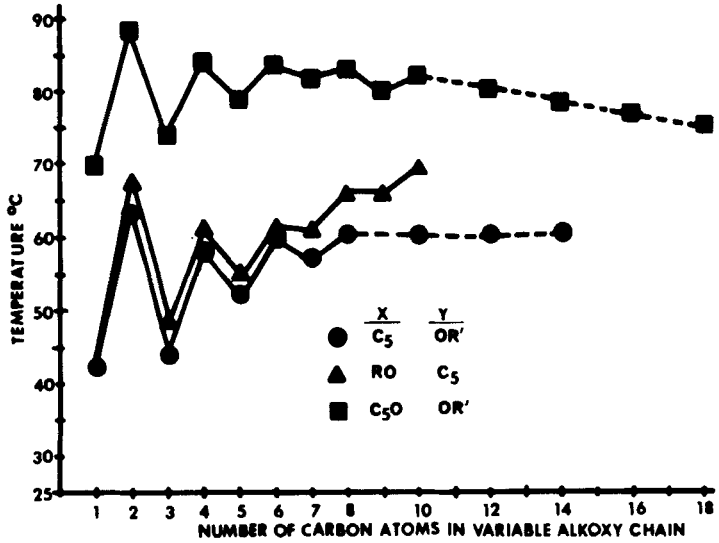
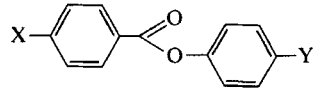



FIGURE 3 Nematic-to-isotropic transition temperatures versus alkoxy chain length for



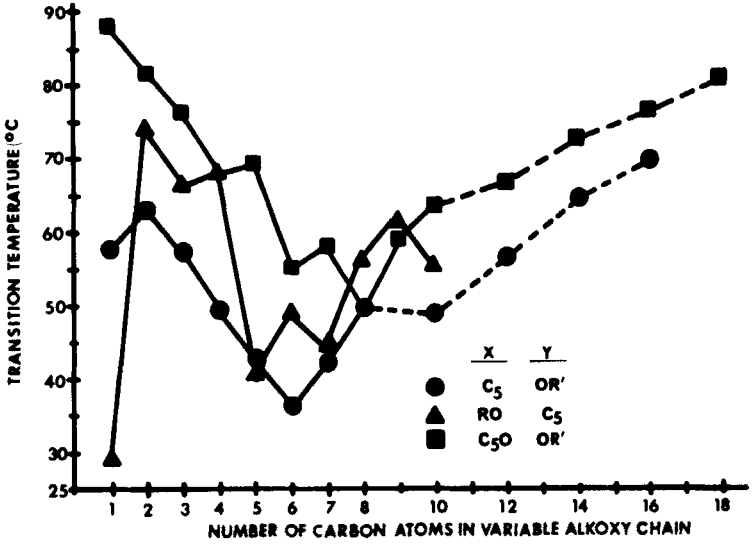
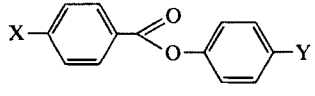




FIGURE 4 Melting temperatures versus alkoxy chain length for



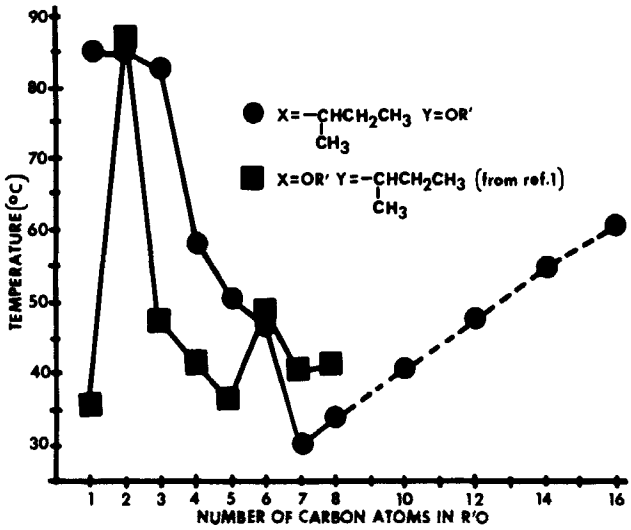



FIGURE 5 Melting temperatures versus alkoxy chain length for

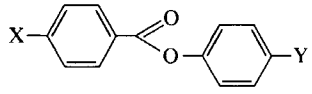
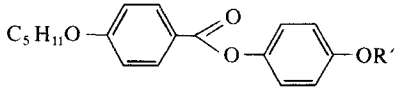


TABLE IV

Transition temperatures (°C) for



| R′ | C[a] | N | I |
|---|---|---|---|
| $C_6$ | (46.2)[b] | 55 | 84[c] |
| $C_8$ | (42.8) | 49 | 83[c] |
| $C_{10}$ | (57.4) | 63.0–63.4 | 82.0 |
| $C_{12}$ | (54.7) | 65.4–66.6 | 80.0 |
| $C_{14}$ | (62.6) | 71.4–72.5 | 78.2 |
| $C_{16}$ | (71.8) | 76.1–76.4 | 76.5 |
| $C_{18}$ | (75.9) | (74.7)[d] | 80.0–80.8 |

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

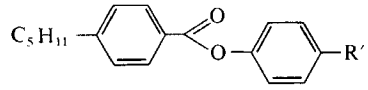
[b] ( ) indicates a monotropic transition temperature.

[c] Reported in Ref. 7.

[d] Obtained on cooling 10°/min; a heating transition temperature could not be obtained before crystallization occurred.

TABLE V

Transition temperatures of



| R′ | C | N | I |
|---|---|---|---|
| $C_1$ | (4.3) | (15.2) | 44.3–45.4 |
| $C_2$ | (−6.5) | (−0.6) | 25.2–26.2 |
| $C_3^c$ | (−3.5) | (2.7) | 18.7 |
| $C_4^c$ | (−20°)[a] | | −7.2 to −4.2 |
| $C_5$ | (20.9) | (25.9) | 33.4–34.8 |
| $C_6$ | (23.1) | | 31.2–33.5 |
| $C_8$ | | (24) | 32[b] |
| $C_9$ | (34.9) | | 35.4–35.9 |

[a] Crystals formed only when cover slide was moved.
[b] Data from Ref. 9.
[c] Materials not purified.

Data are also plotted in Figures 3 and 4 for the related 4′-alkyloxyphenyl 4-pentyloxybenzoate series (Ref. 7 and Table IV) to compare with the **1a** and **1b** series; insufficient data were available to include plots for the dialkyl ester series (see Table V). As can readily be seen, the corresponding transition temperatures are higher for the dialkoxy members than for **1a** and **1b**; melting data show parallel trends (i.e. fall and then rise) but with a minimum $\cong R'O = C_8$. The nematic-isotropic plot shows a gentle fall-off with succeeding members beyond $R'O \simeq C_6$. Simple inspection of the data for the 4′-alkylphenyl 4-pentylbenzoates (Table V) suggests that the melting point minimum may be at $R' = C_4$ (note lower purity for these materials, however.) Although data are still incomplete, we do not expect to observe smectic behavior for the dialkyl esters.

A plot of the nematic phase temperature range versus R′O— chain length for straight chain **1a** series compounds (heating data, Figure 6) illustrates that the maximum nematic range (25.7°) occurs for these compounds when $R = C_5$, $R'O = C_6$ and decreases for either shorter or longer alkyl (R) chains. The nematic range can be increased for mixtures, as expected; two examples are illustrated by Figures 7 and 8. These transition temperature versus composition diagrams were prepared from data obtained with the polarizing microscope (heating previously melted and re-frozen mixtures, see Experimental) and probably do not represent temperatures which would be observed for true equilibrium conditions.

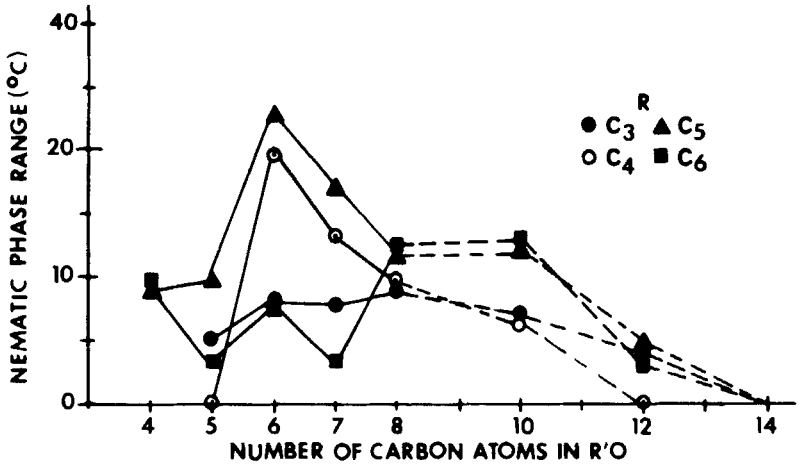
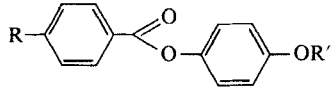



FIGURE 6 Nematic phase range versus alkoxy chain length for



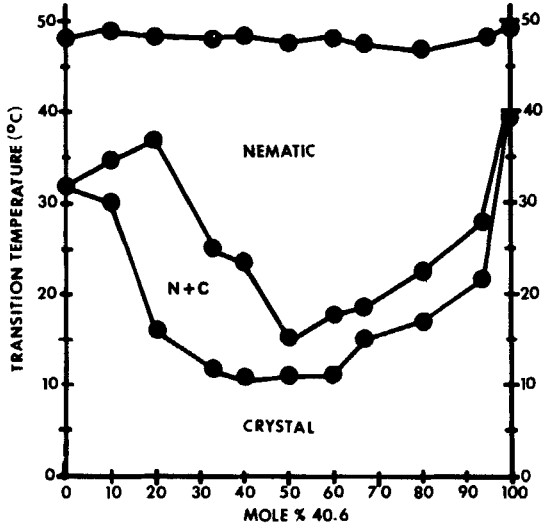




FIGURE 7 Transition temperatures versus composition diagram for mixtures of 40.6 in 60.4.

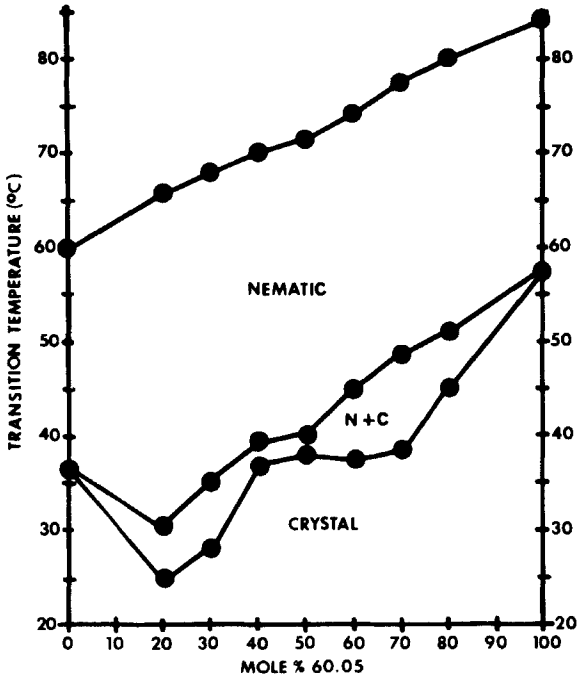


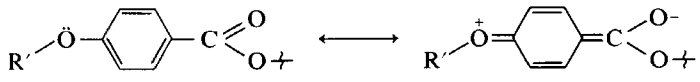

FIGURE 8 Transition temperature versus composition diagram for mixtures of 60.05 in 60.5.

The diagram for mixtures of 40.6 (**1a**, R = $C_6$, R′O = $C_4$; see Ref. 1 for the explanation of these numerical abbreviations) with 60.4 (**1a**, R = $C_4$, R′O = $C_6$) in which the two end carbon chains are interchanged shows a minimum for melting at the $\simeq$50 mole percent composition and with a nematic range $\sim$32.5°. As is usually the case for such mixtures of closely related isomers, the nematic-isotropic transition temperatures are not appreciably lowered but melting temperatures are significantly depressed. Two separate crystalline phases as well as a nematic phase were identifiable within the mixed phase region for 10 and 20 mole percent 40.6. Crystalline material persisted to temperatures *above* the melting point of pure 60.4 for the 10 and 20 mole percent 40.6; this was reproducible but probably reflects non-equilibrium conditions, i.e. a heating rate of 2°/min. was too high. Only one crystalline phase could be detected for 30 mole percent 40.6 and greater.

The transition temperature *vs* composition diagram for mixtures of a **1a** series ester (60.4; R = $C_5$, C′O = $C_6$) with a dialkoxy ester (60.05; X = $C_5O$, Y = $C_6O$) is given in Figure 8. The lowest melting temperature was observed for the 20 mole percent 60.05 composition which also coincided with the largest nematic range ($\sim$35.4°). These compounds appeared

to be more miscible than did the 40.6/60.4 mixture; separate crystal forms were not simultaneously present and the mixed phase region was narrower throughout all compositions. The extremely narrow range of the mixed phase region for the ~50 mole percent composition and the shape of the melting curve there suggests the possibility of compound formation.

Smectic phases were not observed in **1a** series esters when $R \leq C_6$, $R'O \leq C_{16}$, although smectic A phases were present for **1b** esters with $R = C_8$, $R'O \geq C_3$.[1,4] The early appearance of smectic phases in **1b** esters is consistent with the belief that these mesophases result when strong lateral intermolecular attractive forces[10–12] are associated with the aromatic core and in this instance represent the large dipole contributed by "through-resonance" in the alkoxybenzoate moiety; i.e. **ii** is an important



**i** **ii**

contributor to the electronic structure of these compounds. This is not possible in the **1a** series; the appearance of smectic phases only when *longer* end chains are present must be due to the additional intermolecular attraction resulting from their polarizability. The smaller permanent dipoles of the carbonyl and ether linkages in the **1a** series are insufficient in themselves to induce smectic behavior for short end chains.

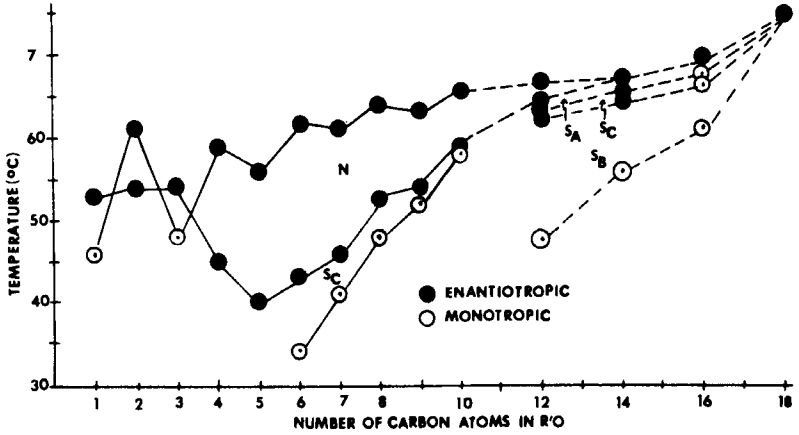
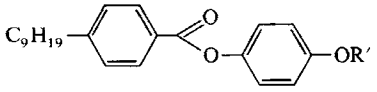



FIGURE 9 Transition temperatures versus alkoxy chain length for



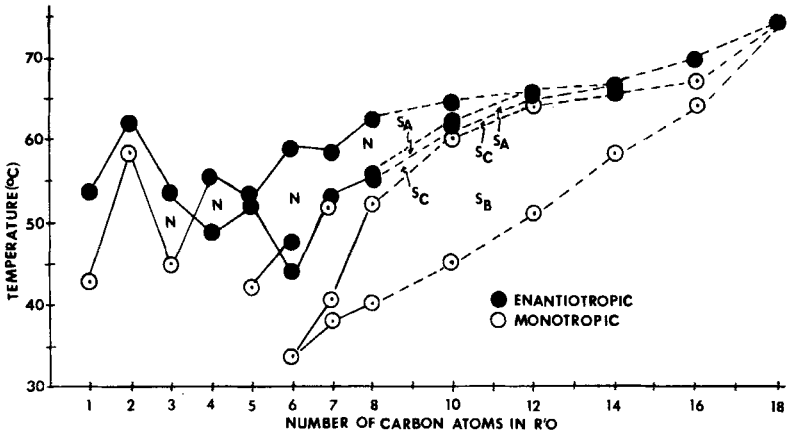
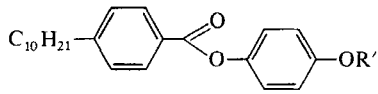



FIGURE 10 Transition temperatures versus alkoxy chain length for




(somewhat simplified, see Table II).

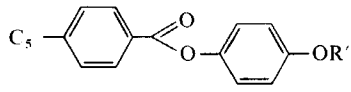
Smectic A phases predominate in the **1b** series esters with the longest chains reported being R = $C_9$, R′O = $C_{10}$[3a] and R = $C_{10}$, R′O = $C_8$[4] although we have found a short range monotopic smectic C phase for R = $C_{10}$, R′O = $C_{12}$ [72.9–74.2° (C → $S_A$), 75.2–75.4° ($S_A$ → 1), (65.6–66.0°)($S_C$ → $S_A$), and 65.1° ($S_C$ → C)]. Smectic C phases are predominant in the **1a** series, however, in which R = $C_9$ and $C_{10}$. Both series then show multiple smectic phases (A, C and B) of short range with longer R′O chain lengths (Figures 9 and 10. The latter is somewhat simplified; see Table II).

The smectic C phases in these compounds appear to have temperature dependent tilt angles as shown by the subtle continuous changes observed in their microscope textures. The smectic B phases showed a uniaxial cross in conoscopic studies and transition bars between smectic A or C and smectic B phases (see Ref. 2 for typical texture photographs).

The appearance of smectic C for lower homologs (R′O = $C_6$–$C_{10}$) *before* smectic A (R′O ≥ $C_{11}$), in the **1a**, R = $C_9$ series, is unusual. Presumably the balance between dipole placement and molecular shape permits a tilted packing arrangement with higher order until a certain chain length is reached. The smectic A phase range is, however, extremely narrow and for R′O ≥ $C_{12}$, the more ordered smectic B phase predominates. It seems apparent that a more subtle interplay of intermolecular forces is present for the **1a** series than for the **1b** series. The strong dipole owing to "through-resonance" and already remarked upon for the **1b** series must play a dominant role and the lack of polymorphism here must be closely related. Further

TABLE VI

Thermodynamic values (from DSC) for mesophase transitions for



| R′ | Melting ΔH (kcal/mole) | Melting ΔS (cal/mole/°K) | Nematic to isotropic ΔH (kcal/mole) | Nematic to isotropic ΔS (cal/mole/°K) |
|---|---|---|---|---|
| $C_1$ | 6.77 | 20.5 | 0.144 | 0.456 |
| $C_2$ | 7.97 | 23.8 | 0.195 | 0.579 |
| $C_3$ | 6.33 | 19.2 | 0.140 | 0.441 |
| $C_4$ | 6.23 | 19.4 | 0.175 | 0.529 |
| $C_5$ | 4.68 | 14.8 | 0.146 | 0.449 |
| $C_6$ | 3.69 | 12.0 | 0.222 | 0.666 |
| $C_7$ | 6.01 | 19.2 | 0.216 | 0.653 |
| $C_8$ | 6.62 | 20.5 | 0.249 | 0.746 |

speculation concerning the role molecular structure must play in determining the differences in smectogenic behavior between the two series must await more detailed physical measurements which elucidate both intermolecular packing arrangements and molecular distances.

The nematic-to-isotropic transition temperature curves for the $C_9$ and $C_{10}$ series show the normal odd-even alternating effect as did the shorter chain series but now there is a gradual rise in these transition temperatures with increasing R′O— chain length. As for the shorter R— chain series, the melting temperatures show a minimum at R′O = $C_5$ (R = $C_9$) and R′O = $C_6$ (R = $C_{10}$) and then rise rapidly.

Transition enthalpies were determined (DSC) and are presented together with calculated transition entropies for the **1a** series, R = *n*-$C_5$, R′O = $G_1$–$C_8$ in Table VI. These entropy values are presented as a plot against R′O— carbon number in Figure 11 (nematic-isotropic transition) and Figure 12 (melting transition) as well as similar data for the two **1b** series R = *n*-$C_5$ and R = 2-methylbutyl (R′O from $C_1$ to $C_8$).

The odd-even alternation for ΔS but with nearly "flat" slope until after R′O > $C_5$, then rapid increase, for the nematic-isotropic transition of the **1a** set (Figure 11) is quite typical for homologous series of nematogenic compounds. The reasonable argument that this represents the effect of increasing flexibility for longer alkyl chains has been presented,[13] i.e. greater disorder, or increased freedom, results for the isotropic liquid relative to the nematic phase.

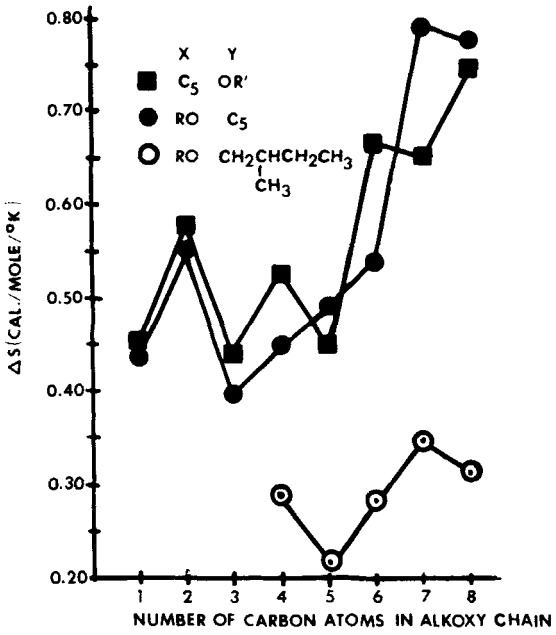
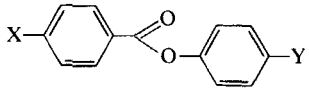



FIGURE 11 $\Delta S$ values for nematic to isotropic transition versus alkoxy chain length for




Two perturbations in the comparable plot for the **1b** series (Figure 11) are worthy of note; there is an initial downward trend in $\Delta S$ values (for R'O = $C_1$ to $C_4$), then a short "linear" section (for R'O = $C_3$ to $C_6$) before the sharp rise which parallels that for the **1a** set (one must as usual, ignore the odd-even alternating effect in making this observation). The initially lower $\Delta S$ values may reflect the increased molecular rigidity (present in *both* phases) due to "through-resonance" between R'O and acyl (i.e. large contribution of **ii**, see earlier discussion of this feature). When the R'O— length reaches $C_5$, the tendency to greater freedom of rotation in the isotropic phase may reduce such "through-resonance" interaction. This would be reflected in an "abnormal" rise in $\Delta S$ for this homolog (fortuitously resulting in a linear plot) following which behavior is no different than for the **1a** series.

The lower nematic-isotropic transition entropies for the R-branched **1b** series reflects a lesser difference between the freedom of the end chains in the two phases.[4] One may qualitatively relate this to a less closely packed

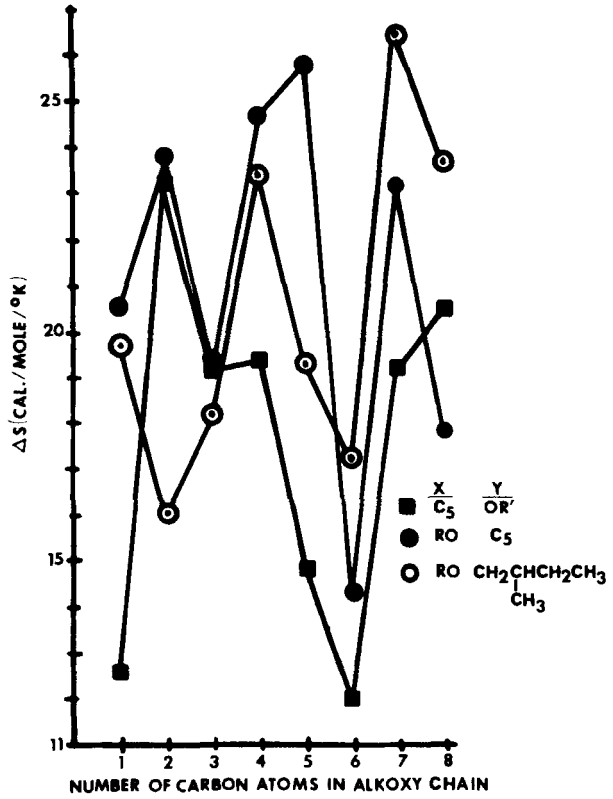
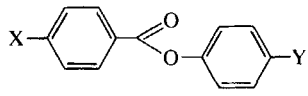



FIGURE 12 $\Delta S$ values for melting versus alkoxy chain length for




structure in the nematic phase than would exist without the branching (this reduces attractive forces, i.e., lower $\Delta H$).[1,4] Further, the branched end would have fewer conformational possibilities in *both* phases.

Point-by-point analysis of the entropy data for melting (Figure 12) in these series is not practical since the higher phase is not always the same (e.g. R'O $\simeq$ $C_8$ is nematic in **1a** series but smectic A in the **1b**). It is interesting to note the grossly parallel trends in $\Delta S$ for similar R'O— chain lengths from $C_5$ through $C_7$ for the 4'-(2-methylbutyl)phenyl 4-alkoxybenzoates as well as for the **1a** and **1b** series, however. This suggests that for these closely related compounds, assuming that ordering in the crystalline state is quite similar, then melting involves the same kind of disordering.

## CONCLUSIONS

It is well known that long terminal alkyl chains on mesogenic compounds tend to favor formation of smectic rather than nematic phases.[10] The data presented here for several homologous series of phenyl benzoates substituted with alkyl and alkoxy end groups indicate that the kind of interaction between the end group and the core portion of the molecule plays an important role in determining the effect of increased length in the end group. Thus "through-resonance" limits conformational possibilities for the end group and adds to core rigidity whereas branching can both weaken intermolecular attractive forces and alter conformational freedom of the end group.

Comparison of the mesomorphic properties of the **1a** and **1b** series of phenylbenzoate esters suggests that "early" (e.g. short end groups) appearance of smectic behavior may occur when a very strong dipole is present in the core but that polymorphic behavior is more likely when there are several weaker dipoles in the central core. The liklihood of polymorphic behavior is also concommitant with the increasing importance of London forces for the longer chain members of the series. The relationship between alkoxy chain length and the type of mesophase observed for **1a** members with R = $C_9$ and $C_{10}$ may be summarized:

| Phase | R=$C_9$ R′ | R=$C_{10}$ R′ |
|---|---|---|
| N | $C_1$–$C_{12}$ | $C_1$–$C_{10}$ |
| $S_A$ | $C_{12}$–$C_{16}$ | $C_5$–$C_{12}$ |
| $S_C$ | $C_6$–$C_{16}$ | $C_7$–$C_{16}$ |
| $S_B$ | $C_{12}$–$C_{16}$ | $C_6$–$C_{16}$ |

## EXPERIMENTAL

4-Alkoxybenzoyl chlorides and 4-alkoxyphenols were prepared as described in Ref. 14; 4-alkylbenzoyl chlorides as in Ref. 15, 4-alklyl phenols as in Refs. 1 and 16 and the esters as described in Ref. 1. The esters were recrystallized three times from abs. EtOH; structure determinations of intermediates and the esters are described in the preceding references.

Transition temperatures and textures were determined using a Leitz–Wetzler Ortholux polarizing microscope fitted with a calibrated, modified[17] Mettler FP–2 heating stage at a heating rate of 2°/min unless otherwise noted. Both fan and pseudoisotropic textures (conoscopic studies) were used for identifying smectic phases. Identification of phases have not been

cross-confirmed by admixture studies. Additional details on the methods used and examples of the textures observed can be found in Ref. 2.

Samples for mixture studies were prepared by melting together the appropriate amounts of each ester. This melt was sandwiched between a slide and a cover slip, cooled to the crystalline phase during which approximate transition temperatures were obtained and then reheated at 2°/min to obtain the reported values.

DSC analyses for the $C_5$ series were determined using a Perkin-Elmer DSC-1B instrument at a heating rate of 2.5°/min. Peak areas were determined using a planimeter from which $\Delta H$ values were obtained. $\Delta S$ values were calculated from these.



## Acknowledgements

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