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Liquid Crystalline Properties of Alkyl 4-[4-(4-Methoxybenzoyloxy)benzylideneamino]benzoates and 4-[4-(4-Methoxybenzylideneamino)benzoyloxy]benzoates

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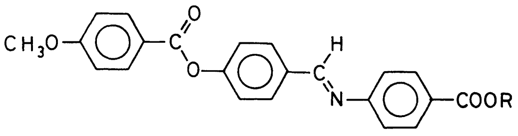
The mesomorphic properties of homologous series of alkyl 4-[4-(4-methoxybenzoyloxy)benzylideneamino]-benzoates and the isomeric compounds, 4-[4-(4-methoxybenzylideneamino)benzoyloxy]benzoates have been studied, employing thirty ester alkyl groups. The nematic phase appearing in the former series is thermally more stable than that in the latter: even the *t*-butyl and 1,1-dimethylpropyl esters are nematogenic. The mesophases in these esters are significantly promoted relative to those in the isopropyl and 1-methylpropyl esters, respectively. An alternation in the thermal stability of the nematic phase occurs when the branching methyl group is moved progressively to the penultimate carbon of the chain in both series. In the second series, the stabilization of the smectic A phase by 3- or 4-methylation is observed for both butyl and pentyl esters.

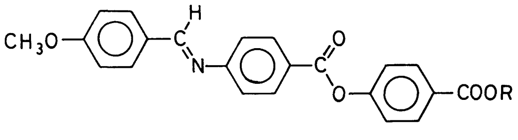
Gray and Harrison were the first to systematically study the effects of the branching of ester alkyl groups on the liquid crystalline properties. The compounds chosen for their work were 4-(4-X-substituted benzylideneamino)cinnamates, where X=CN and Ph.[1,2] While the esters are purely nematogenic when X=CN, those with X=Ph are purely smectogenic. Branching of the ester alkyl groups diminishes the thermal stabilities of the nematic and smectic A phases. The effects of a 1-methyl group is so serious that the nematic phases become monotropic, or are even completely eliminated. As the methyl group is moved towards the end of a given chain, the effect becomes smaller. Branching at any carbon of the chain has a greater effect on the nematic than on the smectic thermal stability, at least in these series. The general pattern of effects on liquid–crystal transition temperatures shown by these cinnamates was supported by further work on some other types of mesogen including cyanobiphenyls and *p*-terphenyls with branched terminal alkyl groups connected directly to the aromatic nuclei.[3]

On the other hand, our earlier studies on 4-(4-phenyl- and 4-(4-alkoxybenzylideneamino)benzoates carrying branched ester alkyl groups revealed the emergence of a nematic phase by 2-methylation in a number of purely smectogenic butyl and pentyl esters.[4–6] This finding is in marked contrast with the trends cited above. Furthermore, our recent study on dialkyl 4,4′-[1,4-phenylenebis(methylidynenitrilo)]bis[benzoates] disclosed a pronounced alternating variation in the nematic–isotropic transition temperature by a shift of the branching methyl group from the first carbon of the chain towards the end of the chain,[7] though such a variation was not detected with the monoester series studied before.[4–6]

Evidently, further work, especially on compounds which have molecular frameworks different from the above-mentioned and/or exhibit both nematic and smectic phases, are needed in order to clarify the effects of chain branching on the liquid crystalline properties. Interest in this problem led us to examine alkyl 4-[4-(4-methoxybenzoyloxy)benzylideneamino]-benzoates (**1**) and 4-[4-(4-methoxybenzylideneamino)-benzoyloxy]benzoates (**2**), empolying thirty ester alkyl groups. A similar, but less extensive, study has been carried out by the present authors on alkyl 4-(4-phenylbenzylideneamino)benzoates.[4]



(**1**)



(**2**)

Experimental

Materials. 4-(4-Methoxybenzoyloxy)benzaldehyde was obtained by a condensation reaction between 4-methoxybenzoyl chloride and 4-hydroxybenzaldehyde dissolved in pyridine. Alkyl 4-aminobenzoates were prepared as described in our previous work.[7] Compounds **1** were synthesized by condensing the above-mentioned benzaldehyde derivative and alkyl 4-aminobenzoates in boiling ethanol. The reaction between 4-methoxybenzaldehyde and 4-aminobenzoic acid produces 4-(4-methoxybenzylideneamino)benzoic acid. Alkyl 4-hydroxybenzoates were prepared by the esterification of 4-hydroxybenzoic acid with appropriate alcohols in boiling benzene, employing sulfuric acid as a catalyst.[8] Compounds **2** were synthesized by the reaction of 4-(4-methoxybenzylideneamino)benzoic acid with alkyl 4-hydroxybenzoates in chloroform, following a procedure of Hassner and Alexanian.[9]

Measurements. The mesophases were identified by examining their textures with the aid of a polarizing microscope in conjunction with a heated stage. The transition temperatures and associated enthalpy changes were determined by calorimetric curves recorded on a Rigaku Denki Thermoflex differential scanning calorimeter.

Results and Discussion

The melting points and liquid-crystal transition temperatures measured for these closely-related two series are presented in Tables 1 and 2. Here, crystalline, smectic A, nematic, and isotropic liquid phases are denoted by K, S_A, N, and I, respectively.

The thermal stability of the nematic phase of the compound in series **1** tends to be higher than that in the corresponding member in series **2**; that is, the N-I transition temperatures were 267 °C vs. 258 °C for the propyl esters (No. 5) and 214 °C vs. 209 °C for the heptyl esters (No. 30). On the other hand, the smectic A phase appearing in series **2** is thermally more stable than that in series **1**. As a matter of fact, all of the compounds in series 2 except for methyl, ethyl and 1,2,2-trimethylpropyl esters (Nos. 1, 2, and 12) exhibit a stable smectic A phase, whereas the corresponding member in series **1** is either not smectogenic at all or the phase is mostly metastable.

To our surprise, even compounds carrying two branching methyl groups at the 1 position in series **1** are mesogenic. Thus, the *t*-butyl and 1,1-dimethylpropyl esters (Nos. 4 and 8) produce a stable nematic phase, the temperature ranges of the existence being as wide as 81 and 97 °C respectively. It must be emphasized that the mesophase in the former ester is enhanced by as much as 66 °C by the second methyl group introduced to the 1 position. While the 1,1,2-trimethylpropyl ester (No. 11) exhibits a nematic phase stable over 11 °C as well as a metastable smectic A phase, the 1,1-dimethylbutyl ester (No. 19) is purely smectogenic. It was not possible to study the corresponding compounds in series **2** because of the difficulty in preparing the precursors, alkyl 4-hydroxybenzoates.

N-I Transition and Chain Branching. The change in the N-I transition temperature by the introductin of a branching methyl group to propyl, butyl, and pentyl groups and also by the shift to the end of the alkyl chains can be fully examined in series **1** because all the members exhibit a stable nematic phase. As is shown in Fig. 1, the nematic property of the propyl ester is reduced by 1-methylation by as much as 83 °C. The 2-methylpropyl ester (No. 7) gives an N-I transition temperature lower only by 12 °C than the unbranched propyl ester. The relation between the transition temperature and the position of the methyl group

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **1**$^{a)}$

No.	Alkyl group	K		S_A		N		I
1	CH_3	.			210 (55)	.	316 (—)	.
2	CH_2CH_3	.			201 (52)	.	282 (0.6)	.
3	$CH(CH_3)_2$	.	161 (39)	[.	145 (0.3)]	.	212 (0.1)	.
4	$C(CH_3)_3$	.			197 (57)	.	278 (0.5)	.
5	$CH_2CH_2CH_3$	.			165 (46)	.	267 (0.5)	.
6	$CH(CH_3)CH_2CH_3$	.	151 (42)	[.	129 (1.1)]	.	184 (0.1)	.
7	$CH_2CH(CH_3)_2$	.			139 (39)	.	255 (0.4)	.
8	$C(CH_3)_2CH_2CH_3$	.			193 (52)	.	290 (0.5)	.
9	$CH(CH_3)CH(CH_3)_2$	.	146 (41)	[.	125 (0.2)]	.	217 (0.1)	.
10	$CH_2C(CH_3)_3$	.	135 (30)	[.	115 (0.1)]	.	230 (0.2)	.
11	$C(CH_3)_2CH(CH_3)_2$	.	129 (38)	[.	115 (0.2)]	.	140 (0.2)	.
12	$CH(CH_3)C(CH_3)_3$	.	154 (48)	[.	128 (0.5)]	.	163 (0.2)	.
13	$CH(CH_2CH_3)_2$	.			149 (58)	[.	139 (0.5)]	.
14	$CH[CH(CH_3)_2]_2$	.	142 (31)	[.		100 (1.5)]		.
15	$CH_2CH_2CH_2CH_3$	.			171 (58)	.	237 (0.3)	.
16	$CH(CH_3)CH_2CH_2CH_3$	.	141 (37)	[.	134 (0.6)]	.	158 (0.1)	.
17	$CH_2CH(CH_3)CH_2CH_3$	.	122 (29)	[.	114 (—)]	.	223 (0.3)	.
18	$CH_2CH_2CH(CH_3)_2$	.	155 (46)	[.	150 (0.5)]	.	213 (0.5)	.
19	$C(CH_3)_2CH_2CH_2CH_3$	.	111 (21)	.		120 (2.4)		.
20	$CH(CH_3)CH_2CH(CH_3)_2$	.	143 (30)	.		152 (0.3)		.
21	$CH(CH_2CH_3)CH_2CH_2CH_3$	.	139 (39)	.		126 (2.3)		.
22	$CH_2CH(CH_2CH_3)_2$	.	122 (28)	[.	121 (0.1)]	.	193 (0.2)	.
23	$CH_2CH_2CH_2CH_2CH_3$	.			161 (54)	.	237 (0.5)	.
24	$CH(CH_3)CH_2CH_2CH_2CH_3$	.	133 (33)	.	141 (0.7)	.	150 (0.2)	.
25	$CH_2CH(CH_3)CH_2CH_2CH_3$	.			110 (38)	.	219 (0.3)	.
26	$CH_2CH_2CH(CH_3)CH_2CH_3$	.	160 (48)	[.	153 (0.3)]	.	203 (0.2)	.
27	$CH_2CH_2CH_2CH(CH_3)_2$	.			153 (44)	.	216 (0.5)	.
28	$CH_2CH_2CH_2CH_2CH_2CH_3$	.	151 (57)	[.	139 (0.1)]	.	217 (0.5)	.
29	$CH_2CH(CH_3)CH_2CH_2CH_2CH_3$	.	108 (35)	.	123 (0.1)	.	204 (0.3)	.
30	$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	.			150 (66)	.	214 (0.5)	.

a) The latter quantities are in parentheses. The braced quantities represent monotropic transitions.

Table 2. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **2**[a)]

No.	Alkyl group	K		S_A		N		I
1	CH_3	.		212 (56)		.	301 (0.8)	.
2	CH_2CH_3	.		185 (53)		.	268 (0.6)	.
3	$CH_2(CH_3)_2$	.	153 (38)	.	177 (1.7)	.	205 (0.4)	.
4	$C(CH_3)_3$							
5	$CH_2CH_2CH_3$	.	159 (52)	.	161 (0.1)	.	258 (0.3)	.
6	$CH(CH_3)CH_2CH_3$	.	144 (36)	.	168 (1.4)	.	184 (0.1)	.
7	$CH_2CH(CH_3)_2$	.	134 (41)	.	156 (0.3)	.	246 (0.9)	.
8	$C(CH_3)_2CH_2CH_3$							
9	$CH(CH_3)CH(CH_3)_2$	.	147 (27)	.	162 (0.7)	.	182 (0.1)	.
10	$CH_2C(CH_3)_3$	.	145 (39)	.	164 (0.7)	.	224 (0.8)	.
11	$C(CH_3)_2CH(CH_3)_2$							
12	$CH(CH_3)C(CH_3)_3$	.	166 (48)	[.	157 (1.9)]	[.	165 (0.2)]	.
13	$C(CH_2CH_3)_2$	.	145 (33)	.		153 (2.6)		.
14	$C[CH(CH_3)_2]_2$	.	119 (31)	.		139 (3.7)		.
15	$CH_2CH_2CH_2CH_3$	.	157 (55)	.	170 (0.5)	.	231 (0.5)	.
16	$CH(CH_3)CH_2CH_2CH_3$	.	125 (31)	.		169 (3.3)		.
17	$CH_2CH(CH_3)CH_2CH_3$	.	126 (34)	.	163 (0.5)	.	221 (0.4)	.
18	$CH_2CH_2CH(CH_3)_2$	.	145 (41)	.	185 (1.5)	.	209 (0.5)	.
19	$C(CH_3)_2CH_2CH_2CH_3$							
20	$CH(CH_3)CH_2CH(CH_3)_2$	.	121 (34)	.		171 (4.2)		.
21	$CH(CH_2CH_3)CH_2CH_2CH_3$	.	124 (32)	.		151 (3.9)		.
22	$CH_2CH(CH_2CH_3)_2$	.	114 (21)	.	159 (0.6)	.	194 (0.2)	.
23	$CH_2CH_2CH_2CH_2CH_3$	.	150 (29)	.	172 (0.4)	.	228 (0.8)	.
24	$CH(CH_3)CH_2CH_2CH_2CH_3$	.	119 (32)	.		164 (3.3)		.
25	$CH_2CH(CH_3)CH_2CH_2CH_3$	.	105 (34)	.	158 (0.3)	.	217 (1.2)	.
26	$CH_2CH_2CH(CH_3)CH_2CH_3$	.	146 (40)	.	184 (1.1)	.	203 (0.4)	.
27	$CH_2CH_2CH_2CH(CH_3)_2$	.	150 (46)	.	182 (0.8)	.	212 (0.7)	.
28	$CH_2CH_2CH_2CH_2CH_2CH_3$	.	145 (50)	.	178 (0.5)	.	213 (0.7)	.
29	$CH_2CH(CH_3)CH_2CH_2CH_2CH_3$	.	92 (26)	.	165 (0.6)	.	207 (0.6)	.
30	$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	.	142 (51)	.	181 (0.5)	.	209 (0.7)	.

a) The latter quantities are in parentheses. The braced quantities represent monotropic transitions.

observed for the propyl ester is reproduced by chain branching in the butyl and pentyl esters, although the transitions in the latter two are located, more or less, at lower temperatures. The following findings regarding the 3-methylbutyl and 3-methyl- and 4-methylpentyl esters (Nos. 18, 26, and 27) may be particularly noteworthy. We can see in Fig. 1 that the shift of a methyl group from the 2 position to the 3 position in the butyl ester decreases the nematic stability by 10 °C. A similar tendency is found by comparing the 2-methyl- and 3-methylpentyl esters; a decrease by 16 °C. The transition temperature given by the 4-methylpentyl ester (No. 27) is lower by 3 °C than that of the 2-methylpentyl ester, even though it is higher by 13 °C than that of the 3-methylpentyl ester. Regarding series **2**, the corresponding esters are not necessarily nematogenic; nevertheless, the above-mentioned tendencies may also be noted in Fig. 2. These observations agree qualitatively with those made earlier for the diesters.[7)] Examining the effects of methyl branching at the penultimate carbon of a chain ($-(CH_2)_nCH(CH_3)_2$ groups), Gray and Harrison pointed out that quite large alternation in the nematic stabilities occurs as *n* changes progressively.[1,2)] Their conclusion may be regarded being one part of other more general tendencies disclosed in the present work.

One of the most fascinating findings is an enhancement of the nematic stability by methylation, observed for the following two esters in series **1** (see Fig. 3). The nematic thermal stability in the 1,1-dimethylpropyl ester (No. 8) is promoted by 106 °C and that in the 1,2-dimethylpropyl ester (No. 9) by 33 °C compared with that of the 1-methylpropyl ester (No. 6), whereas the transition temperature in the 1,2-dimethylpropyl ester is lower by as much as 38 °C than that of the 2-methylpropyl ester (No. 7). In contrast, the N–I transition in the 1,2-dimethylpropyl ester in series **2** occurs at a slightly lower temperature than that in the 1-methylpropyl ester.

The 1-ethyl- and 2-ethylbutyl esters (Nos. 21 and 22) are mesogenic and their data provide the means for comparing the effects of branching methyl and ethyl groups. The depression of the nematic phase relative to the unbranched alkyl ester by 1-alkylation is quite large and the assessment cannot be complete (namely, 70 °C by a methyl group vs. more than 111 °C by an ethyl group in series **1** and 74 °C vs. more than 105 °C in series **2**). In the case of 2-alkylation, the following values are obtained: 14 °C vs. 44 °C in series **1** and 10 °C vs. 36 °C in series **2**. Furthermore, the effects of branching 1-methyl and isopropyl groups may be compared on the basis of the data for the esters

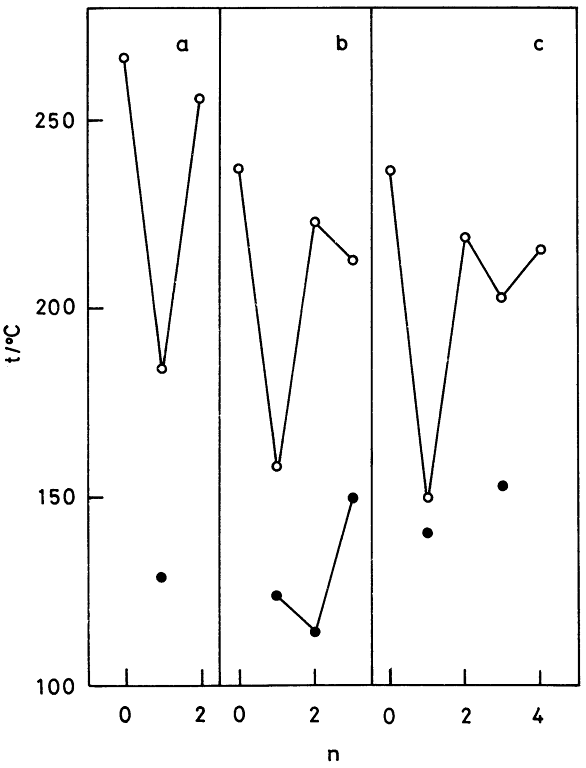


Fig. 1. Plots of the S_A-N (●) and N-I (○) transition temperatures against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl esters in series 1.

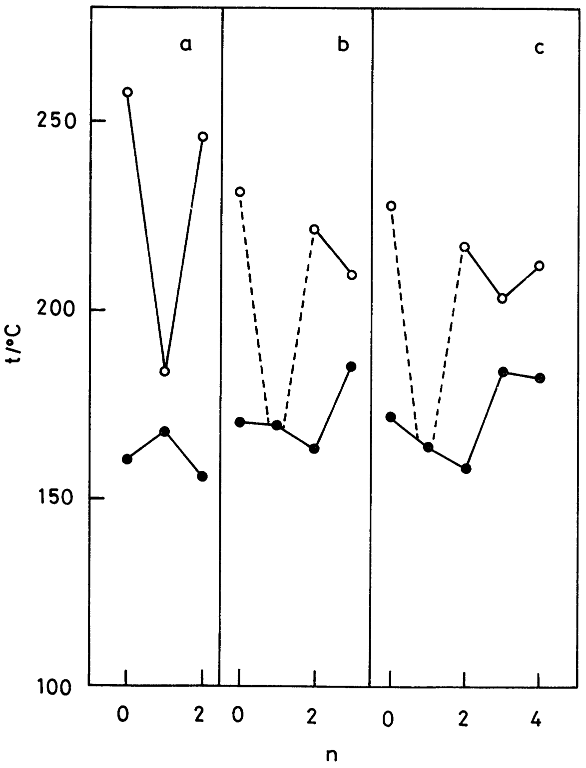


Fig. 2. Plots of the S_A-N/S_A-I (●) and N-I (○) transition temperatures against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl esters in series 2.

Nos. 7, 9, and 14. The depressions are follows: 38 °C vs. more than 155 °C in series **1** and 22 °C vs. more than 107 °C in series **2**.

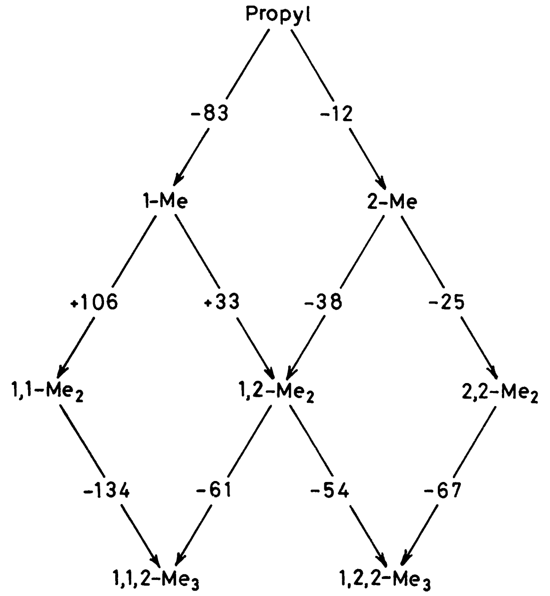


Fig. 3. The change in the N-I transition temperature (°C) of the propyl ester in series 1 by the introduction of a branching methyl group.

S_A-I or S_A-N Transition and Chain Branching. Although the S_A-N transitions measurable for series **1** are very limited, the smectic A phase in the 2-methylbutyl ester is transformed into the nematic phase certainly at a lower temperature than that of the 1-methylbutyl ester (see Fig. 1b). Complete data available for series **2** are very remarkable as depicted in Fig. 2. 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 opposite effects. The methyl group at the 2 position diminished the smectic thermal stability relative to the unbranched ester and the magnitude increases upon the elongation of the alkyl chain. These observations indicate that the effect of chain branching on the smectic behavior is not independent of the length of the alkyl group to which a branching methyl group is introduced. It must be added that the smectic A phases given by the 3-methylbutyl and 3-methyl- and 4-methylpentyl esters (Nos. 18, 26, and 27) are considerably more stable compared not only to that given by the 2-methyl derivatives (Nos. 17 and 25) but also to the unbranched esters (Nos. 15 and 23). The stabilization of a smectic A phase by chain branching is not entirely a new finding. The smectic A phase in butyl 4-(4-phenylbenzylideneamino)benzoate was found to be stabilized by 3-methylation; however, molecular manipulation by methylation at the other positions or by using the other alkyl groups did not give such a change in that series.[4] In addition to these findings, which are not in conformity with the trend described by Gray and Harrison, it may be noted that the S_A–N transition in the 4-methylpentyl ester is located at a lower temperature than that in the 3-methylpentyl ester.

Finally, the effects of methyl, ethyl, and isopropyl groups on the thermal stability of smectic A phase may be compared with each other, employing the data of the aforementioned branched alkyl esters. The changes relative to the unbranched esters can be estimated only for series **2**. In the case of 1-alkylation of the butyl ester, the depression is merely 1 °C by a methyl groups vs. 19 °C by an ethyl group (compare Nos. 16 and 21 with No. 15). Similarly, 7 °C vs. 11 °C is obtained in the case of 2-alkylation (Nos. 17 and 22). The transition temperature of the 2-methylpropyl ester (No. 7) is increased by 6 °C by a methyl group and is decreased by 23 °C by an isopropyl group (Nos. 9 and 14). Apparently, the smectic behavior is less affected by these substituents.

The mesomorphic properties of a compound are determined, in principle, by the features of molecule as a whole. The results presented here firmly establish that the change in the local molecular organization by chain branching in nematic and smectic phases depends appreciably upon the molecular framework as well as upon the length of the alkyl chain to which branching groups are to be introduced. Since the nature of a substituent located at the other end of the molecule is known to be an important structural parameter in determining the mesomorphic properties, this terminal substituent could exert a considerable influence upon the effects of the chain branching under investigation. Work employing substituents other than a methoxyl group will be reported in forthcoming papers.

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, *Bull. Chem. Soc. Jpn.*, **62**, 3417 (1989).

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.