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Mesomorphic Properties of 3-Pyridyl 4-(4-Alkoxybenzyleneamino) benzoates and Isomeric Compounds

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The nematic-isotropic transition temperature of 3-pyridyl 4-(4-propoxybenzylideneamino) benzoate is higher by 13°C than that of the phenyl analogue and the smectic A-nematic/isotropic transition is also promoted by the replacement of the terminal moiety as much as 23°C. The enhancement of both the nematic and smectic thermal stabilities decreases as the terminal alkyl chain length increases. Similar changes in the mesomorphic properties by the replacement are recorded for N- [4-(4-alkoxybenzoyloxy) benzylidene] anilines and other isomeric compounds.

Keywords: nematic; smectic; 3-pyridyl group

INTRODUCTION

The generation of a smectic A phase by the 3-halogenation of the phenyl moiety of purely nematogenic 4-(benzylideneamino)phenyl 4-alkoxybenzoates and 4-(4-alkoxybenzylideneamino)phenyl benzoates was revealed in our previous papers [1,2]. For example, the smectic A-nematic (S_A -N) transition temperature of the octyloxy member of the former compound is located at 113°C for the F derivative, 100°C for the Cl derivative, and 89°C for the Br derivative [1]. These temperatures are higher than 87°C where the nematic melt of the parent compound solidifies. The promotion of the S_A -N transition temperature by the incorporation of a 3-halogeno substituent to the terminal phenyl moiety accompanied by the depression of the nematic-isotropic (N-I) transition temperature is in sharp

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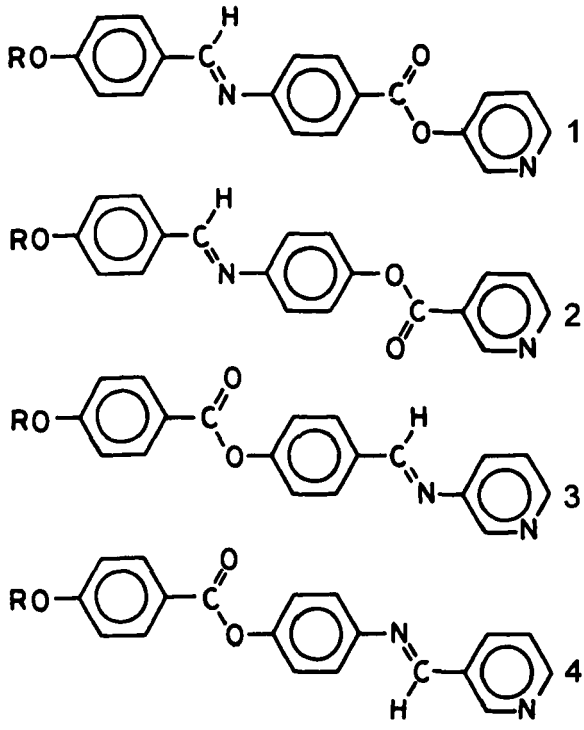
contrast to the observations reported by Gray and Worrall for 3'-X-4'-octyloxybiphenyl-4-carboxylic acid; namely, the introduction of a lateral substituent depresses the smectic thermal stability more than the nematic thermal stability [3].



Our study on phenyl 4-(4-alkoxybenzylideneamino)benzoates disclosed that the smectic A thermal stability may be enhanced or depressed by the 3-halogeno substitutent depending upon the size of the substituent and the terminal alkyl chain length [4]. When the alkyl chain is short, the entropy of the S_A -N transition of the parent compound is small. In such a case, the molecular ordering in the smectic phase is relatively low and the lateral polar substituents may facilitate the formation of the smectic phase by enhancing the lateral molecular attraction. On the other hand, the lamellar packing in the smectic phase of the higher homologous members with relatively large S_A -N transition entropies is better ordered and may be disrupted by the steric effects of the lateral substituent. If this proposition is right, 3-pyridyl 4-(4-alkoxybenzylideneamino)benzoates (1) and

isomeric compounds (2–4) may exhibit the enhanced smectic thermal stability compared with the phenyl analogues regardless of the alkyl chain length as the 3-pyridyl moiety increases the lateral polarity of the molecule without increasing the size of the terminal moiety. This situation bears some similarity to that recorded by Gray and Jones for 5-substituted 6-alkoxy-2-naphthoic acids in which a chloro or bromo substituent can be accommodated at the 5-position without noticeably broadening the molecule [5,6]. The dipole of the 5-halogeno substituent strengthens the intermolecular attractions and promotes both the S-N and N-I transition temperatures because of the absence of any breadth increase, the S-N transition being more affected.

EXPERIMENTAL

3-Hydroxypyridine, 3-aminopyridine, nicotinic acid, pyridine-3-aldehyde were commercially available. The desired compounds were obtained by the procedures similar to those employed for the preparation of the phenyl analogues [1,2,4,7]. Transition temperature measurement and mesophase identification were carried out using a Rigaku differential scanning calorimeter, model TAS-300 DSC240D and a Yanaco melting point apparatus, model PV-500V, with the aid of a polarizing microscope (magnification 60×).

RESULTS AND DISCUSSION

The liquid crystalline transition temperatures and the associated enthalpies of compounds 1 to 4 are presented in Table I. Here, K, S_A, N, and I stand for the crystalline, smectic A, nematic, and isotropic phases, respectively. The smectic A phase has a strong tendency to be homeotropic and a short-lived focal conic texture could be observed on cooling the higher temperature phase. The N-I and S_A -N/I transition temperatures of compound 1 are plotted in Figure 1 against the number of carbon atoms in the alkoxy group (n). The data of the phenyl analogues taken from our previous paper [4] are also shown in the same figure for the sake of comparison. The N-I transition temperature is markedly raised compared with that of the phenyl analogue; for example, 16°C for the methoxy member, confirming that the increased lateral polarity is a factor favorable to the stabilization of the nematic phase. The extent of the promotion decreases by lengthening the alkyl chain which may serve to dilute the core-core interactions, exhibiting the even-odd alternation. The pronounced promotion of the S_A -N/I

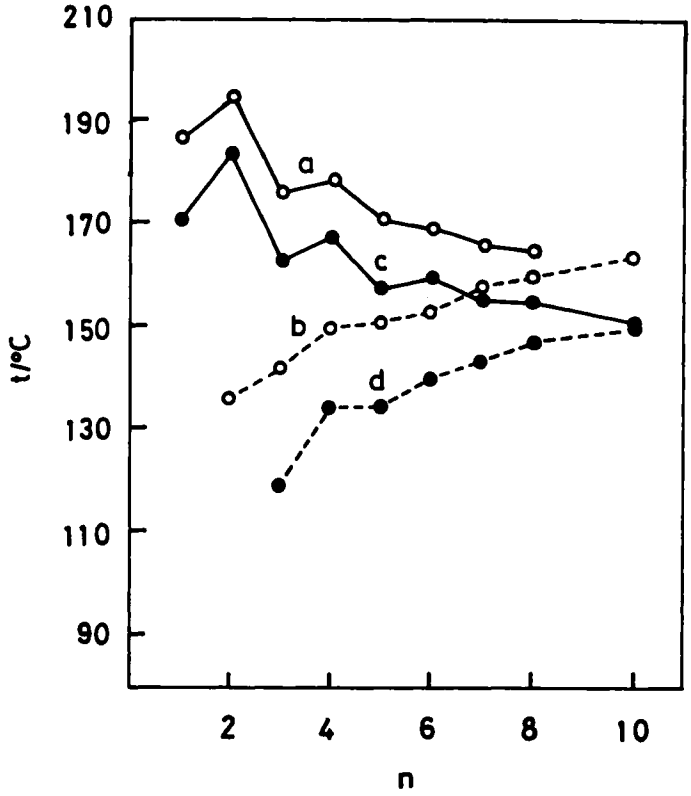


FIGURE 1 Variation of the transition temperatures with the number of carbon atoms in the alkoxy group, n. (a) N-I and (b) S-N/I transitions of compounds 1 indicated by open circles. (c) N-I and (d) S-N transitions of the phenyl analogues indicated by shaded circles

transition can be noted in Figure 1; that is, 23°C for the propoxy member and 14°C for the decyloxy member. It must be added that the melting point is not much affected by the replacement and is markedly reduced in the case of the ethoxy member. These observations are in conformity with the mesomorphic properties described by Nash and Gray; namely, the N-I transition temperature of 4-(benzylideneamino)-4′-methoxybiphenyl is raised from 175.5°C to 195.2°C by the replacement of the terminal phenyl group with the 3-pyridyl group and the S_A -I transition of the 4′-octyloxy analogue from 169°C to 194°C [8].

The S_A -N/I and N-I transition temperatures of compound 2 and its phenyl analogue, 4-(4-alkoxybenzylideneamino)phenyl benzoate are plotted in Figure 2. The N-I transition temperature of the present phenyl analogue is the highest among the four isomeric compounds. For the methoxy member, the transition

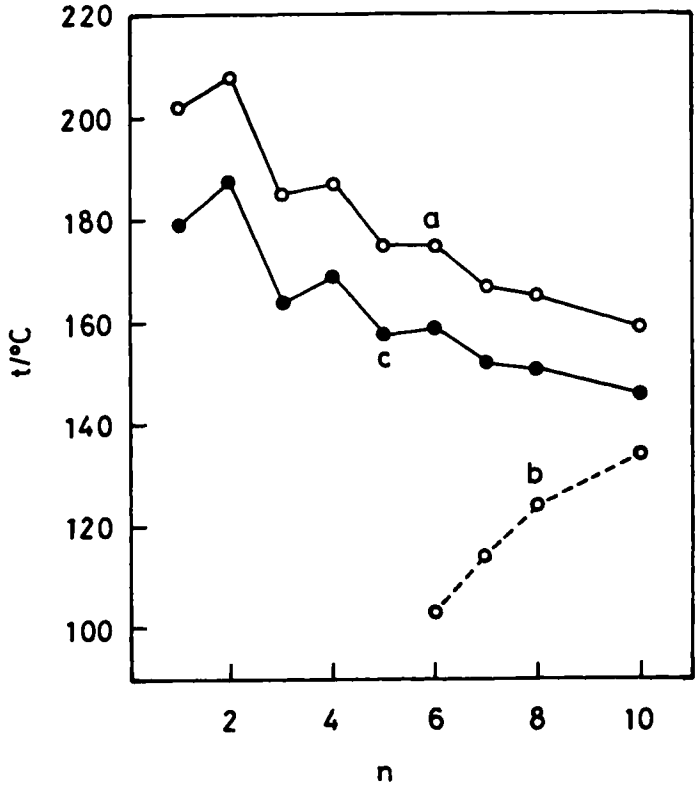


FIGURE 2 Variation of the transition temperatures with the number of carbon atoms in the alkoxy group, n. (a) N-I and (b) S-N transitions of compounds 2 indicated by open circles. (c) N-I transitions of the phenyl analogues indicated by shaded circles

temperature is found between 179°C of 4-(4-alkoxybenzylideneamino)phenyl benzoate [2] and 170°C of 4-(benzylideneamino)phenyl 4-alkoxybenzoate, the phenyl analogue of compound 4 [1]. The difference in the N-I transition temperature is nearly doubled by the replacement of the phenyl group with the 3-pyridyl group; the methoxy member of compound 2 exhibits the highest transition temperature, 202°C, and those of compounds 1 and 3 exhibit the lowest, 187°C. The enhancement by the replacement of the phenyl group with the 3-pyridyl group is also large in compound 2; namely, 23°C for the methoxy member and 14°C for the octyloxy member. While the smectogenic behavior of the phenyl analogue of compound 1 is completely eliminated by the inversion of the carbonyloxy group, a smectic A phase is found for the hexyloxy and higher homologous members of compound 2, naturally the temperature being lower than that of compound 1. As

the nematic melt of the octyloxy member of the phenyl analogue is solidified at 90°C [2], the smectic stability is enhanced by the replacement more than 34°C for this member.

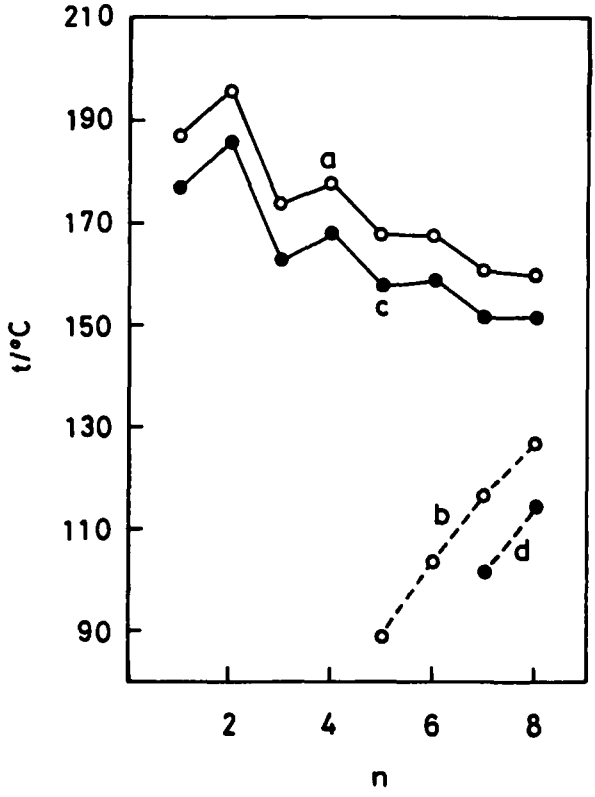


FIGURE 3 Variation of the transition temperatures with the number of carbon atoms in the alkoxy group, n. (a) N-I and (b) S-N transitions of compounds 3 indicated by open circles. (c) N-I and (d) S-N transitions of the phenyl analogues indicated by shaded circles

Figure 3 presents plots of the transition temperatures of compound 3 and its phenyl analogue, N-[4-(4-alkoxybenzoyloxy)benzylidene]aniline [7], against the number of carbon atoms in the alkyl group. The difference in the N-I transition temperature between these two series is the smallest among the isomeric compounds; merely 10°C for the lower homologous members and a slight decrease by the increase of the alkyl chain length. The heptyloxy and octyloxy members of the phenyl analogue are known to be smectogenic [4]. The enhancement of the smectic thermal stability is more than the nematic thermal stability by the replacement; namely, 15°C for the heptyloxy member and 12°C for the octyloxy member.

TABLE I Transition temperatures (°C) and associated enthalpy changes (kJ mol^{-1})* of compounds 1–4

n^a	K	S_A	N	I
		Compound 1		
1	. 135(38)		. 187(0.3)	.
2	. 138(31)	[. 137(1.7)][b]	. 195(0.4).	.
3	. 136(31)	. 143(2.3)	. 176(0.3)	.
4	. 118(36)	. 151(1.8)	. 179(0.5)	.
5	. 95(39)	. 152(2.1)	. 171(0.5)	.
6	. 100(39)	. 154(1.9)	. 169(0.6)	.
7	. 87(42)	. 159(2.4)	. 166(0.6)	.
8	. 91(33)	. 161(3.3)	. 165(1.0)	.
10	. 83(51)	. 164(5.5)		.
		Compounds 2		
1	. 133(41)		. 202(0.6)	.
2	. 133(34)		. 208(0.9)	.
3	. 120(36)		. 185(0.6)	.
4	. 111(41)		. 187(0.6)	.
5	. 113(44)		175(0.5)	.
6	. 110(45)	[. 103(0.2)][b]	175(0.7)	.
7	. 116(53)	[. 114(0.3)][b]	167(0.8)	.
8	. 113(53)	. 124(0.6).	165(0.8)	.
10	. 117(57)	. 134(0.7)	. 159(0.9)	.
		Compounds 3		
1	. 121(31)		. 187(0.5)	.
2	. 128(38)		. 196(0.6)	.
3	. 122(39)		. 174(0.4)	.
4	. 101(35)		. 178(0.7)	.
5	. 113(39)	[. 89(0.1)][b]	. 168(0.6)	.
6	. 105(35)	[. 104(0.2)][b]	. 168(0.6)	.
7	. 94(46)	. 117(0.3)	. 161(0.7)	.
8	. 91(35)	. 127(0.4)	. 160(0.8)	.
		Compounds 4		
1	. 132(35)		. 191(0.8)	.
2	. 116(34)		. 198(0.8)	.
3	. 118(39)		. 175(0.7)	.
4	. 117(41)		. 177(0.8)	.
5	. 129(49)		. 167(0.7)	.
6	. 111(42)		165(0.8)	.
7	. 97(31)	[. 94(0.2)][b]	159(0.8)	.
8	. 79(39)	. 108(0.3)	. 158(1.0)	.

* Values in parentheses.

a. The number of carbon atoms in the alkoxy group.

b. Monotropic transition.

In Figure 4, the transition temperatures of compound 4 are compared with those of the phenyl analogue, 4-(benzylideneamino)phenyl 4-alkoxybenzoate [1]. The second largest promotion of the N-I transition by the replacement is found for this compound; namely, 21°C for the methoxy member and 14°C for the octyloxy member. The phenyl analogue is purely nematogenic but the S_A -N transition is detected for the last two members in Table I. The promotion of the smectic thermal stability is estimated to be more than 21°C for the octyloxy member as the nematic melt of the phenyl analogue solidified at 87°C [1].

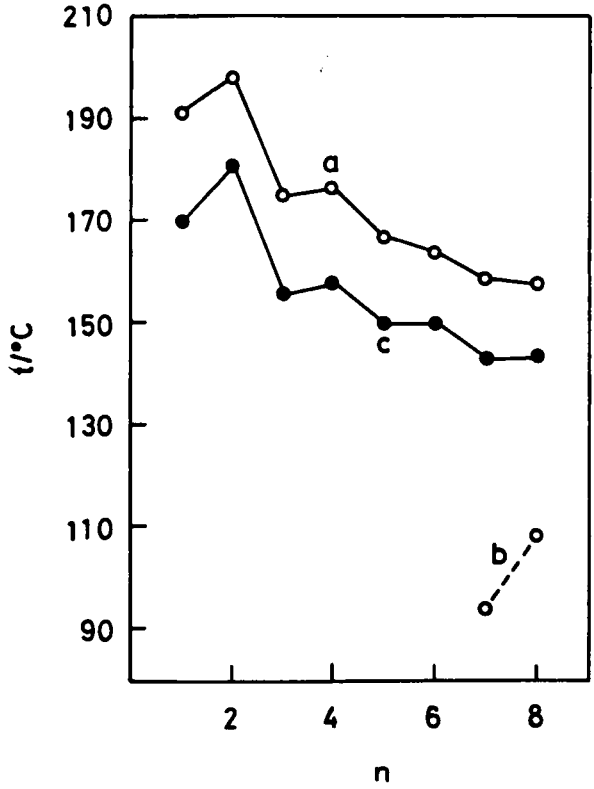


FIGURE 4 Variation of the transition temperatures with the number of carbon atoms in the alkoxy group, n. (a) N-I and (b) S-N transitions of compounds 4 indicated by open circles. (c) N-I transitions of the phenyl analogues indicated by shaded circles

It may be interesting to compare the enhancement of the smectic thermal stability by the replacement of the terminal phenyl group with the 3-pyridyl group with that by the introduction of the 3-F substituent which is the most efficient

one among the 3-halogeno substituents. Pyridine is known to have a larger dipole moment than fluorobenzene. However, the extents of enhancement of the smectic thermal stability found for the propoxy and butoxy members of compound 1 are less by 6°C than those by the 3-F substitution. Although the extent decreases as the alkyl chain length increases, the 3-pyridyl moiety becomes more effective than the 3-F substituent. For the next two members, the S_A -N transition temperature of compound 1 is in coincidence with that of the corresponding 3-F derivative, and then becomes progressively higher; that is, by 4°C for the heptyloxy member, by 5°C for the octyloxy member, and by 9°C for the decyloxy member.

The enthalpies associated with the S_A -N transition of compound 1 are consistently smaller than those of the 3-F derivative; for example, 1.7 kJ mol^{-1} vs. 3.1 kJ mol^{-1} for the ethoxy member and 5.5 kJ mol^{-1} vs. 6.7 kJ mol^{-1} for the decyloxy member. Therefore, the entropy change by the S_A -N/I transition of compound 1 is less than that of the corresponding member of the 3-F derivative, suggesting that the 3-pyridyl moiety is not so efficient for ordering in the smectic phase as the 3-F substituent. As a matter of fact, the entropy change in the decyloxy member is comparable to that in the heptyloxy member of the 3-F derivatives. The smaller entropy changes throughout the present homologous series seem to be compatible with the observed moderate and gradual enhancement of the smectic thermal stability by the increase of the alkyl chain length.

As to compounds 2, 3 and 4, a smectic A phase is detected only for the higher homologous members. The same is true for the 3-F derivatives of the phenyl analogues. Therefore, the S_A-N transition temperature of the octyloxy members may be compared with each other. As is expected, the present compounds have lower transition temperatures than the 3-F derivatives; 124°C (compound 2) vs. 133°C, 127°C (compound 3) vs. 139°C, and 108°C (compound 4) vs. 113°C. The associated enthalpies are smaller in agreement with the above-mentioned observation made for compound 1; 0.7 kJ mol^{-1} (compound 2) vs. 1.5 kJ mol^{-1}, 0.4 kJ mol^{-1} (compound 3) vs. 3.1 kJ mol^{-1}, and 0.3 kJ mol^{-1} (compound 4) vs. 1.2 kJ mol^{-1}. Thus, the effects of replacing the phenyl group with the 3-pyridyl group on the smectogenic behavior appear to resemble each other among the four compounds.

The trend of the smectogenic behavior of the 3-pyridyl compounds differs distinctly from that of the 3-F derivatives of the phenyl analogues. The S_A -N transition temperature of the 3-pyridyl compound is higher than that of the parent compound regardless of the terminal alkyl chain length, reflecting the absence of steric effects. Secondly, the 3-pyridyl moiety is less efficient than the 3-F substituent for ordering in the smectic A phase as indicated by low entropy values at the S_A -N transition. This finding may imply that the polarity of the 3-pyridyl moiety is markedly affected by becoming a part of the conjugated system. Our observation that the promotion of the nematic thermal stability by the replacement of the

phenyl group with the 3-pyridyl group varies significantly by the arrangement of the linking groups seems to be consistent with this view.

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