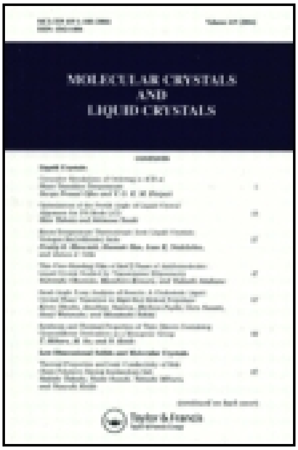

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Mesomorphic Behavior of 4-t-Butylphenyl 4-(4-Alkoxybenzylideneamino) benzoates and 4-(4-Alkoxybenzylideneamino)-phenyl4-t-Butylbenzoates

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Mesomorphic Behavior of 4-*t*-Butylphenyl 4-(4-Alkoxybenzylideneamino)benzoates and 4-(4-Alkoxybenzylideneamino)-phenyl 4-*t*-Butylbenzoates

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Phenyl 4-(4-alkoxybenzylideneamino)benzoates become more strongly smectogenic by the incorporation of the 4-*t*-butyl group to the phenyl moiety and only the methoxy member is purely nematogenic. The ethoxy to pentyloxy members exhibit both a nematic phase and a smectic A phase. The higher homologous members are no longer nematogenic and a smectic C phase is additionally generated. The *t*-butyl group gives a decrease in the nematic thermal stability by 26 to 6°C relative to that of the unsubstituted phenyl esters depending upon the alkyl chain length. The mesomorphic properties of the 4-ethylphenyl and 4-isopropyl esters are presented for comparison. A smectic C phase is observed for the hexyloxy and higher members of the latter ester. In contrast, the isomeric 4-(4-alkoxybenzylideneamino) phenyl 4-*t*-butylbenzoates produce no smectic phase.

Keywords: *t*-butyl group; isopropyl group; nematic; smectic A; smectic C

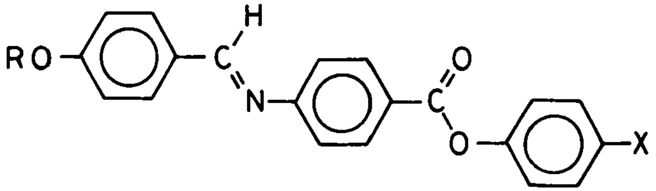
INTRODUCTION

Gray and Harrison carried out the first systematic study on the effects of branching of ester alkyl chains on the mesomorphic behavior employing a range of Schiff's bases derived from alkyl 4-aminocinnamates, particularly those with a terminal cyano or phenyl substituent in the benzylidene moiety [1, 2]. They found that 1-methylation greatly decreases the nematic-isotropic (N–I) transition temperature and the effect on the temperature becomes smaller by the movement of the methyl group to the 2-, 3-, or 4-position. For smectogenic esters, 1-methylation has a much smaller effect on the smectic A – isotropic ($S_A - I$) transition temperatures, and as the methyl group is moved to the end of the chain, the temperature depression becomes smaller.

We examined a number of compounds containing branched ester alkyl groups [3–8]. An alternation in the N – I transition temperature occurring when the first branching methyl group is moved progressively to the penultimate carbon of the chain is in accordance with that established for the cinnamate esters by Gray and Harrison, but the second and/or third methyl groups were found to either further depress or enhance the transition temperature, depending upon the nature of the terminal substituent located at the other end of the molecule. Furthermore, the stabilization of the smectic A phase by branching was often noted.

While the effects of branching of ester alkyl chains on the mesomorphic behavior have been extensively studied, not much attention has been paid to the alkyl chains directly attached to an aromatic ring. Gray and Kelly examined 4-alkoxy- and 4-alkyl-4′-cyanobiphenyls and 4-alkyl-4″-cyano-*p*-terphenyls and concluded that the effects on the N – I transition temperatures approximate those found by the works on benzoates and cinnamates [9]. In no case was the branching methyl group located at the 1-position of the alkyl group. To the author's best knowledge, the *t*-butyl group has never been evaluated as a terminal substituent with the exception of 4-*t*-butyl-1, 2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] in which the smectic thermal stability is markedly enhanced by the introduction of a *t*-butyl group into the 4-position of the 1,2-phenylene moiety but the nematic phase is completely lost [10].

As the size of the *t*-butyl group ($44.34\,\mathrm{cm^3\,mol^{-1}}$) is nearly the same as that of the phenyl group ($45.84\,\mathrm{cm^3\,mol^{-1}}$) [11], the effects of this bulky nonpolar group directly attached to the molecular core on the mesomorphic properties might not be predictable on the basis of the above-mentioned results. This paper will report on the mesomorphic behavior of the 4-*t*-butylphenyl 4-(4-alkoxybenzylideneamino)benzoates (1, X = *t*-butyl) and isomeric 4-(4-alkoxybenzylideneamino)phenyl 4-*t*-butylbenzoates (2, X = *t*-butyl). The data of the 4-ethylphenyl and 4-isopropylphenyl esters (X = ethyl and isopropyl) will be presented for consideration of effects of branching methyl groups.



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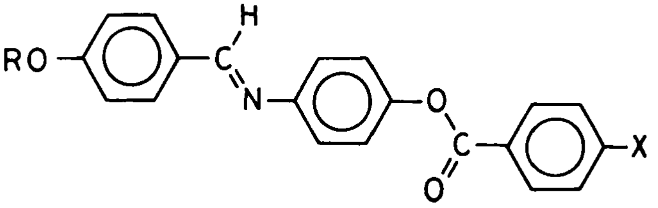

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EXPERIMENTAL

All the 4-alkoxybenzaldehydes, 4-alkylphenols, and 4-alkylbenzoic acids were commercially available. 4-(4-Alkoxybenzylideneamino)benzoic acids prepared by condensing 4-alkoxybenzaldehydes with 4-aminobenzoic acid were esterified by the carbodiimide method with unsubstituted, 4-ethyl-, 4-isopropyl, and 4-*t*-butylphenol, respectively [12]. For the preparation of the isomeric compounds, 4-aminobenzoic acid was replaced with 4-aminophenol and 4-alkylphenol with 4-alkylbenzoic acid. The products were recrystallized from toluene- or chloroform-ethanol until sharp constant transition temperatures were observed. Mesophase identification and transition temperature measurements were performed using a Yanaco melting point apparatus, model PV-500V, with the aid of a polarizing microscope (magnification 60 ×) and also a Rigaku differential scanning calorimeter, model TAS-300 DSC8240D.

RESULTS AND DISCUSSION

The liquid crystal transition temperatures and enthalpy changes of the esters of 4-(4-alkoxybenzylideneamino)benzoic acids (1) are listed in Table I. Here, K, S_C, S_A, N, and I stand for crystalline, smectic C, smectic A, nematic, and isotropic liquid phases, respectively. The smectic A phase was identified by its fan-shaped texture and also the homeotropic alignment and the smectic C phase by its schlieren texture.

TABLE I Transition temperatures (°C) and enthalpy changes (kJ mol^{-1})[a] of 4-*X*-phenyl 4-(4-alkoxybenzylideneamino) benzoates

n[b]	*K*	S_c	S_A	*N*	*I*
			X = *t*-Butyl		
1	.165(38)			[.145(0.4)][c]	·
2	.173(39)		[.154(0.4)][c]	[.171(0.8)][c]	·
3	.157(40)		[.148(1.0)][c]	[.155(0.8)][c]	·
4	.167(43)		[.160][c,e]	[.161][c,e]	·
5	.164(45)		[.151][c,f]	[.152][c,f]	·
6	.156(51)		[.154 (3.6)][c]		·
7	.154(48)	[.107][c,d]	[.149 (3.3)][c]		·
8	.131(37)	[.116 (---)][c]	.152(4.4)		·
10	.129(31)	[.122(0.2)][c]	.148(4.1)		·
			X = Hydrogen		
1	.136(34)			.171(0.3)[i]	·
2	.163(46)			.184(0.4)[j]	·
3	.121(39)		[.120(1.3)][c]	.163(0.3)	·
4	.115(32)		.135(1.3)	.168(0.5)	·
5	.116(41)		.135(1.4)	.158(0.4)	·
6	.103(38)		.141(1.6)	.160(0.6)	·
7	. 88(41)		.144(2.1)	.156(0.6)	·
8	. 89(41)		.148(2.5)	.156(0.8)	·
10	. 92(48)		.150[g]	.151[g]	·
			X = Ethyl		
1	.138(31)			.255(0.9)	·
2	.156(40)			.261(1.3)	·
3	.125(33)			.243(1.1)	·
4	.106(29)		.133(0.3)	.238(1.2)	·
5	. 89(22)		.145(0.5)	.225(1.2)	·
6	. 93(33)		.159(0.7)	.219(1.2)	·
7	. 80(39)		.167(0.9)	.210(1.2)	·
8	. 87(35)		.173(1.1)	.206(1.2)	·
10	. 84(37)		.179(1.7)	.197(1.2)	·
			X = Isopropyl		
1	.131(30)			.206(0.5)	·
2	.146(37)			.217(0.7)	·
3	.140(40)			.201(0.7)	·
4	.133(27)		.153(0.4)	.200(0.7)	·
5	.117(35)		.153(0.5)	.188(0.7)	·
6	.112(32)	[. 80][c,d]	.162(0.9)	.187(0.9)	·
7	. 97(37)	[.102][c,d]	.163(1.0)	.180(1.1)	·
8	.100(29)	[.106][c,d]	.166(1.1)	.178(1.1)	·
10	. 90(38)	[.113][c,d]	.167[h]	.170[h]	·

[a] Values in parentheses.
[b] The number of carbon atoms in the alkoxy group.
[c] Monotropic transition.
[d] Microscopic observation.
[e] The combined enthalpy value is 3.7 kJ mol^{-1}.
[f] The combined enthalpy value is 3.3 kJ mol^{-1}.
[g] The combined enthalpy value is 5.1 kJ mol^{-1}.
[h] The combined enthalpy value is 4.6 kJ mol^{-1}.
[i] 139°C (32 kJ mol^{-1}) and 174°C (0.4 kJ mol^{-1}) by Funakoshi *et al.* (Ref. 13).
[j] 161°C (36 kJ mol^{-1}) and 182°C (0.5 kJ mol^{-1}) by Funakoshi *et al.* (Ref. 13).

The molecule is elongated without increasing the molecular width by the incorporation of the terminal substituent; nevertheless, the N – I transition temperature of the 4-*t*-butylphenyl esters is depressed relative to that of the unsubstituted phenyl esters. The depression is 26°C for the methoxy member but only 6°C for the pentyloxy member. It may be noted that the 4-*t*-butylphenyl esters are more strongly smectogenic than the unsubstituted phenyl esters in qualitative agreement with the above-mentioned observations made on 1,2-phenylene analogues in which the nematic phase is completely eliminated and the smectic A thermal stability is enhanced by the 4-*t*-butyl substituent [10]. The nematic phase of the higher members of the present parent compounds is also lost by the *t*-butyl substitution. Not only a smectic A phase is generated by the substitution to the ethoxy member but also the S_A-N transition temperature in the higher members is promoted compared to that of the corresponding phenyl ester; for example, by 28°C for the propoxy member. Moreover, the substitution generates a smectic C phase in the heptyloxy to decyloxy members.

The crystalline phase in most members is stabilized by the incorporation of a 4-*t*-butyl group. For example, the difference in the melting point between the phenyl and *t*-butylphenyl esters is 10°C for the ethoxy member and increases up to 66°C for the heptyloxy member, suggesting that the bulky rigid alkyl group in the present series gives rise to an efficient molecular packing in the crystalline phase. If a similar situation is expected more or less in the mesophases, it might explain the tendency of stabilizing smectic phases.

The afore-mentioned mesomorphic behavior may be discussed from the standpoint of effects of branching methyl groups. To do so, we must examine the behavior of the 4-ethylphenyl and 4-isopropylphenyl esters. Upon the introduction of the 4-ethyl group to the phenyl moiety, the nematic phase appearing in the methoxy to octyloxy members is thermally stabilized by 50°C (for the octyloxy member) to 80°C (for the propoxy member). Even though the existence range of the nematic phase of the decyloxy member of the unsubstituted phenyl ester nearly vanishes, the corresponding member of the 4-ethylphenyl ester gives a thermodynamically stable nematic phase over a range of 18°C. The terminal ethyl group stabilizes also the smectic A phase by 10°C for the pentyloxy member to 25°C for the octyloxy member. The only exception is the butoxy member in which the S_A-N transition is located at a temperature 2°C lower than that of the same member of the unsubstituted phenyl ester.

The first branching methyl group reduces the thermal stability of the nematic phase of the methoxy member by 49°C. The extent of destabilization by the 1-methylation decreases on ascending the series, namely, to 27°C for the decyloxy member (compare plots a and b in Fig. 1). It should be noted that these depressions are unexpectedly small. Gray and Kelly observed a depression of 44.5°C by the 2-methylation of 4-butyl-4′-cyanobiphenyl and that of 117.5°C by the 1-methylation of 4-butoxy-4′-cyanobiphenyl [9]. If one assumes the behavioral trends similar to those established for the benzoate and cinnamate esters, the depressions in our compounds must be larger than theirs. The second branching methyl group produces a little larger reduction of the nematic thermal stability for the lower three members and almost the same for the next two (see plot c in Fig. 1).

The effects on the stability of the smectic phases are not simple. An enhancement as large as 20°C is found for the butoxy member by the first branching methyl group but a smaller effect by the second one. On the other hand, the smectic A phase in the higher members in both the 4-ethylphenyl and 4-isopropylphenyl esters is destabilized by the methylation, for example, 12°C for the decyloxy member by the first methyl group and 19°C by the second one. The generation of a smectic C phase by the introduction of the first branching methyl group and the promotion of thermal stability by the second one are interesting, whereas the smectic A phase appearing in the decyloxy member of the 4-ethylphenyl ester could be supercooled to 50°C without a transition to any other phase.

The emergence of a smectic C phase by the introduction of a branching methyl group is not new. We reported earlier that a smectic C phase is generated by the introduction of a branching methyl group to the alkoxycarbonyl groups in bis(4-butyloxycarbonylphenyl) and bis(4-pentyloxycarbonylphenyl) terephthalates [7]. However, a similar structural modification may affect the mesomorphic behavior in the opposite way. The smectic C phase appearing in butyl 4-(4-alkoxybenzylideneamino)-benzoates, where the alkoxy group is butoxy to decyloxy, is eliminated by the 2-methylation of the ester butyl group [4]. Therefore, it is difficult to understand how the above-mentioned observations regarding the smectic C behavior is related to the terminal branched alkyl group.

4-(4-Alkoxybenzylideneamino) phenyl benzoates ($2, X = H$), where the carbonyloxy group is inverted, are known to exhibit no smectic phase [14]; therefore, an extension of our work to the 4-*t*-butylbenzoates seemed to be worthwhile. As is shown in Table II, all the examined 4-ethyl-, 4-isopropyl, and 4-*t*-butylbenzoates are purely nematogenic. The N – I transition temperature of the *t*-butylbenzoates is affected only a little by the inversion of the carbonyloxy group except for the methoxy member (compare plots c and d in Fig. 1). The molecular packing in the crystals of the 4-*t*-

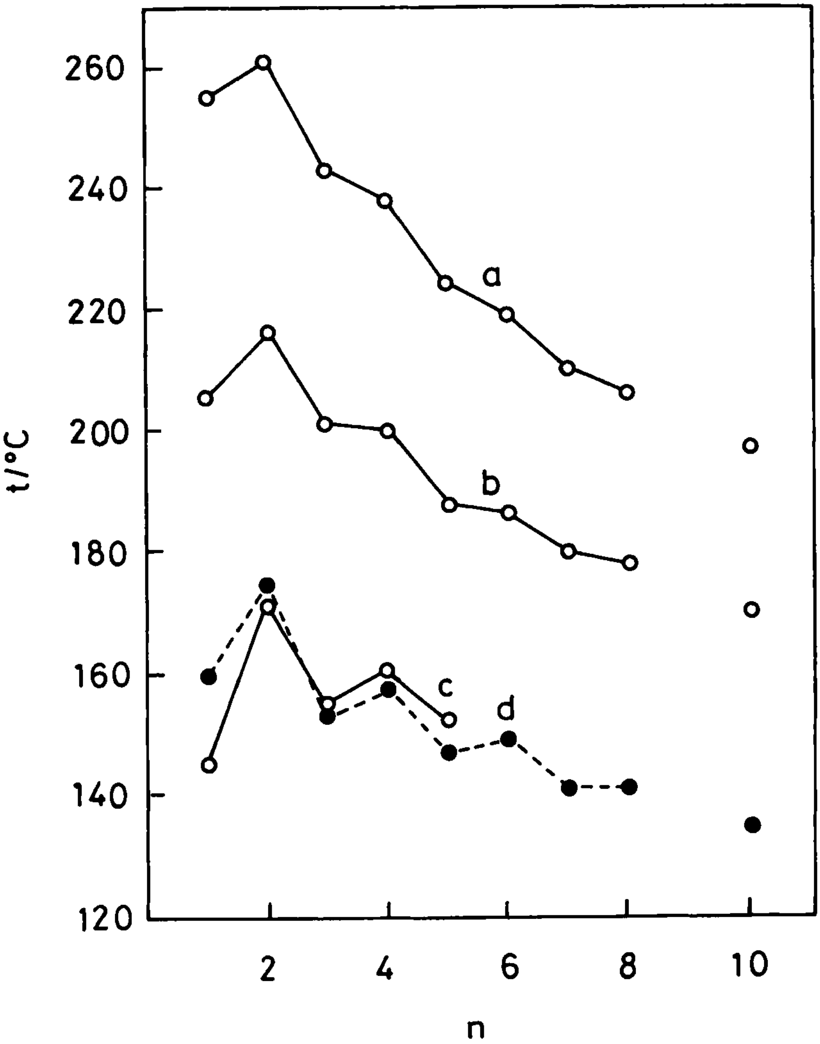

FIGURE 1 Dependence of the N–I transition temperature on the number of carbon atoms (*n*) in the alkoxy group. (a) 4-ethylphenyl 4-(4-alkoxybenzylideneamino)benzoates (1, *X* = ethyl), (b) 4-isopropylphenyl 4-(4-alkoxybenzylideneamino)benzoates (1, *X* = isopropyl), (c) 4-*t*-butyl 4-(4-alkoxybenzylideneamino)benzoates (1, *X* = *t*-butyl, represented by open circles), and (d) 4-(4-alkoxybenzylideneamino) phenyl 4-*t*-butylbenzoates (2, *X* = *t*-butyl, represented by shaded circles).

butylbenzoates appears to be more efficient than that of the 4-*t*-butylphenyl esters as indicated not only by higher K–N transition temperatures but also the large associated enthalpy changes. This situation does not help the

TABLE II Transition temperatures (°C) and enthalpy changes (kJ mol^{-1})[a] of 4-(4-alkoxybenzylideneamino) phenyl 4-*X*-benzoates

n[b]	*K*	*N*	*I*
		X = *t*-Butyl	
1	.193(48)	[.160(0.9)][c]	.
2	.202(54)	[.175(1.7)][c]	.
3	.191(52)	[.153(1.2)][c]	.
4	.184(55)	[.158(1.7)][c]	.
5	.167(50)	[.147(1.3)][c]	.
6	.158(47)	[.149(1.6)][c]	.
7	.142(47)	[.141(1.4)][c]	.
8	.148(47)	[.141(1.5)][c]	.
10	.140(50)	[.135(1.6)][c]	.
		X = Hydrogen	
8	.110(42)	.151(0.8)	.
10	.105(55)	.146(1.0)	.
		X = Ethyl	
8	.96(31)	.209(1.7)	.
10	.88(32)	.196(1.7)	.
		X = Isopropyl	
8	.111(34)	.176(1.5)	.
10	.102(26)	.169(1.5)	.

[a] Values in parentheses.
[b] The number of carbon atoms in the alkoxy group.
[c] Monotropic transition.

thermal stabilities of the nematic phases; however, the entropy changes at the N–I transition of 4-*t*-butylbenzoates nearly twice as large as than those of 4-*t*-butylphenyl esters imply that the nematic phase in the second series is more ordered than that of the first one. The N–I transitions in the ethylbenzoates and isopropylbenzoates are not much affected by the inversion of the carbonyloxy group. In the case of phenyl 4-(4-alkoxybenzylideneamino)benzoates, the smectogenic ability of the molecular core is so strong that the rather small effects of the *t*-butyl group on the smectic thermal stabilities are detectable. When the linking carbonyloxy group is inverted, the molecular core becomes too unfavorable for the generation of a smectic phase and we cannot observe any effect of a terminal alkyl group on the smectic behavior.

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