Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effects of Branching of the Alkyl Chain on the Liquid Crystalline Properties of N-(p-Phenylbenzylidene)-p-Alkoxycarbonylanilines

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To cite this article: Y. Matsunaga & N. Miyajima (1984): Effects of Branching of the Alkyl Chain on the Liquid Crystalline Properties of N-(p-Phenylbenzylidene)-p-Alkoxycarbonylanilines, Molecular Crystals and Liquid Crystals, 104:3-4, 353-359

To link to this article: http://dx.doi.org/10.1080/00268948408070437

Mol. Cryst. Liq. Cryst., 1984, Vol. 104, pp. 353–359
0026-8941/84/1044-0353/$18.50/0

Printed in the United States of America

Effects of Branching of the Alkyl Chain on the Liquid Crystalline Properties of *N*-(*p*-Phenylbenzylidene)-*p*-Alkoxycarbonylanilines

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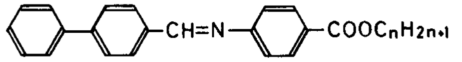
(*Received August 3, 1983*)

The liquid crystal behavior of twenty-three *N*-(*p*-phenylbenzylidene)-*p*-alkoxycarbonylanilines has been examined by optical microscopy and differential scanning calorimetry in order to study the effects of branching of the alkyl groups. Among the results obtained, the following are particularly of interest: (1) the effect of methyl group(s) on the penultimate carbon of the propyl ester on the nematic thermal stabilities is essentially nil or small, (2) the emergence of a nematic liquid crystal is achieved by 2-methylation of the purely smectogenic butyl and pentyl esters, and (3) the thermal stability of smectic phase is not always decreased by methylation but is increased in some cases.

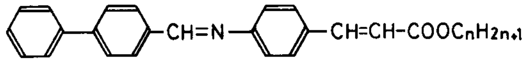
INTRODUCTION

It has been well known that liquid crystalline properties of organic compounds are sensitive to change in molecular structure. According to the systematic studies by Gray and Harrison on alkyl 4-(*p*-substituted benzylideneamino)cinnamates, all the branched chain esters have lower liquid crystal stabilities than the unbranched chain esters.[1,2] Especially, 1-methylation greatly reduces the thermal stability and as the methyl group is moved towards the end of the chain, the transition temperature rises again. Branching at any carbon of the chain was noted to have a greater effect on nematic than on smectic thermal stability. However, as was pointed out by Gray and Harrison themselves, further experimental work is evidently needed to confirm the generality of their observations. Our attention has been particularly paid to the possibility of obtaining a nematic liquid crystal by partial destruction of smectic molecular order. As a nematic is less ordered than a smectic structure, the occurrence of such a situation by chain branching seems to be not unlikely.

This paper presents a study on a series of *N*-(*p*-phenylbenzylidene)-*p*-alkoxycarbonylanilines which have the general structure given below (1) and are closely related to that of the smectogenic compounds studied by Gray and Harrison (2). As a matter of fact, the effects of chain branching on liquid crystal behavior were found to be much more complicated than the empirical correlations cited above. Indeed, the emergence of nematic properties by chain branching was demonstrated with the butyl and pentyl esters.



(1)



(2)

EXPERIMENTAL

Alkyl *p*-aminobenzoates were prepared by the reaction between *p*-nitrobenzoyl chloride and appropriate alcohols and then by the reduction with iron powder and dilute hydrochloric acid as described by Adams *et al.*[3] The Schiff's bases were obtained by the condensation reaction between *p*-phenylbenzaldehyde and the alkyl *p*-aminobenzoates in boiling ethanol. The mesophases were identified by examination of their textures with the aid of a polarizing microscope in conjunction with a heated stage. The transition temperatures were determined by the calorimetric curves recorded on a Rigaku Denki Thermoflex differential scanning calorimeter. The heating rate in the present work was 5 °C min^{-1}.

RESULTS AND DISCUSSION

The methyl, ethyl, two isomeric propyl, four isomeric butyl, eight isomeric pentyl, and fifteen isomeric hexyl derivatives were examined in this work. The eight esters for which we failed to detect any mesophase had the following alkyl groups: methyl, *t*-butyl, 1-ethylpropyl, *t*-pentyl, 2,2-dimethylbutyl, 1-ethyl-2-methylpropyl, 1,1,2-trimethylpropyl, and 1,2,2-trimethylpropyl. Table I summarizes the liquid crystal behavior of twenty-three esters. Here, C, S_B, S_A, N and I stand for crystalline, smectic B, smectic A, nematic, and isotropic phases respectively.

a) Chain Branching of the Ethyl Group

The ethyl ester (No. 1 in Table I) has been known to be smectogenic.[4] The S_A phase stable between 125 and 132 °C can be transformed into a S_B phase at 108 °C if it is well supercooled. Although branching of this short chain makes the S_A phase monotropic because of the lowering of the S_A–I transition temperature as much as 21 °C, no effect is detected on the S_B–S_A transition temperature (see No. 2).

b) Chain Branching of the Propyl Group

The propyl ester (No. 3) is the only unbranched alkyl ester which exhibits enantiotropic S_A and N phases in the present series. By 1-methylation, not only N but also S_A properties are eliminated (see No. 4), whereas the upper limit of S_B temperature range is raised by 9 °C. The effect of the 2-methyl group (see No. 5) is far from what might be expected. In marked contrast to the findings by Gray and Harrison, the branching methyl group has no effect on the N–I transition temperature. The molecular structure rationale for this result, however, is not understood. On the other hand, the S_A phase is destabilized by 10 °C and the S_B phase by 7 °C compared with the corresponding phases of No. 3.

When one more methyl group occupies the 1 position, the liquid crystalline properties of No. 4 are completely destroyed and nonmesogenic *t*-pentyl ester is produced. However, liquid crystalline properties are not much modified when the second branching occurs at the 2 position (compare No. 4 and No. 6). Consequently, the similarity in the phase relationship between the isobutyl ester (No. 5) and the neopentyl ester (No. 7) may not be surprising. While the N–I transition temperature lowers by 8 °C by the second methyl group, the S_B–S_A transition temperature raises by the same amount.

c) Chain Branching of the Butyl Group

The butyl ester (No. 8) is the first member of the unbranched alkyl esters which exhibit stable S_A and S_B phases. Movement of the methyl

TABLE I

Liquid crystal behavior of *N*-(*p*-phenylbenzylidene)-*p*-alkoxycarbonylanilines

No.	Alkyl group	Transition temperatures/ °C
1	CH_2CH_3	$\begin{tikzcd} C \arrow[rr, "125"] & & S_A \arrow[rr, leftrightarrow, "132"] & & I \\ & S_B \arrow[ul] \arrow[ur, leftrightarrow, "108"'] & & & \end{tikzcd}$
2	$CH(CH_3)_2$	$\begin{tikzcd} C \arrow[rrrr, "128"] & & & & I \\ & S_B \arrow[ul] \arrow[r, leftrightarrow, "108"] & S_A \arrow[urr, leftrightarrow, "111"'] & & \end{tikzcd}$
3	$CH_2CH_2CH_3$	$\begin{tikzcd} C \arrow[rr, "114"] & & S_A \arrow[r, leftrightarrow, "128"] & N \arrow[r, leftrightarrow, "133"] & I \\ & S_B \arrow[ul] \arrow[ur, leftrightarrow, "90"'] & & & \end{tikzcd}$
4	$CH(CH_3)CH_2CH_3$	$\begin{tikzcd} C \arrow[rrrr, "107"] & & & & I \\ & S_B \arrow[ul] \arrow[urrr, leftrightarrow, "99"'] & & & \end{tikzcd}$
5	$CH_2CH(CH_3)_2$	$\begin{tikzcd} C \arrow[rr, "124"] & & N \arrow[rr, "133"] & & I \\ & S_B \arrow[ul] \arrow[r, leftrightarrow, "83"] & S_A \arrow[urr, leftrightarrow, "118"'] & & \end{tikzcd}$
6	$CH(CH_3)CH(CH_3)_2$	$\begin{tikzcd} C \arrow[rrrr, "106"] & & & & I \\ & S_B \arrow[ul] \arrow[urrr, leftrightarrow, "94"'] & & & \end{tikzcd}$
7	$CH_2C(CH_3)_3$	$\begin{tikzcd} C \arrow[rr, "119"] & & N \arrow[rr, leftrightarrow, "125"] & & I \\ & S_B \arrow[ul] \arrow[r, leftrightarrow, "91"] & S_A \arrow[urr, leftrightarrow, "117"'] & & \end{tikzcd}$
8	$CH_2CH_2CH_2CH_3$	$C \xrightarrow{91} S_B \xleftrightarrow{98} S_A \xleftrightarrow{121} I$
9	$CH(CH_3)CH_2CH_2CH_3$	$C \xrightarrow{62} S_B \xleftrightarrow{102} I$
10	$CH_2CH(CH_3)CH_2CH_3$	$C \xrightarrow{77} S_B \xleftrightarrow{89} S_A \xleftrightarrow{111} N \xleftrightarrow{113} I$
11	$CH_2CH_2CH(CH_3)_2$	$C \xrightarrow{86} S_B \xleftrightarrow{102} S_A \xleftrightarrow{120} I$
12	$C(CH_3)_2CH_2CH_2CH_3$	$\begin{tikzcd} C \arrow[rrrr, "103"] & & & & I \\ & S_B \arrow[ul] \arrow[urrr, leftrightarrow, "94"'] & & & \end{tikzcd}$
13	$CH(CH_3)CH(CH_3)CH_2CH_3$	$\begin{tikzcd} C \arrow[rrrr, "100"] & & & & I \\ & S_B \arrow[ul] \arrow[urrr, leftrightarrow, "93"'] & & & \end{tikzcd}$
14	$CH(CH_3)CH_2CH(CH_3)_2$	$C \xrightarrow{76} S_B \xleftrightarrow{105} I$
15	$CH_2CH_2C(CH_3)_3$	$\begin{tikzcd} C \arrow[rr, "121"] & & S_A \arrow[rr, leftrightarrow, "125"] & & I \\ & S_B \arrow[ul] \arrow[urrr, leftrightarrow, "105"'] & & & \end{tikzcd}$

TABLE I *Continued*

No.	Alkyl group	Transition temperatures/ ° C
16	$CH(CH_2CH_3)CH_2CH_2CH_3$	$C \xrightarrow{93} S_B \xleftrightarrow{93} I$
17	$CH_2CH(CH_2CH_3)_2$	$C \xrightarrow{95} S_B \xleftrightarrow{97} I$
18	$CH_2CH_2CH_2CH_2CH_3$	$C \xrightarrow{85} S_B \xleftrightarrow{94} S_A \xleftrightarrow{123} I$
19	$CH(CH_3)CH_2CH_2CH_2CH_3$	$C \xrightarrow{70} S_B \xleftrightarrow{92} I$
20	$CH_2CH(CH_3)CH_2CH_2CH_3$	$C \xrightarrow{75} S_B \xleftrightarrow{81} S_A \xleftrightarrow{106} N \xleftrightarrow{113} I$
21	$CH_2CH_2CH(CH_3)CH_2CH_3$	$C \xrightarrow{65} S_B \xleftrightarrow{101} S_A \xleftrightarrow{116} I$
22	$CH_2CH_2CH_2CH(CH_3)_2$	$\begin{tikzcd} C \arrow[rr, "111"] \arrow[dr] & & S_A \arrow[r, leftrightarrow, "121"] & I \\ & S_B \arrow[ur, "104"'] & & \end{tikzcd}$
23	$CH_2CH_2CH_2CH_2CH_2CH_3$	$C \xrightarrow{77} S_B \xleftrightarrow{91} S_A \xleftrightarrow{119} I$

group from the 1 position to 3 position of this alkyl chain gives the following drastic changes in liquid crystal behavior. The 1-methyl group eliminates S_A properties and raises the upper limit of the S_B temperature range by 4°C (see No. 9). The emergence of an N phase is achieved by the 2-methyl substitution even though its temperature range is as narrow as 2°C (see No. 10). By this methylation, the S_A thermal stability is recovered. The 3-methyl group raises the S_A–I transition temperature to within 1°C of the butyl ester (see No. 11), eliminating the possibility of appearance of an N phase. Moreover, the S_B–S_A transition temperature is raised 4°C above that of No. 8.

The temperatures given for No. 10 in Table I are those observed with the optically active ester; therefore, the phase indicated by N is actually cholesteric–nematic. The phase relationship of the racemic ester is essentially the same as that of the active one. With the exception of the C–S_B transition temperature, the temperatures observed with the racemic ester are slightly lower (1°C or less).

The esters from No. 12 to No. 15 have two methyl groups introduced into the butyl group. In contrast to the *t*-butyl and *t*-pentyl esters, a monotropic S_B phase is observable with No. 12. The ester having methyl groups on the 1 and 2 positions (No. 13) behaves similarly. It may be noted that the phase relationship found with these two is of the same type as that of No. 6. When the methyl groups are located on the 1 and 3 positions, a stable S_B phase is regenerated (see No. 14). The small difference in the transition temperature between No. 9 and No. 14 implies that the presence of the 3-methyl group is not very important in determining the mesomorphic properties of No. 14. This conclusion is supported by the phase relationship exhibited by No. 15; that is, a stable S_A phase emerges and both the S_B–S_A and S_A–I transitions occur at temperatures higher than those of No. 8.

As was noted at the beginning of this section, mesophases are often completely eliminated by ethyl substitution; however, a stable S_B phase can be detected with No. 16 and No. 17. The mesomorphic temperature range in the former ester is less than 1°C. The endothermic peaks due to the C–S_B and S_B–I transitions are entirely overlapped in the calorimetric curve recorded in the process of heating but they are well separated on the curve obtained in the process of cooling because of the retarded solidification. The large effect of this voluminous substituent on the S_B thermal stability is clearly reflected by its narrow temperature range compared with the range of 40°C in No. 9. Movement of the ethyl group to the 2 position slightly eases this effect. Namely, the S_B temperature range in No. 17 covers about 2°C. It must be emphasized that this ester behaves very differently from the corresponding methyl derivative (No. 10).

d) Chain Branching of the Pentyl Group

The mesomorphic properties of the pentyl ester are very close to those of the butyl ester (see No. 18), whereas the destabilization of S_B phase by the 1-methylation is considerably greater in the longer alkyl ester (compare No. 9 and No. 19). The methyl substitution at the 2 position results in the emergence of an N phase. It must be noted that the temperature ranges of the N and S_A phases in No. 20 are wider than those in No. 10. The 3-methyl-substituted pentyl ester (No. 21) behaves similarly to the 3-methyl-substituted butyl ester (No. 11). In these two cases, the presence of a methyl group promotes the S_B–S_A transition (compare with No. 8 and No. 18 respectively). When a methyl group is located at the penultimate carbon in the pentyl ester, the phase relationship is quite different from that of No. 11 but resembles that of No. 15. Here again, the S_B–S_A transition temperature is enhanced compared with that of the unsubstituted pentyl ester. Finally, the hexyl ester (No. 23) is found to behave in the same way as the butyl and the pentyl esters (No. 8 and No. 18).

CONCLUDING REMARKS

Comparison between the results reported by Gray and Harrison and ours reveals that the effects of chain branching on the liquid crystalline properties greatly vary with the features of molecular structure. Particularly, the following observations made with *N*-(*p*-phenylbenzylidene)-*p*-alkoxycarbonylanilines distinctly differ from those by the earlier workers.

1. When methyl group(s) occupies the penultimate carbon of the ester propyl chain, the effect on the nematic thermal stabilities is essentially nil or small (see No. 5 and No. 7).
2. A nematic liquid crystal emerges by 2-methylation of the purely smectogenic butyl and pentyl esters (see No. 10 and No. 20).
3. Methylation not always reduces the thermal stability of S_B phase but in some cases promotes this mesophase (see No. 11, No. 15, No. 21, and No. 22).
4. An increase of the S_A thermal stability by chain branching is found in No. 15 (compare with No. 8 and No. 11).

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