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Emergence of Nematic Phase in Purely Smectogenic Alkyl 4-(4-Substituted Benzylideneamino)benzoates by Chain Branching of the Ester Alkyl Group

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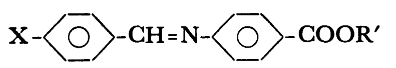
Synopsis. 2-Methylation of the ester butyl and pentyl groups in the phenyl-substituted compounds and also of the ester propyl, butyl, and pentyl groups in a number of the alkoxy-substituted compounds resulted in the production of nematic liquid crystals.

Gray and Harrison systematically studied the effects of branching of alkyl chain on the liquid crystalline behavior of 4-(4-substituted benzylideneamino)cinnamates.[1,2] Methylation at any carbon of the ester alkyl chain was found to decrease liquid crystal stability. They noted that branching has a greater effect on nematic than on smectic thermal stability. However, there may be cases where nematic liquid crystals arise by partial destruction of smectic ordered arrangement due to methylation of the alkyl chain as subtle changes in molecular structure can strongly influence the liquid crystalline behavior. Thus, we began a study of the effects of chain branching specifically paying attention to such a possibility. In this note, we wish to report the formation of nematic liquid crystals by 2-methylation of alkyl chains (R′) in fourteen purely smectogenic compounds of the following type.



The mesogenic compounds first studied by us were alkyl 4-(4-phenylbenzylideneamino)benzoates (X=Ph) which are closely related in molecular structure to the compounds studied by Gray and Harrison. The ethyl and isopropyl esters are purely smectic in behavior. Stable nematic and smectic A phases are given by the propyl ester. As the butyl and pentyl esters exhibit only smectic properties, search for nematic phases was undertaken with all the possible methylbutyl and methylpentyl esters. The emergence is limited to the 2-methyl derivatives. The transition temperatures determined by differential scanning calorimetry are presented in Table 1 together with those of the unbranched alkyl esters. The mesophases were identified by examination of their textures with the aid of a polarizing microscope in conjunction with a heated stage.

Further examples were provided by some alkyl 4-(4-alkoxybenzylideneamino)benzoate (X=RO) series. The alkoxyl group includes all the members from methoxyl to decyloxyl. Among the propyl esters, the first two members are nematogenic, whereas the higher members are purely smectogenic (see Table 2).

We have found that five members from the propoxy to heptyloxy derivatives in the isobutyl esters exhibit nematic behavior. As in shown in Table 2, the nematic phase in the propoxy derivative is monotropic. Nevertheless, the temperature range of existence is as wide as 12 °C in this compound, and progressively decreases with lengthening of the alkoxyl group. Above octyloxy derivative a smectic A phase becomes the only observable mesophase. Thus, none of the isobutyl esters gives smectic B phase found with most of the propyl esters.

The butyl 4-(4-alkoxybenzylideneamino)benzoate series has been examined by Fishel and Patel.[3] The methoxy derivative gives no mesophase but a metastable smectic A phase is observable with the ethoxy derivative. All the higher members were reported to be purely smectic in behavior. The methoxy and ethoxy derivatives of the racemic 2-methylbutyl esters examined by us form nematic liquid crystals (see Table 3); however, the higher members give only smectic A

Table 1. Transition temperatures (°C) for alkyl 4-(4-phenylbenzylideneamino)benzoates

Ester alkyl group	Transition temperatures[a]
Butyl	$C \xrightarrow{91} S_B \xleftrightarrow{98} S_A \xleftrightarrow{\quad 121 \quad} I$
2-Methylbutyl	$C \xrightarrow{77.5} S_B \xleftrightarrow{88} S_A \xleftrightarrow{110} N \xleftrightarrow{112} I$
Pentyl	$C \xrightarrow{84.5} S_B \xleftrightarrow{94.5} S_A \xleftrightarrow{\quad 123 \quad} I$
2-Methylpentyl	$C \xrightarrow{75} S_B \xleftrightarrow{80.5} S_A \xleftrightarrow{106} N \xleftrightarrow{113} I$

a) C, S_B, S_A, N, and I stand for crystalline, smectic B, smectic A, nematic, and isotropic phases respectively.

Table 2. Transition temperatures (°C) for propyl and isobutyl 4-(4-substituted benzylideneamino)benzoates

Substituent	Propyl esters	Isobutyl esters
Propoxyl	$C \xrightarrow{58} S_A \xleftrightarrow{70.5} I$	$\begin{tikzcd} C \arrow[rrr, "74.5"] & & & I \\ & S_A \arrow[ul] \arrow[r, leftrightarrow, "56.5"] & N \arrow[ur, leftrightarrow, "68.5"'] & \end{tikzcd}$
Butoxyl	$\begin{tikzcd} C \arrow[rr, "55"] & & S_A \arrow[rr, leftrightarrow, "90"] \arrow[dl, leftrightarrow, "47.5"] & & I \\ & S_B \arrow[ul] & & & \end{tikzcd}$	$C \xrightarrow{74} S_A \xleftrightarrow{74.5} N \xleftrightarrow{80} I$
Pentyloxyl	$\begin{tikzcd} C \arrow[rr, "56.5"] & & S_A \arrow[rr, leftrightarrow, "85"] \arrow[dl, leftrightarrow, "36.5"] & & I \\ & S_B \arrow[ul] & & & \end{tikzcd}$	$C \xrightarrow{66} S_A \xleftrightarrow{71} N \xleftrightarrow{75} I$
Hexyloxyl	$\begin{tikzcd} C \arrow[rr, "61"] & & S_A \arrow[rr, leftrightarrow, "91"] \arrow[dl, leftrightarrow, "38"] & & I \\ & S_B \arrow[ul] & & & \end{tikzcd}$	$C \xrightarrow{59.5} S_A \xleftrightarrow{77} N \xleftrightarrow{79.5} I$
Heptyloxyl	$\begin{tikzcd} C \arrow[rr, "62.5"] & & S_A \arrow[rr, leftrightarrow, "90.5"] \arrow[dl, leftrightarrow, "35.5"] & & I \\ & S_B \arrow[ul] & & & \end{tikzcd}$	$C \xrightarrow{52} S_A \xleftrightarrow{81} N \xleftrightarrow{82} I$

Table 3. Transition temperatures (°C) for butyl and 2-methylbutyl 4-(4-substituted benzylideneamino)-benzoates

Substituent	Butyl esters	2-Methylbutyl esters
Methoxyl	$C \xrightarrow{57.5} I$	$$\begin{tikzcd} C \arrow[rr, "34.5"] & & I \arrow[dl, leftrightarrow, "3.5"] \\ & N \arrow[ul] & \end{tikzcd}$$
Ethoxyl	$$\begin{tikzcd} C \arrow[rr, "98"] & & I \\ & S_A \arrow[ul] \arrow[ur, leftrightarrow, "63.5"'] & \end{tikzcd}$$	$C \xrightarrow{35} S_A \xleftrightarrow{47.5} N \xleftrightarrow{53} I$

phase. These results contrast greatly with those described for the isobutyl ester series and also the findings with the 2-methylpentyl esters to be presented in next paragraph.

In the series of pentyl esters, the methoxy and ethoxy derivatives were found to be nonmesogenic and nematogenic respectively. All the other members give smectic A phase. Upon 2-methylation, the members from the propoxy to heptyloxy derivatives exhibit nematic properties (see Table 4). In this series too, the metastable phase in the propoxy derivative appears over the widest temperature range. The phase is enantiotropic in the next three members but monotropic again in the heptyloxy derivative and the range is as narrow as 1 °C in the last. Finally we add that neither the 3-methylpentyl nor 4-methylpentyl ester exhibits nematic behavior except for the methoxy derivative in the latter series. A monotropic isotropic-nematic transition occurs at 16 °C for this compound.

In conclusion, we wish to emphasize that methylation of the ester alkyl chain not only diminishes the thermal stability of smectic A mesophase, as confirmed by the ample examples presented in the four tables, but also gives rise to the appearance of nematic phase in a number of smectogens by partial destruction of the molecular order, the magnitude of which seems to be just right, in general, when the methyl group is located at the 2 position.

Table 4. Transition temperatures (°C) for pentyl and 2-methylpentyl 4-(4-substituted benzylideneamino)benzoates

Substituent	Pentyl esters	2-Methylpentyl esters
Propoxyl	$C \xrightarrow{45} S_A \xleftrightarrow{58} I$	$$\begin{tikzcd} C \arrow[rrr, "41.5"] & & & I \arrow[dl, leftrightarrow, "37"] \\ & S_A \arrow[ul] \arrow[r, leftrightarrow, "31.5"] & N & \end{tikzcd}$$
Butoxyl	$C \xrightarrow{29} S_A \xleftrightarrow{77.5} I$	$$\begin{tikzcd} C \arrow[rr, "49.5"] & & N \arrow[r, leftrightarrow, "53"] & I \\ & S_A \arrow[ul] \arrow[ur, leftrightarrow, "49"'] & & \end{tikzcd}$$
Pentyloxyl	$C \xrightarrow{47.5} S_A \xleftrightarrow{74.5} I$	$C \xrightarrow{38} S_A \xleftrightarrow{43.5} N \xleftrightarrow{47.5} I$
Hexyloxyl	$C \xrightarrow{60} S_A \xleftrightarrow{79} I$	$C \xrightarrow{34} S_A \xleftrightarrow{54} N \xleftrightarrow{57} I$
Heptyloxyl	$C \xrightarrow{57} S_A \xleftrightarrow{79} I$	$$\begin{tikzcd} C \arrow[rrr, "57"] & & & I \arrow[dl, leftrightarrow, "56.5"] \\ & S_A \arrow[ul] \arrow[r, leftrightarrow, "55.5"] & N & \end{tikzcd}$$

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