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

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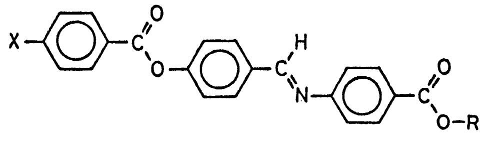
The mesomorphic properties of five homologous series of alkyl 4-[4-(4-X-substituted benzoyloxy)benzylideneamino]benzoates, where X=CN, NO_2, CH_3, Cl, and CH_3COO, have been studied. The ester alkyl groups employed were the following eleven types: ethyl and propyl and their mono-, di-, and trimethyl-substituted ones. Although the introduction of the first branching methyl group to the ester alkyl chain depresses the nematic stability, the second and/or third groups may either further depress or enhance the stability, depending upon the nature of the substituent X. While all of the members of the cyano and nitro derivatives are purely nematogenic, many members of the other three series display a smectic A phase, as well as a nematic phase. In addition to the above-mentioned esters, the butyl, pentyl, and their monomethyl-substituted esters were examined in order to demonstrate that the effects on the thermal stability of the smectic A phase of the branching of the ester alkyl chain and those of the substituent X are also interdependent.

Continuing our studies on the effects of branching of the ester alkyl group on the mesomorphic properties,[1–4] we recently described the properties of two closely-related homologous series: alkyl 4-[4-(4-methoxybenzoyloxy)benzylideneamino)benzoates and 4-[4-(4-methoxybenzylideneamino)benzoyloxy]benzoates.[5] The nematic phase appearing in the former series is so stable that the *t*-butyl and 1,1-dimethylpropyl esters are mesogenic. Moreover, the mesophases in these two esters are significantly stabilized relative to those in the isopropyl and 1-methylpropyl esters, respectively. An odd-even alternation in the thermal stability of their nematic phase occurs when the branching methyl group is shifted progressively to the penultimate carbon of the chain in both series.

These findings are not in conformity with those reported by Gray and Harrison.[6,7] According to their work on alkyl 4-(4-substituted benzylideneamino)cinnamates, the thermal stabilities of the nematic and smectic phases of all the branched chain esters are lower than those of the unbranched alkyl esters. The nematic thermal stability is more affected by branching at any carbon of the chain than the smectic thermal stability. The former properties are so reduced by 1-methylation that the phases become monotropic or are completely eliminated. Regarding the shift of the methyl group towards the end of the chain, the transition temperature again rises. The mesomorphic properties of some cyanobiphenyls and -*p*-terphenyls with branched terminal alkyl groups have also been reported by Gray and Kelly.[8] The general pattern of the effect on the liquid-crystal transition temperatures was found to be in accord with that observed with cinnamate esters.

It seemed to us quite reasonable that the effects of the branching of the ester alkyl chain on both the nematic and smectic thermal stabilities are substantially affected not only by the molecular framework but also by the nature of substituent; we have therefore undertaken an extension of our work to alkyl 4-[4-(4-X-substituted benzoyloxy)benzylideneamino]benzoates (**1**), where X=CN, NO_2, CH_3, Cl, and CH_3COO.



(1)

Experimental

Materials. 4-(4-X-Substituted benzoyloxy)benzaldehydes were prepared by a reaction between 4-X-substituted benzoic acid or its chloride and 4-hydroxybenzaldehyde. The desired compounds were obtained by condensing the above-mentioned benzaldehyde derivatives with alkyl 4-aminobenzoates in boiling ethanol. For example, Found: C, 75.31; H, 6.32; N, 3.30%. Calcd for $C_{27}H_{28}NO_4$ (the 1,1-dimethylpropyl ester of the methyl derivative): C, 75.50; H, 6.34; N, 3.26%.

Measurements. The mesophases were identified by an examination of their textures with the aid of a polarizing microscope in conjunction with a heated stage. The transition temperatures were determined by calorimetric traces recorded on a Rigaku Denki Thermoflex differential scanning calorimeter, as described in our previous papers.[4,5]

Results and Discussion

The melting points and liquid-crystal transition temperatures measured for the cyano, nitro, chloro, methyl, and acetoxy derivatives are presented in Tables 1 to 5 with the associated enthalpy changes. Here, K, S_A, N, and I stand for the crystalline, smectic A, nematic, and isotropic liquid phases respectively.

N-I Transition and Chain Branching. All of the members in the cyano derivatives are purely nematogenic, including the *t*-butyl and 1,1-dimethylpropyl esters. The clearing point of the ethyl ester is depressed by as much as 60 °C by the first branching methyl group, but by only 34 °C by the second one. The changes in the clearing point arising from the introducton of a branching methyl group are summarized

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Cyanobenzoyloxy)benzylideneamino]benzoates[a)]

No.	Alkyl group	K		N		I
1	CH_2CH_3	.	181(36)	.	306(0.3)	.
2	$CH(CH_3)_2$	.	168(38)	.	246(0.3)	.
3	$C(CH_3)_3$	.	205(26)	.	212(—)	.
4	$CH_2CH_2CH_3$	.	133(34)	.	258(—)	.
5	$CH(CH_3)CH_2CH_3$	.	153(38)	.	213(0.1)	.
6	$CH_2CH(CH_3)_2$	.	126(37)	.	276(0.1)	.
7	$C(CH_3)_2CH_2CH_3$	.	201(33)	[.	199(0.1)]	.
8	$CH(CH_3)CH(CH_3)_2$	.	141(22)	.	203(0.4)	.
9	$CH_2C(CH_3)_3$	.	150(32)	.	248(0.4)	.
10	$C(CH_3)_2CH(CH_3)_2$	.	181(28)	[.	173(0.1)]	.
11	$CH(CH_3)C(CH_3)_3$	.	176(31)	[.	164(0.1)]	.

a) The latter quantities are in parentheses. Brackets indicate monotropic transitions.

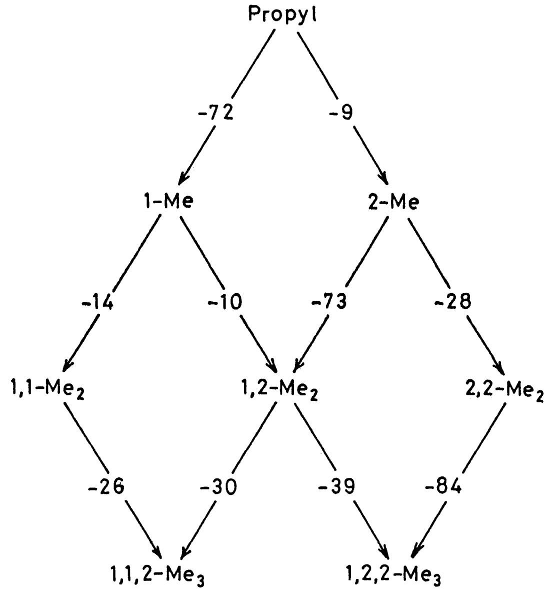


Fig. 1. The change in the N-I transition temperature (°C) of the propyl ester of the cyano derivative by the introduction of a branching methyl group.

for the propyl ester in Fig. 1. The clearing point is progressively depressed by the introduction of branching methyl groups. The reduction of the nematic thermal stability by the 1-methylation of the propyl ester is eight-times larger than that by the 2-methylation. The effects of a branching methyl group introduced to the 1 position is represented by the following order of the temperature decrease:

2,2-dimethylpropyl > 2-methylpropyl > propyl >
1,2-dimethylpropyl > 1-methylpropyl.

Thus, the reduction of the nematic thermal stability by a branching 1-methyl group is augmented by the presence of 2-methyl group(s) (compare the reduction of the clearing point of the propyl ester, −72 °C, with that of the 2-methylpropyl ester, −73 °C, and also that of the latter with that of the 2,2-dimethylpropyl ester, −84 °C). However, it is diminished by the presence of a 1-methyl group (compare the reduction of the clearing point of the propyl ester with that of the 1-methylpropyl ester, −14 °C, and also that of the 2-methylpropyl ester with that of the 1,2-dimethylpropyl ester, −30 °C). Thus, the effects of these methyl groups cannot be assessed by the additivity rule. On the other hand, the depression of the nematic thermal stability by a branching 2-methyl group is enlarged by the presence of a methyl group at any position in the propyl group. The magnitude of the depression falls off in the following order:

1,2-dimethylpropyl > 2-methylpropyl >
1.1-dimethylpropyl > 1-methylpropyl > propyl.

The reduction is augmented more by the presence of a 2-methyl group than by the presence of 1-methyl group(s). For example, the reduction of the clearing point of the 1-methylpropyl ester, −10 °C, and that of the 2-methylpropyl ester, −28 °C, may be compared with that of the propyl ester, −9 °C. Because of these effects, the 1-methylation of a given methyl-substituted propyl ester does not necessarily destabilize the nematic phase more than 2-methylation does. In Fig. 1 one can see that the clearing point of the 1,2-dimethylpropyl ester is depressed more by 2-methylation than by 1-methylation: 39 °C versus 30 °C. On the basis of these results, one may assume that the metastable nematic phase in the 1,1,2,2-tetramethylpropyl ester would appear around 120 °C if the melt were sufficiently supercooled.

The effects of a first branching methyl group introduced to the propyl ester of the purely nematogenic nitro derivatives are analogous to those found for the cyano derivatives. Nevertheless, the behavior of the methyl-substituted propyl esters (summarized in Fig. 2) differs remarkably from that found for the cyano derivatives. Specifically, the depression in the nematic thermal stability caused by a branching 1-methyl group is diminished by the presence of any

Table 2. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Nitrobenzoyloxy)benzylideneamino]benzoates[a)]

No.	Alkyl group	K		N		I
1	CH_2CH_3	.	175(40)	.	280(—)	.
2	$CH(CH_3)_2$	.	178(42)	.	231(0.6)	.
3	$C(CH_3)_3$	.	175(42)	.	185(0.1)	.
4	$CH_2CH_2CH_3$	.	141(32)	.	271(—)	.
5	$CH(CH_3)CH_2CH_3$	.	149(18)	.	161(0.5)	.
6	$CH_2CH(CH_3)_2$	.	142(37)	.	258(0.4)	.
7	$C(CH_3)_2CH_2CH_3$	.	194(40)	[.	185(0.1)]	.
8	$CH(CH_3)CH(CH_3)_2$	.	145(32)	.	186(0.3)	.
9	$CH_2C(CH_3)_3$	.	178(41)	.	219(0.1)	.
10	$C(CH_3)_2CH(CH_3)_2$	.	177(44)	.	286(—)	.
11	$CH(CH_3)C(CH_3)_3$	.	186(36)	[.	178(0.1)]	.

a) The latter quantities are in parentheses. Brackets indicate monotropic transitions.

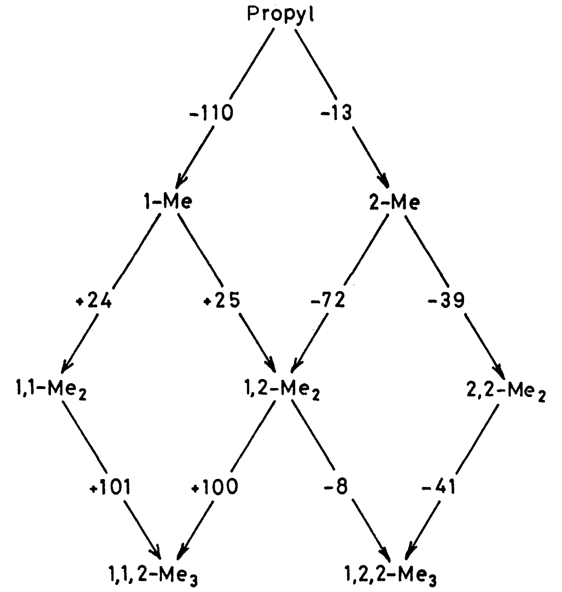


Fig. 2. The change in the N-I transition temperature (°C) of the propyl ester of the nitro derivative by the introduction of a branching methyl group.

branching methyl group. The magnitude decreases in the following order:

propyl > 2-methylpropyl > 2,2-dimethylpropyl >
1-methylpropyl > 1,2-dimethylpropyl.

It may be noteworthy that 1-methylation of the last two esters gives rise to the promotion of the transition temperature as much as by 24 °C and 100 °C.

The change in the thermal stability by 2-methylation is also different from that found for the cyano derivatives. The following order of the depression is obtained:

2-methylpropyl > propyl > 1,2-dimethylpropyl >
1-methylpropyl > 1,1-dimethylpropyl.

Here again, the promotion of the transition temperature by an additional methyl group is observed for esters carrying the last two alkyl groups. Consequently, a stable nematic phase may appear in the 1,1,2,2-tetramethylpropyl ester. It may be added that, on the two routes starting from the 1-methylpropyl ester and ending at the 1,1,2-trimethylpropyl ester, the 1- and 2-methyl groups affect the clearing point of the precursors to almost the same extent.

The *t*-butyl and 1,1-dimethylpropyl esters in the methyl derivatives are not mesogenic at all. The observed clearing point depression arising from 1-methylation diminishes in the following order and the stabilization of the nematic occurs in the last two:

propyl > 2-methylpropyl > 2,2-dimethylpropyl
> 1,2-dimethylpropyl.

Judging from this order, it must be said that the absence of a nematic phase in the 1,1-dimethylpropyl ester (for which the result of elemental anlysis is given in Experimental) is anomalous; therefore, the accumulated methyl groups in the present derivative cause more complex effects on the nematic thermal stability than those found for the cyano and nitro derivatives.

The accumulation of methyl groups in different ways results in a promotion of the nematic thermal stability: namely, by 3 °C in the 2,2-dimethylpropyl ester and by 98 °C in the 1,2-dimethylpropyl ester. The order of the clearing point depression given by the 2-methylation is as follows:

2-methylpropyl > 1,2-dimethylpropyl > propyl
> 1-methylpropyl > 1,1-dimethylpropyl.

Table 3. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Methylbenzoyloxy)benzylideneamino]benzoates[a)]

No.	Alkyl group	K		S_A		N		I
1	CH_2CH_3	.	181(46)			.	250(0.5)	.
2	$CH(CH_3)_2$	.	183(35)	[.	156(—)]	[.	177(0.1)]	.
3	$C(CH_3)_3$	.	193(36)					.
4	$CH_2CH_2CH_3$	.	150(40)	[.	134(—)]	.	236(0.3)	.
5	$CH(CH_3)CH_2CH_3$	.	156(37)	[.	146(2.9)]	[.	155(0.1)]	.
6	$CH_2CH(CH_3)_2$	.	136(37)	[.	127(—)]	.	229(0.3)	.
7	$C(CH_3)_2CH_2CH_3$	.	161(36)					.
8	$CH(CH_3)CH(CH_3)_2$	.	160(39)	[.	139(1.7)]	[.	154(0.2)]	.
9	$CH_2C(CH_3)_3$	.	145(30)			[.	140(0.8)]	.
10	$C(CH_3)_2CH(CH_3)_2$	.	181(52)			.	252(0.4)	.
11	$CH(CH_3)C(CH_3)_3$	.	166(31)	[.	131(—)]	[.	143(0.2)]	.
12	$CH_2CH_2CH_2CH_3$	.	136(37)	.	149(0.1)	.	209(0.3)	.
13	$CH(CH_3)CH_2CH_2CH_3$	.	146(36)	[.	145(3.1)]			.
14	$CH_2CH(CH_3)CH_2CH_3$	.	119(26)	.	136(0.9)	.	199(0.4)	.
15	$CH_2CH_2CH(CH_3)_2$	.	135(28)	.	164(1.9)	.	194(0.2)	.
16	$CH_2CH_2CH_2CH_2CH_3$	.	139(41)	.	147(0.5)	.	206(0.5)	.
17	$CH(CH_3)CH_2CH_2CH_2CH_3$	.	150(44)	[.	142(3.9)]			.
18	$CH_2CH(CH_3)CH_2CH_2CH_3$	.	121(32)	.	129(1.7)	.	196(0.4)	.
19	$CH_2CH_2CH(CH_3)CH_2CH_3$	.	147(35)	.	161(1.6)	.	184(0.3)	.
20	$CH_2CH_2CH_2CH(CH_3)_2$	.	136(30)	.	162(0.8)	.	198(0.3)	.

a) The latter quantities are in parentheses. Brackets indicate monotropic transitions.

Table 4. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Chlorobenzoyloxy)benzylideneamino]benzoates$^{a)}$

No.	Alkyl group	K	S_A	N	I
1	CH_2CH_3	. 211(48)	. 218(11)	. 266(0.4)	.
2	$CH(CH_3)_2$	. 156(26)	. 204(8.3)		.
3	$C(CH_3)_3$	. 211(57)	. 218(11)	. 263(0.5)	.
4	$CH_2CH_2CH_3$	. 174(38)	. 199(2.8)	. 250(0.3)	.
5	$CH(CH_3)CH_2CH_3$	. 130(27)	. 187(5.7)		.
6	$CH_2CH(CH_3)_2$	. 132(54)	. 178(1.6)	. 238(0.3)	.
7	$C(CH_3)_2CH_2CH_3$	. 208(43)	. 219(1.0)	. 293(0.1)	.
8	$CH(CH_3)CH(CH_3)_2$	. 138(33)	. 165(3.0)	. 169(0.3)	.
9	$CH_2C(CH_3)_3$	. 146(30)	. 154(10)	. 210(0.3)	.
10	$C(CH_3)_2CH(CH_3)_2$	. 209(54)	. 219(12)	. 266(0.6)	.
11	$CH(CH_3)C(CH_3)_3$	. 180(36)	[. 145(2.2)]	[. 151(0.3)]	.
12	$CH_2CH_2CH_2CH_3$	. 155(37)	. 201(0.4)	. 224(0.3)	.
13	$CH(CH_3)CH_2CH_2CH_3$	. 122(26)	. 184(6.3)		.
14	$CH_2CH(CH_3)CH_2CH_3$	. 118(28)	. 179(2.2)	. 212(0.3)	.
15	$CH_2CH_2CH(CH_3)_2$	. 148(30)	. 207(4.0)	. 215(0.3)	.
16	$CH_2CH_2CH_2CH_2CH_3$	. 145(38)	. 201(2.7)	. 221(0.4)	.
17	$CH(CH_3)CH_2CH_2CH_2CH_3$	. 135(34)	. 174(5.9)		.
18	$CH_2CH(CH_3)CH_2CH_2CH_3$	. 99(31)	. 170(0.9)	. 208(0.3)	.
19	$CH_2CH_2CH(CH_3)CH_2CH_3$	. 159(36)	. 198(5.9)		.
20	$CH_2CH_2CH_2CH(CH_3)_2$	. 149(41)	. 198(4.4)	. 205(0.4)	.

a) The latter quantities are in parentheses. Brackets indicate monotropic transitions.

Clearly, the virtual nematic thermal stability in the 1,1-dimethylpropyl ester is strongly promoted by 2-methylation.

All of the chloro derivatives examined were smectogenic. In Table 4, one can find a strong tendency that the 1-methylation eliminates the nematic phase. Nonetheless, the presence of any methyl group diminishes the reduction of the nematic thermal stability by a branching 1-methyl group. The clearing point depression is found to fall off in the following order:

propyl > 2-methylpropyl > 2,2-dimethylpropyl
> 1,2-dimethylpropyl > 1-methylpropyl.

Since the nematic phase in the 1-methylpropyl and the 1,2-dimethylpropyl esters is stabilized by about 100 °C by the added 1-methyl group, the presence of a 1-methyl group is an extremely dominant factor in controlling the effect of a newly added 1-methyl group. On the other hand, the clearing point seems to be only slightly and irregularly affected by the presence of a 2-methyl group(s). Regarding 2-methylation, the following order was obtained:

2-methylpropyl ≈ 1,1-dimethylpropyl
> 1,2-dimethylpropyl ≈ propyl.

Table 5. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Alkyl 4-[4-(4-Acetoxybenzoyloxy)benzylideneamino]benzoates$^{a)}$

No.	Alkyl group	K	S_A	N	I
1	CH_2CH_3	. 146(23)	. 150(0.1)	. >310	.
2	$CH(CH_3)_2$	. 147(31)	. 168(0.1)	. 256(0.1)	.
3	$C(CH_3)_3$	. 181(38)		[. 165(0.1)]	.
4	$CH_2CH_2CH_3$	. 132(21)	. 155(0.1)	. >300	.
5	$CH(CH_3)CH_2CH_3$	. 144(34)	. 165(0.5)	. 227(0.3)	.
6	$CH_2CH(CH_3)_2$	. 133(32)	. 146(0.1)	. 275(0.3)	.
7	$C(CH_3)_2CH_2CH_3$	. 187(43)		[. 182(0.1)]	.
8	$CH(CH_3)CH(CH_3)_2$	. 156(36)	[. 160(0.7)]	. 213(0.2)	.
9	$CH_2C(CH_3)_3$	. 160(28)		. 253(0.1)	.
10	$C(CH_3)_2CH(CH_3)_2$	. 187(43)		[. 178(0.1)]	.
11	$CH(CH_3)C(CH_3)_3$	. 182(42)	[. 159(—)]	. 199(0.3)	.
12	$CH_2CH_2CH_2CH_3$	. 151(41)	. 162(0.2)	. 256(0.4)	.
13	$CH(CH_3)CH_2CH_2CH_3$	. 135(30)	. 167(1.5)	. 180(0.1)	.
14	$CH_2CH(CH_3)CH_2CH_3$	. 122(29)	. 143(0.1)	. 233(0.3)	.
15	$CH_2CH_2CH(CH_3)_2$	. 141(34)	. 170(0.4)	. 233(0.3)	.
16	$CH_2CH_2CH_2CH_2CH_3$	. 125(32)	. 161(0.1)	. 242(0.4)	.
17	$CH(CH_3)CH_2CH_2CH_2CH_3$	. 123(25)	. 172(1.5)	. 178(0.2)	.
18	$CH_2CH(CH_3)CH_2CH_2CH_3$	. 127(31)	. 150(0.1)	. 238(0.5)	.
19	$CH_2CH_2CH(CH_3)CH_2CH_3$	. 124(28)	. 168(0.5)	. 211(0.3)	.
20	$CH_2CH_2CH_2CH(CH_3)_2$	. 115(28)	. 150(0.1)	. 212(0.1)	.

a) The latter quantities are in parentheses. Brackets indicate monotropic transitions.

This order suggests a destabilization of the nematic phase by methyl branching at any position; however, the clearing points given by the 1,1-dimethylpropyl and 1,2,2-trimethylpropyl esters are not in accordance with this suggestion.

In the acetoxy derivatives, the presence of any methyl group in the propyl ester diminishes the clearing point depression. Regarding 1-methylation, the following order was established:

propyl > 2-methylpropyl > 2,2-dimethylpropyl
> 1-methylpropyl > 1,2-dimethylpropyl.

Regarding 2-methylation:

propyl > 2-methylpropyl > 1-methylpropyl
= 1,2-dimethylpropyl > 1,1-dimethylpropyl.

Thus, the presence of a methyl group(s) gives rise to the suppression of the clearing point depression by an added methyl group; however, their effects are not so significant that the promotion of the nematic thermal stability by a branching methyl group is never achieved in this series.

Finally, the methoxy derivatives reported in our previous paper may be summarized in the same way. The 1-methylation gives the following order:

propyl > 2,2-dimethylpropyl > 1,2-dimethylpropyl
> 2-methylpropyl > 1-methylpropyl.

Although the presence of a 1-methyl group gives rise to a promotion of the clearing point, the accumulation of methyl groups produces no drastic effect. In the case of 2-methylation, the following order was obtained:

1,1-dimethylpropyl > 1,2-dimethylpropyl >
2-methylpropyl > propyl > 1-methylpropyl.

In this order too, a remarkable change is seen in the influence of 1-methyl groups: that is, the incoming 2-methyl group promotes mesophase stability in the presence of a single 1-methyl group, whereas the same methyl group greatly depresses the stability when two 1-methyl groups exist in the chain.

It is often said that the centers of mass of the molecules in the nematic phase have three translational degrees of freedom, and are thus distributed at random. Such a picture is known to be too simple. Leadbetter et al. carried out detailed X-ray diffraction measurements on five nematogens and concluded that the structures of the different types of compounds in the nematic phase differ appreciably.[9] Thus, Schiff's bases carrying only alkyl and alkoxyl groups form rather simple structures with no strong correlations in the local order; the Schiff's base carrying a cyano group, however, has a quasi-crystalline local ordering. Most strikingly, the repeat distance along the molecular alignment in cyanobiphenyls is of about 1.4 molecular lengths, which is interpreted as arising from an overlapping head-to-tail arrangement of molecules, resulting in a quasi-smectic A structure on the local scale. The diversity in the nematic properties disclosed by the present esters can probably be understood in terms of the difference in such a local quasi-crystalline ordering in the nematic phase. In other words, the nature of terminal substituent exerts significant effects on the molecular packing adopted in the nematic phase, resulting in quite different effects of chain branching of the ester alkyl group on the mesomorphic properties.

$\mathrm{S_A}$-I or $\mathrm{S_A}$-N Transition and Chain Branching. Smectic A phases are of a higher degree of order than nematic phases; therefore, thermal stability may be more susceptive to branching of the ester alkyl chain. If so, the effect on the smectic properties of the present compounds may be as complicated as we have seen for the nematic properties. In order to check such a possibility, the methyl, chloro, and acetoxy derivatives carrying butyl, pentyl, and their monomethyl-substituted groups were included in the present work. As is clear from Tables 3 to 5, these esters are all smectogenic. Indeed, the change in the thermal stability of the smectic A phase by chain branching depends strikingly upon the nature of the substituent and also upon the alkyl chain length.

When the terminal substituent is a methyl group, the introduction of a branching methyl group to the 1

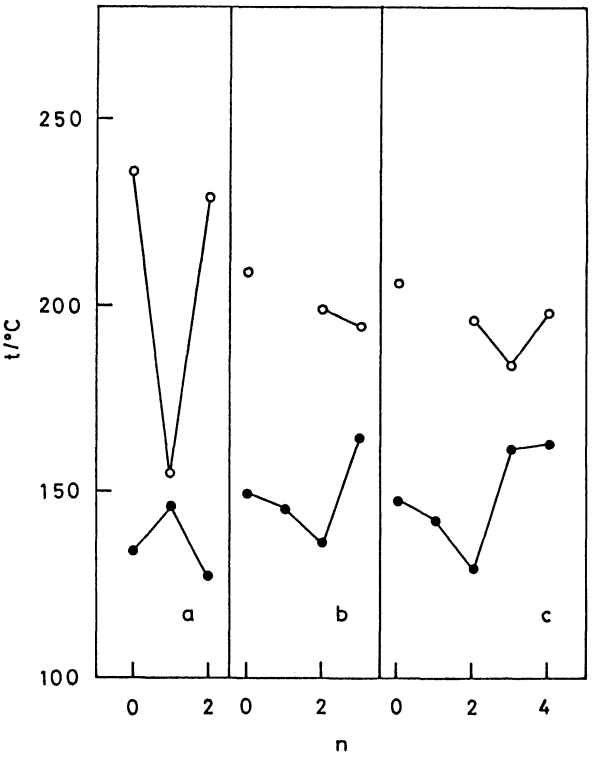


Fig. 3. Plots of the $\mathrm{S_A}$-N/$\mathrm{S_A}$-I (●) and N-I (○) transition temperatures against the position of the branching methyl group. The unmethylated alkyl ester is denoted by 0. (a) propyl, (b) butyl, and (c) pentyl esters of the methyl derivative.

position of the propyl ester enhances the smectic properties but that to the 2 position gives rise to the depression as depicted in Fig. 3. In contrast, the branching methyl group at the 1 position of the butyl and pentyl esters slightly depresses the smectic properties; in other words, a decrease in the transition temperature by 4 to 5 °C was observed. The methyl group at the 2 position further decreases the transition temperature. It must be added that the change is more than twice that caused by the 1-methyl group. A marked odd-even alternation in the nematic thermal stability by the shift of a branching methyl group, which is analogous to that found for the methoxy derivatives, was partially exhibited by these esters.

In the chloro derivatives, the depression of the transition temperature by the 1-methyl group increases as the ester alkyl becomes longer. The depression by the 2-methyl group is larger than that by the 1-methyl group in all of the three esters, and the magnitude also increases with increasing the alkyl chain length.

The effects of a branching methyl group on the propyl ester of the acetoxy derivatives closely resemble those found for the propyl ester of the methyl derivatives. However, the alternation in the transition temperature by the shift of the branching methyl group to the end of the chain continues to occur in the butyl and pentyl esters.

In conclusion, the effects of a branching of the ester alkyl chain on both the nematic and smectic properties are much more complicated than those demonstrated in early studies. Evidently, all of the positions of the branching methyl groups, the length of the alkyl chain, the nature of the terminal substituent, and the molecular framework are important factors which affect the molecular interactions responsible for the formation of mesophases. They are also strongly interdependent. Therefore, much remains to be studied about the relationship between the molecular structure and the properties of mesophases.

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