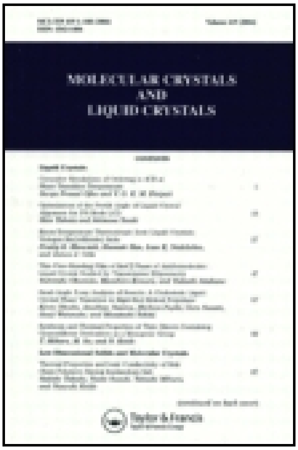


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Effects of Branching of the Ester Alkyl Chain on the Liquid Crystalline Properties of Alkyl 4-[4-(4-Substituted benzylideneamino)benzoyloxy]benzoates

Y. Matsunaga [a] & N. Miyajima [a]
[a] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan

To cite this article: Y. Matsunaga & N. Miyajima (1990): Effects of Branching of the Ester Alkyl Chain on the Liquid Crystalline Properties of Alkyl 4-[4-(4-Substituted benzylideneamino)benzoyloxy]benzoates, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 157-165

To link to this article: http://dx.doi.org/10.1080/00268949008042716

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 157–165
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Effects of Branching of the Ester Alkyl Chain on the Liquid Crystalline Properties of Alkyl 4-[4-(4-Substituted benzylideneamino)benzoyloxy]benzoates

Y. MATSUNAGA and N. MIYAJIMA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

(*Received June 19, 1989; in final form August 28, 1989*)

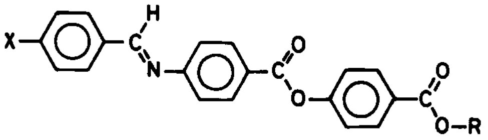
The liquid crystalline properties of four homologous series of alkyl 4-[4-(4-X-substituted benzylideneamino)benzoyloxy]benzoates, where X = NO_2, Cl, CH_3, and CH_3O, have been compared with each other. The ester alkyl groups employed were the following twelve; propyl, butyl, pentyl, and their monomethyl-substituted ones. While all the members of the nitro derivatives are purely nematogenic, the other three series exhibit both nematic and smectic A phases but the former mesophase is mostly eliminated by 1-methylation. The nematic-isotropic transition temperature varies alternately when the branching methyl group shifts from the odd to even position in the alkyl chain. The change in the thermal stability of the smectic A phase by chain branching depends considerably upon the alkyl chain length and also upon the nature of the substituent X located at the other end of the molecule. Some branched alkyl esters attain a smectic A-nematic transition temperature higher than that of the corresponding unbranched alkyl ester.

Keywords: liquid crystals, nematic, smectic, branching of ester alkyl chain

INTRODUCTION

The effects of branching of the ester alkyl group upon the liquid crystalline properties of alkyl 4-(4-substituted benzylideneamino)cinnamates have been studied by Gray and Harrison.[1,2] The thermal stabilities of the mesophases of all the branched chain esters are lower than those of the unbranched alkyl esters. Nematic properties are so reduced by 1-methylation that the phases become monotropic or are completely eliminated. On the shift of the methyl group towards the end of the chain, the transition temperature rises again. Nematic thermal stability is more affected by branching at any carbon of the chain than smectic thermal stability. Gray and Kelly have extended their work to some cyano-biphenyls and -p-terphenyls with branched terminal alkyl groups and concluded that the general pattern of effects on the liquid crystal transition tempertures is consistent with that observed with the cinnamate esters.[3]

In contrast to the tendencies cited above, the emergence of a nematic phase by 2-methylation in a number of purely smectogenic butyl and pentyl esters was found by our earlier studies on 4-(4-phenyl- and 4-(4-alkoxybenzylideneamino)benzoates.[4-6] Moreover, our recent study on dialkyl N,N'-[1,4-phenylenebis(methylidyne)]bis[4-aminobenzoates] revealed that the nematic-isotropic transition temperature varies alternately as the branching methyl group shifts from the odd to even position in the alkyl chain,[7] whereas the monoester series studied before did not show such a variation.[4-6] The change in the nematic and smectic thermal stabilities by chain branching is expected to depend substantially upon the molecular framework; therefore, we decided to extend our work to alkyl 4-[4-(4-X-substituted benzylideneamino)benzoyloxy]benzoates (1), where X = NO_2, Cl, CH_3, and CH_3O.



(1)

EXPERIMENTAL

4-(4-X-Substituted benzylideneamino)benzoic acids were prepared by the condensation reaction between 4-X-substituted benzaldehyde and 4-aminobenzoic acid in boiling alcohol. Alkyl 4-hydroxybenzoates were obtained by the esterification of 4-hydroxybenzoic acid with appropriate alcohol in boiling benzene, employing sulfuric acid as a catalyst.[8] 4-(4-X-Substituted benzylideneamino)benzoic acid and alkyl 4-hydroxybenzoate were condensed in chloroform by the method proposed by Hassner and Alexanian.[9]

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 as described in our previous papers.[4,7]

RESULTS AND DISCUSSION

The melting points and liquid crystal transition temperatures measured for the nitro, chloro, methyl, and methoxy derivatives are summarized in Tables I to IV. Here, K, S_A, N. and I stand for crystalline, smectic A, nematic, and isotropic liquid phases respectively.

N-I transition temperature.

The alteration in the N-I transition temperature by the introduction of a branching methyl group and also by the shift to the end of the alkyl chain is best exemplified by the nitro derivatives, all the members of which are nematogenic (see Figure 1). The depression of the nematic property of the pentyl ester by 1-methylation is as

TABLE I

Transition Temperatures (°C) and Enthalpy Changes (kJ mole^{-1}) of Aklyl 4-[4-(4-Nitrobenzylideneamino)benzoyloxy] benzoates[a)]

Alkyl group	K		N		I
$CH_2CH_2CH_3$	•	149(37)	•	266(0.5)	•
$CH(CH_3)CH_2CH_3$	•	169(33)	•	193(0.3)	•
$CH_2CH(CH_3)_2$	•	153(32)	•	251(0.4)	•
$CH_2CH_2CH_2CH_3$	•	119(37)	•	239(0.5)	•
$CH(CH_3)CH_2CH_2CH_3$	•	137(36)	•	158(0.2)	•
$CH_2CH(CH_3)CH_2CH_3$	•	125(31)	•	223(0.4)	•
$CH_2CH_2CH(CH_3)_2$	•	135(31)	•	215(0.3)	•
$CH_2CH_2CH_2CH_2CH_3$	•	118(34)	•	233(0.6)	•
$CH(CH_3)CH_2CH_2CH_2CH_3$	•	115(30)	•	154(0.2)	•
$CH_2CH(CH_3)CH_2CH_2CH_3$	•	133(39)	•	218(0.4)	•
$CH_2CH_2CH(CH_3)CH_2CH_3$	•	119(27)	•	210(0.2)	•
$CH_2CH_2CH_2CH(CH_3)_2$	•	136(36)	•	216(0.4)	•

a) The latter quantities are in parentheses.

much as 79°C. The 2-methylpentyl ester gives a lower N-I transition temperature by only 15°C compared to that of the unbranched pentyl ester. And, the 3-methylpentyl ester produces a nematic phase thermally less stable than that of the 2-methylpentyl ester. The transition temperature given by the 4-methylpentyl ester is lower than that of the 2-methylpentyl ester even though it is higher than that of the 3-methylpentyl ester. The even-odd effect exhibited by the pentyl ester is well reproduced by the branching in the butyl and propyl esters although all the transitions in the latter two occur in somewhat higher temperature ranges. The local molecular organization in the nematic phase may not be identical when the nature of substituent X is quite different[10]; nevertheless, the other three series have the tendencies described above irrespective of substituent X.

S_A-I or S_A-N transition temperature.

As smectic A phases are of a higher degree of order than nematic phases, the thermal stability may be more susceptive of the specific feature of local molecular

TABLE II

Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Chlorobenzylideneamino) benzoyloxy] benzoates[a)]

Alkyl group	K		S_A		N		I
$CH_2CH_2CH_3$	.	168(35)	.	198(1.9)	.	236(0.4)	.
$CH(CH_3)CH_2CH_3$	.	168(40)	.	180(4.9)			.
$CH_2CH(CH_3)_2$	.	137(31)	.	190(1.8)	.	233(0.6)	.
$CH_2CH_2CH_2CH_3$	.	151(38)	.	205(3.7)	.	220(0.4)	.
$CH(CH_3)CH_2CH_2CH_3$	.	134(33)	.	168(5.6)			.
$CH_2CH(CH_3)CH_2CH_3$	.	126(26)	.	187(2.1)	.	206(0.4)	.
$CH_2CH_2CH(CH_3)_2$	.	151(36)	.	209(6.3)			.
$CH_2CH_2CH_2CH_2CH_3$	.	139(35)	.	204(3.2)	.	216(0.4)	.
$CH(CH_3)CH_2CH_2CH_2CH_3$	.	125(34)	.	164(3.4)			.
$CH_2CH(CH_3)CH_2CH_2CH_3$	.	119(37)	.	178(1.3)	.	205(0.4)	.
$CH_2CH_2CH(CH_3)CH_2CH_3$	.	156(39)	.	200(6.0)			.
$CH_2CH_2CH_2CH(CH_3)_2$	.	153(42)	.	201(4.3)	.	204(0.4)	.

a) The latter quantities are in parentheses.

packing. Indeed, the dependence of the S_A-I or S_A-N transition temperature on the position of a branching methyl group is not so straightforward as that found for the N-I transition temperature. As it turns out below, the smectic behavior changes by chain branching in a rather complicated way, depending upon the alkyl chain length and also upon the nature of the substituent X located at the other end of the three-ring system.

In the chloro derivatives, where the smectic behavior is most promoted among the compounds examined here, the S_A-N transition temperature is depressed by the methyl group introduced to the 1 position, and then is raised as the methyl group is shifted to the 2 and 3 positions in agreement with what Gray and Harrison demonstrated.[1,2] As is shown in Figure 2, the magnitude of the temperature change is clearly dependent on the alkyl chain length. The depression given by the 1-methyl group is merely 18°C in the propyl ester but twice as large in the butyl and pentyl esters. The difference in the transition temperature between the 1-methyl- and 2-methylalkyl esters is similar to that between the 2-methyl- and 3-methylalkyl esters;

TABLE III

Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Methylbenzylideneamino) benzoyloxy] benzoates[a)]

Alkyl group	K		S_A		N		I
$CH_2CH_2CH_3$	.	149(41)	.	150(0.3)	.	222(0.5)	.
$CH(CH_3)CH_2CH_3$	.	170(47)	[.	147(3.1)]			.
$CH_2CH(CH_3)_2$	.	150(43)	[.	137(0.2)]	.	206(0.4)	.
$CH_2CH_2CH_2CH_3$	.	140(39)	.	157(0.7)	.	198(0.6)	.
$CH(CH_3)CH_2CH_2CH_3$	.	141(35)	.	144(3.7)			.
$CH_2CH(CH_3)CH_2CH_3$	.	136(34)	.	147(0.6)	.	188(0.3)	.
$CH_2CH_2CH(CH_3)_2$	.	143(33)	.	167(2.1)	.	177(0.4)	.
$CH_2CH_2CH_2CH_2CH_3$	.	127(35)	.	159(0.5)	.	198(0.4)	.
$CH(CH_3)CH_2CH_2CH_2CH_3$	.	133(35)	.	141(4.0)			.
$CH_2CH(CH_3)CH_2CH_2CH_3$	.	119(37)	.	143(0.3)	.	185(0.4)	.
$CH_2CH_2CH(CH_3)CH_2CH_3$	.	137(37)	.	162(1.8)	.	171(0.3)	.
$CH_2CH_2CH_2CH(CH_3)_2$	.	136(38)	.	162(1.0)	.	181(0.3)	.

a) The latter quantities are in parentheses.

namely, 19°C versus 22°C in the butyl ester and 14°C versus 22°C in the pentyl ester. As a result, the 3-methyl group raises the S_A-N transition temperature close to that of the unbranched alkyl ester and the 4-methyl group gives a transition temperature essentially the same as the 3-methyl group. It must be noted that the S_A-I transition in the 3-methylbutyl ester is located at a temperature a little bit higher than the S_A-N transition in the unbranched butyl ester.

The effects of chain branching on the transition temperature in the methyl derivatives are somewhat unusual as depicted in Figure 3. The S_A-I transition of the sec-butyl ester is located at a lower temperature than that of the propyl ester but only by a few degrees. In contrary to the case of the chloro derivatives, the isobutyl ester exhibits the S_A-N transition at a temperature 10°C lower than that of the sec-butyl ester. When the alkyl chain length becomes longer, the depression by 1-methyl group increases; namely, 13°C in the butyl ester and 18°C in the pentyl ester. On the other hand, the change by chain branching at the 2 position is so reduced that the S_A-N transition temperature of the 2-methylbutyl ester is higher than that of the 1-methylbutyl ester. The smectic A phase exhibited by the 3-

TABLE IV

Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Methoxybenzylideneamino) benzoyloxy] benzoates[a]

Alkyl group	K		S_A		N		I
$CH_2CH_2CH_3$	.	159(52)	.	161(0.1)	.	258(0.3)	.
$CH(CH_3)CH_2CH_3$	.	144(36)	.	168(1.4)	.	184(0.1)	.
$CH_2CH(CH_3)_2$	.	134(41)	.	156(0.3)	.	246(0.9)	.
$CH_2CH_2CH_2CH_3$	.	157(55)	.	170(0.5)	.	231(0.5)	.
$CH(CH_3)CH_2CH_2CH_3$	.	125(31)	.	169(3.3)			.
$CH_2CH(CH_3)CH_2CH_3$	.	126(34)	.	163(0.5)	.	221(0.4)	.
$CH_2CH_2CH(CH_3)_2$	.	145(41)	.	185(1.5)	.	209(0.5)	.
$CH_2CH_2CH_2CH_2CH_3$	.	150(29)	.	172(0.4)	.	228(0.8)	.
$CH(CH_3)CH_2CH_2CH_2CH_3$	.	119(32)	.	164(3.3)			.
$CH_2CH(CH_3)CH_2CH_2CH_3$	.	105(34)	.	158(0.3)	.	217(1.2)	.
$CH_2CH_2CH(CH_3)CH_2CH_3$	.	146(40)	.	184(1.1)	.	203(0.4)	.
$CH_2CH_2CH_2CH(CH_3)_2$	.	150(46)	.	182(0.8)	.	212(0.7)	.

a) The latter quantities are in parentheses.

methylbutyl ester is appreciably more stable than that of the 2-methylbutyl ester. Similar temperature changes may be found in the branched pentyl esters. It must be noted that the 3-methylbutyl, 3-methylpentyl, and 4-methylpentyl esters have S_A-N transitions definitely higher than the corresponding unbranched alkyl esters.

The variation in the thermal stability of the smectic A phase of the methoxy derivatives by chain branching shown in Figure 4 is more striking than that depicted in Figure 3. While the introduction of a methyl group to the 1 position of the propyl chain enhances the smectic properties, a similar modification to the butyl and pentyl chains gives rise to the opposite effects. The methyl group at the 2 position decreases the temperature relative to the unbranched ester and the magnitude enlarges upon the elongation of the alkyl chain. Thus, the effect of chain branching found for the butyl ester of the methoxy derivative resembles, to some extent, that found for the propyl ester of the methyl derivative shown in Figure 3. Nevertheless, the depression by 2-methylation continues to be larger than that by 1-methylation in the pentyl ester in contrast to the case in the methyl derivative. Therefore, one cannot conclude that the effects observed with the methoxy derivatives are simply

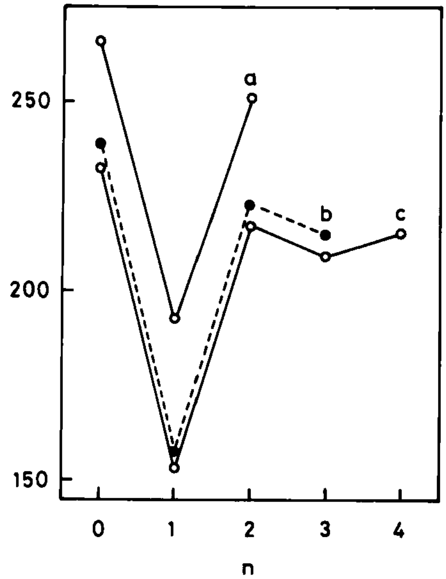


FIGURE 1 Plot of the N-I transition temperature against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl 4-[4-(4-nitrobenzylideneamino)benzoyloxy]benzoates.

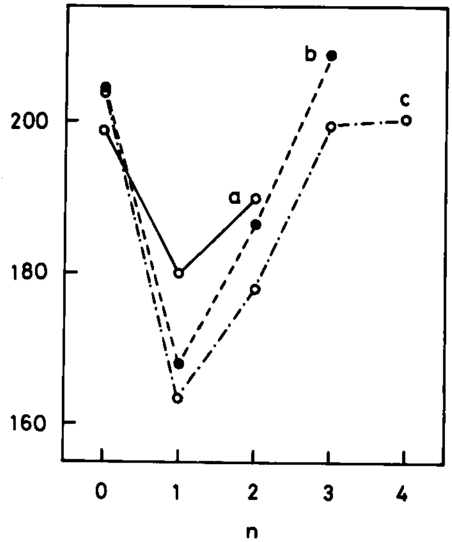


FIGURE 2 Plot of the S_A-N or S_A-I transition temperature against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl 4-[4-(4-chlorobenzylideneamino)benzoyloxy]benzoates.

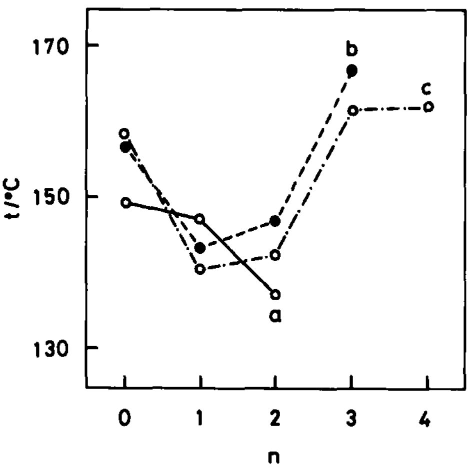


FIGURE 3 Plot of the S_A-N or S_A-I transition temperature against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl 4-[4-(4-methylbenzylideneamino)benzoyloxy]benzoates.

more pronounced than those observed with the methyl derivatives. The smectic A phases appearing in the 3-methylbutyl and 3-methyl- and 4-methylpentyl esters are significantly more stable compared not only to those in the 2-methylbutyl and 2-methylpentyl esters but also those in the unbranched butyl and pentyl esters. Finally, we note that the S_A-N transition temperature of the 4-methylpentyl ester is lower than that of the 3-methylpentyl ester.

In conclusion, the effects of chain branching on smectic thermal stability are undoubtedly dependent upon the nature of the substituent located at the other end

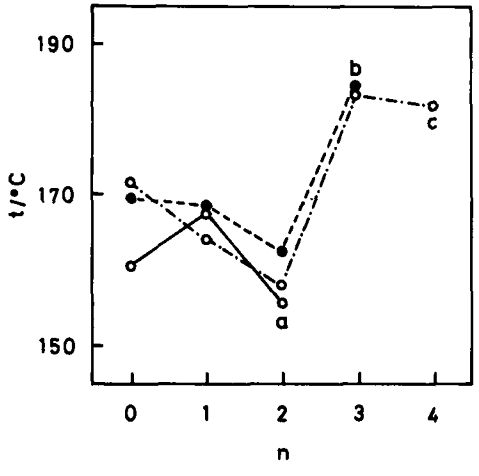


FIGURE 4 Plot of the S_A-N or S_A-I transition temperature against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl 4-[4-(4-methoxybenzylideneamino)benzoyloxy]benzoates.

of the molecule and also upon the alkyl chain length, indicating that much yet remains to be established about the details on the molecular arrangement in smectic A phases.

References

1. G. W. Gray and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).
2. G. W. Gray and K. J. Harrison, *Symp. Faraday Soc.*, **5**, 54 (1971).
3. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **104**, 335 (1984).
4. Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **104**, 353 (1984).
5. Y. Matsunaga and N. Miyajima, *Bull. Chem. Soc. Jpn.*, **57**, 1413 (1984).
6. Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **116**, 207 (1985).
7. Y. Matsunaga and H. Matsuzaki, submitted to *Bull. Chem. Soc. Jpn.*
8. G. W. K. Cavill and J. M. Vincent, *J. Soc. Chem. Ind.* (London), **66**, 175 (1947).
9. A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 1978, 4475.
10. A. J. Leadbetter, R. M. Richardson, and C. N. Colling, *J. Phys.* (Paris), **36**, C1-37 (1975).