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The Effect of Heterocyclic Nitrogen on the Mesomorphic Behavior of 4-Alkoxybenzylidene-2′-alkoxy-5′-aminopyridines

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Abstract—A series of Schiff bases derived from 4-alkoxybenzylidene-2′-alkoxy-5′-aminopyridines were prepared in order to investigate the effect of heterocyclic nitrogen on the mesomorphic behavior. Nematic mesomorphism was obtained when the alkoxy group in the benzaldehyde portion of the molecule was methoxy or ethoxy while the higher homologs exhibited two smectic phases. The higher and lower temperature smectic phases were identified as smectic A and B respectively on the basis of their optical properties and transition enthalpies. Plots of mesomorphic–isotropic transition temperature as a function of the number of carbon atoms in the benzaldehyde portion of these Schiff bases exhibited some unusual odd-even effects which are discussed in terms of current theory. No particularly meaningful trends were observed, however, when the transition entropies were plotted against the number of carbon atoms in the alkoxy chains. The smectogenic tendencies of this series of compounds, compared to the benzene analogs, appeared to be due to the presence of a nitrogen atom.

1. Introduction

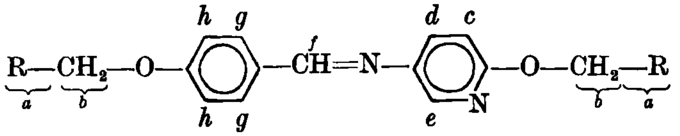
While many series of Schiff bases have been reported to exhibit mesomorphism,(1–3) a comparatively small number of these compounds contained heterocyclic ring systems. Among the latter, several substituted 2,5-diphenylpyrimidines(4) and 2,5-diphenylpyridazines,(5) Schiff bases of 2,3 and 4-pyridinecarboxaldehydes(6) and several derivatives of benzoxazole and benzthiazole(7) have been reported to exhibit liquid crystallinity. In this paper, the preparation and mesomorphic behavior of a new series of heterocyclic Schiff bases are described.

It has been known for some time(8) that a basic requirement for smectic behavior is that the intermolecular lateral attractions be considerably greater than the terminal attractions. Smectic properties are most likely to occur in long chain members of homologous series of mesomorphic compounds because of the increasing separation of the parts of the molecules containing the dipolar and polarizable units. Additionally, smectic behavior is often observed in molecules which possess a very strong dipole moment operating across the long axis of the molecule. Unfortunately it has often been difficult to interpret results in terms of pure dipole–dipole type interactions because of the presence of steric effects. That is, substitution of strong dipolar groups in the lateral position of the molecule produces a strong lateral attractive force but at the expense of molecular breadth. It was our intention, therefore, to examine the effects of a laterally substituted heteroatom on the mesomorphic behavior of homologous series of 4-alkoxybenzylidene-2′-alkoxy-5′-aminopyridines. Particularly important was the fact that the nitrogen atom imparted a lateral dipole moment to the molecule without substantially increasing molecular breadth. Thus, some 42 Schiff bases were prepared from 2-alkoxy-5-aminopyridines and 4-alkoxybenzaldehydes.

2. Experimental

2-*Alkoxy*-5-*aminopyridines*: 2-Chloro-5-nitropyridine (Aldrich Chemical Co.) was treated with various alkoxides in alcohol solution and the resultant 2-alkoxy-5-nitropyridines were reduced to the corresponding amines by the method of Friedman *et al.*(9) The products were purified by distillation until the boiling points of the amines agreed with those reported in the literature.

Schiff bases: Equimolar quantities of the various 4-alkoxybenzaldehydes (Columbia Organic Chemicals) and 2-alkoxy-5-aminopyridines were dissolved in ethanol and refluxed for 30 minutes. Upon cooling, the white crystals which separated from the solution were filtered. The compounds were recrystallized several times from ethanol until sharp and reproducible transition temperatures were obtained. Satisfactory combustion analysis was obtained for each compound. In addition, each compound exhibited sharp infrared absorption bands at 1610–1620 cm^{-1} (CH=N stretching). The nuclear magnetic resonance spectra (Jeolco Minimar 60 MHz, deutero-chloroform, TMS internal std.) showed resonances at δ 0.73–1.83 (multiplet, *a*), 3.67–4.27 (multiplet, *b*), 7.27 (doublet, 1*H*, $J_{cd} = 9$ Hz, *c*), 6.75 (doublet, 2*H*, $J_{hg} = 9$ Hz, *h*), 6.62 (quartet, 1*H*, $J_{dc} = 9$ Hz, $J_{de} = 2$ Hz, *d*), 7.62 (doublet, 2*H*, $J_{gh} = 9$ Hz, *g*) 7.92 (doublet, 1*H*, $J_{ed} = 2$ Hz, *e*) and 8.17 (singlet, 1*H*, *f*).



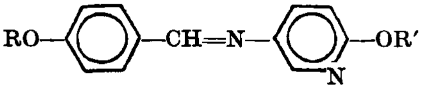
Determination of transition temperatures: Transition temperatures were determined with both a Thomas–Hoover melting point apparatus and a differential scanning calorimeter (DuPont Model 900 Thermal Analyzer). In the latter case, sample sizes were between 5 and 15 mg while the heating rate was 10° per minute. The transition temperatures were reproducible within 1°. The texture of the mesophases were examined with a Bausch and Lomb polarizing microscope equipped with a hot stage (magnifications were between 60 and 120 ×). Transition temperatures, heats and entropies of transitions are presented in Table 1.

3. Results and Discussion

Although a majority of the compounds prepared for this study exhibited smectic mesomorphism, nematic behavior was observed when the alkoxy group in the aldehyde portion of the molecule contained one or two carbon atoms (Fig. 1). Several of these compounds also showed a smectic I phase (Fig. 1b). When the aldehyde portion of the Schiff base contained more than three carbon atoms, smectic phase I and II were observed (Fig. 2).

Since the crystal–smectic II transition could not be observed in capillary tubes, differential scanning calorimetry (DSC) was employed. For example, 4-*n*-butoxybenzylidene-2′-*n*-butoxy-5′-aminopyridine (25) had transitions at 62° ($\Delta S = 19.0$ Cal. mole^{-1} deg^{-1}), 82° ($\Delta S = 2.8$ Cal. mole^{-1} deg^{-1}) and 96° ($\Delta S = 4.7$ Cal. mole^{-1} deg^{-1}). Under the hot stage polarizing microscope only subtle changes in the fan-shaped texture was observed during a smectic II → smectic I

TABLE 1 Physical Constants of 4-Alkoxybenzylidene-2′-alkoxy-5′-aminopyridines



No.	R	R′	Transition	Temp., °C	ΔH Kcal mol^{-1}	ΔS Cal mol^{-1} deg^{-1}
1.	CH_3	CH_3	CI	79.5		
2.	C_2H_5	CH_3	CI	78.0		
3.	C_3H_7	CH_3	CS_1	62.5[a]		
			S_1I	66.5		
4.	C_4H_9	CH_3	CS_1	70.6[a]	6.97	20.3
			S_1I	75.0	2.23	6.4
5.	C_5H_{11}	CH_3	CS_2	68.0[a]		
			S_2S_1	71.0		
			S_1I	74.0		
6.	C_6H_{13}	CH_3	CS_2	65.0[a]	5.76	17.0
			S_2S_1	68.0	0.68	2.0
			S_1I	78.0	1.64	4.7
7.	C_7H_{15}	CH_3	CS_2	62.8[a]	6.98	20.8
			S_2S_1	69.0	0.59	1.7
			S_1I	81.0	1.85	5.2
8.	CH_3	C_2H_5	CI	94.0	7.73	20.9
9.	C_2H_5	C_2H_5	CN	84.0	7.75	21.7
			NI	87.0		
10.	C_3H_7	C_2H_5	CI	89.5	9.37	25.6
11.	C_4H_9	C_2H_5	CS_2	81.7[a]	5.94	16.7
			S_2S_1	86.0	1.08	3.0
			S_1I	91.5	1.91	5.2
12.	C_5H_{11}	C_2H_5	CS_2	62.8[a]	7.27	21.7
			S_2S_1	84.0	1.28	3.6
			S_1I	91.0	2.00	5.5
13.	C_6H_{13}	C_2H_5	CS_2	83.0[a]	7.13	20.0
			S_2S_1	85.0	1.35	3.7
			S_1I	97.0	2.11	5.6
14.	C_7H_{15}	C_2H_5	CS_2	70.8[a]	8.55	24.9
			S_2S_1	84.0	1.10	3.1
			S_1I	97.0	1.94	5.2
15.	CH_3	C_3H_7	CI	55.6	7.44	22.6
			IN[b,c]	18.0		
16.	C_2H_5	C_3H_7	CN	67.0		
			IN	71.0	5.93	17.3
			NS_1[c]	61.0		
17.	C_3H_7	C_3H_7	CI	80.0	6.85	19.3
			IS_1[c]	75.0		

No.	R	R′	Transition	Temp., °C	ΔH Kcal mol^{-1}	ΔS Cal mol^{-1} deg^{-1}
18.	C_4H_9	C_3H_7	CS_2	75.2^a	3.18	9.1
			S_2S_1	90.5	0.99	2.7
			S_1I	93.0	1.65	4.5
19.	C_5H_{11}	C_3H_7	CS_2	52.5^a	3.06	9.4
			S_2S_1	84.5	1.18	3.3
			S_1I	93.0	1.88	5.1
20.	C_6H_{13}	C_3H_7	CS_2	51.3^a	4.32	13.3
			S_2S_1	86.0	1.35	3.8
			S_1I	96.0	2.00	5.4
21.	C_7H_{15}	C_3H_7	CS_2	78.2^a	8.71	24.8
			S_2S_1	83.0	1.68	4.7
			S_1I	94.0	2.08	5.6
22.	CH_3	C_4H_9	CI	60.0	8.63	25.7
			IN^{b,c}	43.0		
23.	C_2H_5	C_4H_9	CN	76.0	3.85	10.8
			NI	84.0	0.09	0.3
			NS_1^{c}	65.0		
24.	C_3H_7	C_4H_9	CS_1	69.0	5.85	17.0
			S_1I	77.0	1.92	5.5
			S_1S_2^{c}	65.0^a		
25.	C_4H_9	C_4H_9	CS_2	62.0^a	6.37	19.0
			S_2S_1	82.0	0.99	2.8
			S_1I	96.0	1.76	4.7
26.	C_5H_{11}	C_4H_9	CS_2	55.8^a	5.61	17.5
			S_2S_1	79.0	1.11	3.1
			S_1I	93.0	1.65	4.5
27.	C_6H_{13}	C_4H_9	CS_2	66.7^a	6.20	18.3
			S_2S_1	84.0	1.24	3.5
			S_1I	99.0	1.96	5.3
28.	C_7H_{15}	C_4H_9	CS_2	72.5^a	6.54	18.9
			S_2S_1	83.0	1.35	3.8
			S_1I	98.0	1.76	4.7
29.	CH_3	C_5H_{11}	CI	51.0	7.09	21.7
			IN^c	35.5		
30.	C_2H_5	C_5H_{11}	CS_1	60.0	6.33	18.9
			S_1N	67.0	0.23	0.7
			NI	78.5	0.16	0.4
31.	C_3H_7	C_5H_{11}	CS_2	45.0^a	4.33	13.6
			S_2S_1	68.0	0.80	2.3
			S_1I	77.0	1.53	6.1
32.	C_4H_9	C_5H_{11}	CS_2	60.5^a	7.35	22.0
			S_2S_1	81.0	0.84	2.4
			S_1I	94.0	1.96	5.3
33.	C_5H_{11}	C_5H_{11}	CS_2	65.0^a	6.32	18.7
			S_2S_1	76.0	1.19	3.4
			S_1I	91.0	1.69	4.6

No.	R	R′	Transition	Temp., °C	ΔH Kcal mol^{-1}	ΔS Cal mol^{-1} deg^{-1}
34.	C_6H_{13}	C_5H_{11}	CS_2	52.4[a]	4.59	14.1
			S_2S_1	78.0	1.53	4.3
			S_1I	96.0	2.40	6.5
35.	C_7H_{15}	C_5H_{11}	CS_2	62.5[a]	6.69	19.9
			S_2S_1	79.0	1.51	4.3
			S_1I	95.0	2.11	5.7
36.	CH_3	C_6H_{13}	CI	53.0	9.83	30.1
			IN[a,c]	42.0		
			NS_1[a,c]	28.0		
37.	C_2H_5	C_6H_{13}	CS_1	56.0	7.43	22.5
			S_1N	69.0	0.09	0.3
			NI	82.0	0.23	0.6
			S_1S_2[a,c]	48.0		
38.	C_3H_7	C_6H_{13}	CS_2	58.2[a]	5.56	16.8
			S_2S_1	64.0	1.02	3.0
			S_1I	78.0	1.31	3.7
39.	C_4H_9	C_6H_{13}	CS_2	47.7[a]	5.89	18.4
			S_2S_1	77.0	0.92	2.6
			S_1I	95.0	1.87	5.1
40.	C_5H_{11}	C_6H_{13}	CS_2	57.2[a]	5.60	17.0
			S_2S_1	72.5	0.93	2.7
			S_1I	91.0	1.90	5.2
41.	C_6H_{13}	C_6H_{13}	CS_2	57.0[a]	5.34	16.2
			S_2S_1	77.0	0.99	2.8
			S_1I	97.0	1.99	5.4
42.	C_7H_{15}	C_6H_{13}	CS_2	69.2[a]	5.22	15.2
			S_2S_1	75.0	0.94	2.7
			S_1I	96.0	1.78	4.8

[a] The transition temperature was determined with a Differential Scanning Calorimeter.

[b] Extrapolated from a curve connecting nematic–isotropic points of the mixtures containing 4-ethoxybenzylidene-2′-*n*-propoxy-5′-aminopyridine.

[c] The transition is monotropic with regard to the crystal–isotropic or crystal–mesomorphic transition.

CI, crystal–isotropic; CN, crystal–nematic; CS_1, crystal–smectic A; S_1S_2, smectic A–smectic B; S_1N, smectic A–nematic; S_1I, smectic A–isotropic; NI, nematic–isotropic transitions.

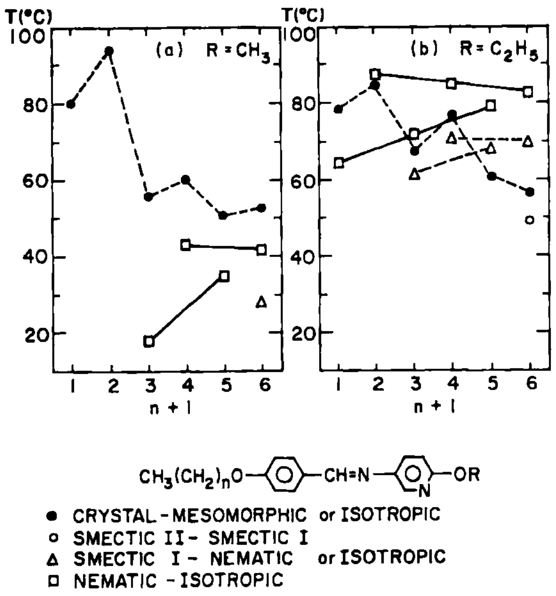


Figure 1. Plot of transition temperatures against the number of carbon atoms in the alkoxy group of aldehyde portion (compound 1–14).

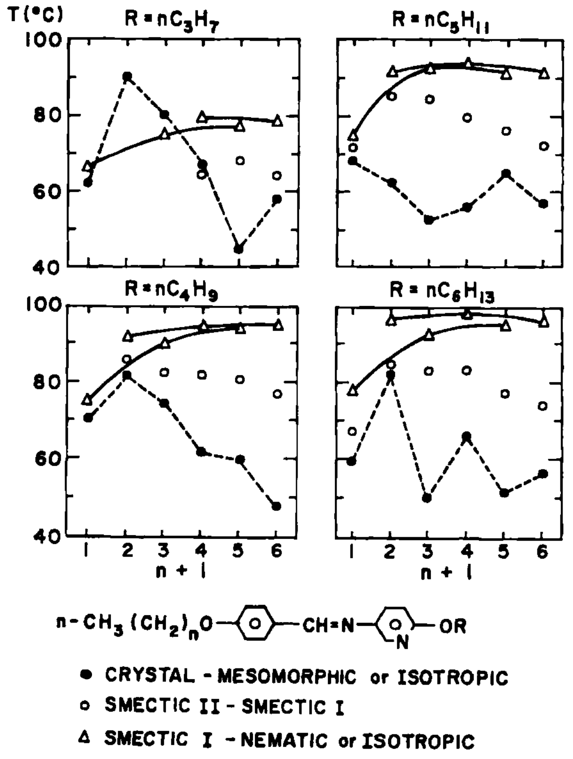


Figure 2. Plot of transition temperatures against the number of carbon atoms in the alkoxy group of aldehyde portion (compound 15–42).

transition. Cooling below 82° did not change the boundaries of the fans, but transient " ripple " appeared to convert the material to a " shaded " fan texture. Heating of this fan texture above 82° produced the original texture with increased discontinuities. Sackman and Demus(10) reported similar texture modifications between two smectic phases in ethyl *p*-(4-ethoxybenzylidene) aminocinnamate. They identified the higher and lower temperature smectic phase as smectic A and B respectively. Furthermore, the entropy change at 82.0° was too high for smectic C → A (0.068 Cal. mole^{-1} deg^{-1}), but was comparable to smectic B → A (1.28 Cal. mole^{-1} deg^{-1}) transition reported by Arnold.(11) Arrora, Taylor and Fergason(12) reported a smectic II → I transition which could not be detected by optical method. This subtle transition had an enthalpy which was much lower than that of smectic A–B. They attributed this observation to the polar ordering of the molecules within the smectic strata. Based on the above mentioned findings, smectic I and II phases of this series of pyridines Schiff bases are tentatively identified as smectic A and B respectively. In order to confirm these phase assignments, mixture liquid crystals were prepared from the pyridine Schiff base and ethyl *p*-ethoxy benzylidene-aminocinnamate and their transition temperatures were plotted vs the mole percentages. As shown in Fig. 3, the identical phase in the two samples exhibited an uninterrupted mixture mesophase.

An examination of the plots of transition temperature against the number of carbon atoms in the alkoxy group of the aminopyridine ring (Fig. 4) revealed some unusual odd–even effects for both mesomorphic–mesomorphic and mesomorphic–isotropic transitions. The odd–even effects for mesomorphic–mesomorphic transitions are most dramatic in the homologs where the alkoxy group of the pyridine portion is *n*-butoxy, *n*-pentyloxy, and *n*-hexyloxy. The curves are generally concave upward having maxima where the aldehyde portion of the Schiff bases have four to six carbon atoms in their alkoxy chain. Similar shaped mesomorphic–isotropic transition curves have previously been reported.(12–14) Although the nematic–isotropic and smectic–isotropic transitions in many known homologs showed odd–even effects, only a few cases are known(15,16) where odd–even effects in mesomorphic–mesomorphic transition were

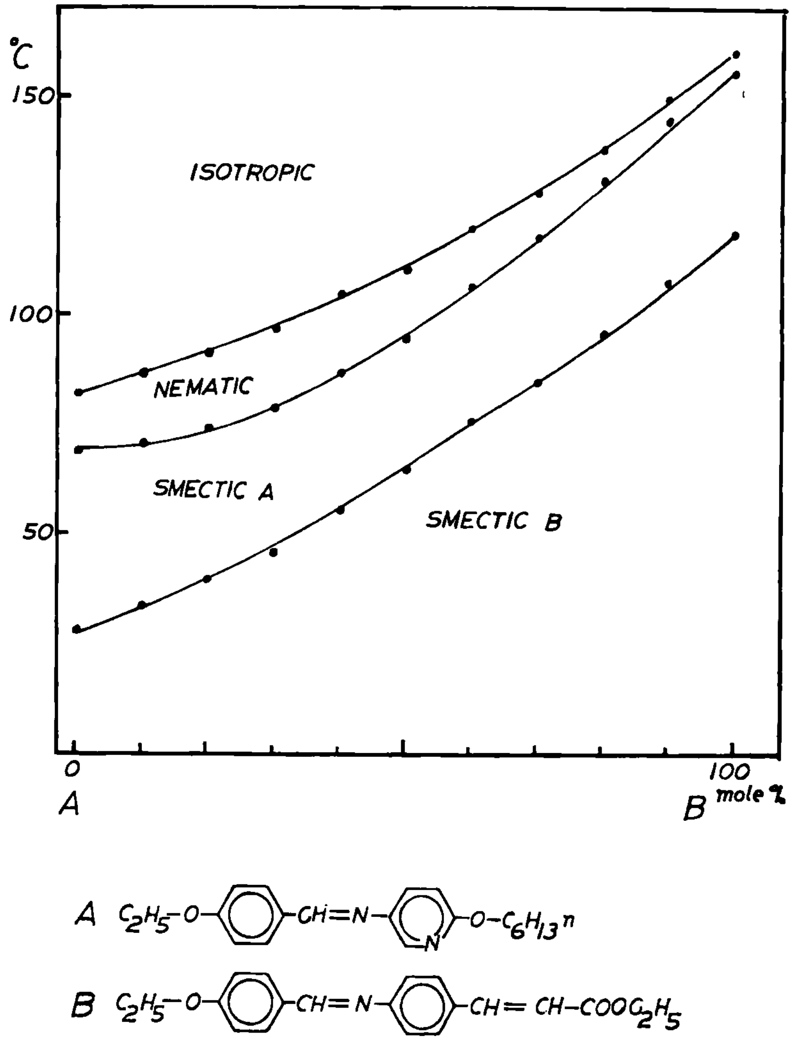


Figure 3. Plot of transition temperatures of the mixture liquid crystals between compound 37 and ethyl *p*-ethoxybenzylideneaminocinnamate against the mole percentages.

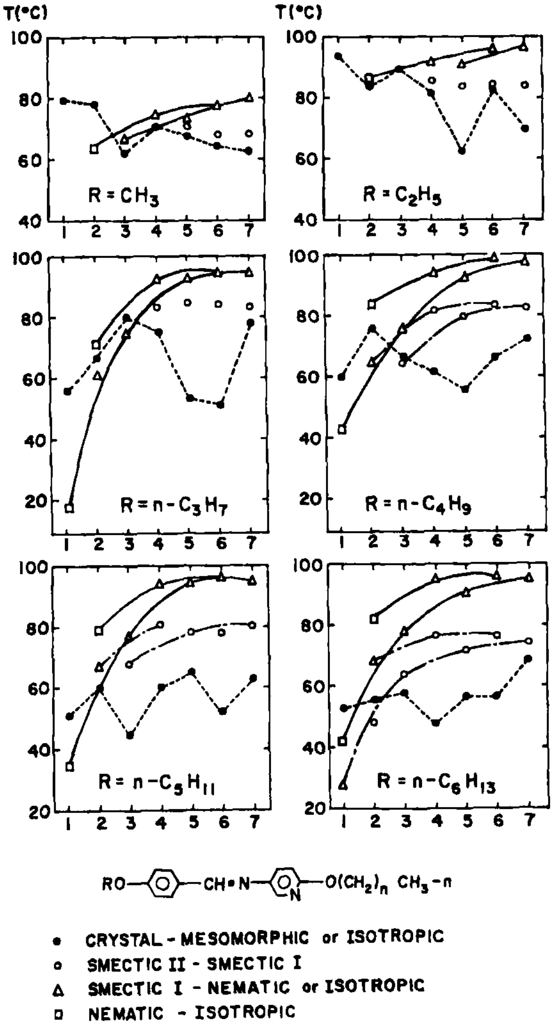


Figure 4. Plot of transition temperatures against the number of carbon atoms in the alkoxy group of aminopyridine portion (compound 1–42).

observed. Gray(17) postulated that the absence of such alternations of mesomorphic–mesomorphic (e.g. smectic–nematic) temperatures indicates that the terminal hydrocarbon chain must convert from a " zig-zag " conformation in the smectic state to the " cog-wheel " conformation in the nematic state. Concerning the alternating smectic–isotropic transition temperatures, he speculated that the " zig-zag " conformation of the hydrocarbon chain becomes " cog-wheel " somewhere before the smectic–isotropic transition point. The present investigation casts doubt over such a postulate. Furthermore, some recent evidence(14) appeared to contradict the widely accepted view that a single conformation of the hydrocarbon chain exists in the mesomorphic state. In the transition temperature plots presented in Fig. 2, the odd–even effects of the mesomorphic–mesomorphic transitions are not so conspicuous, while the mesomorphic–isotropic transition curves still show the alternations. Here again the even members exhibited higher mesomorphic thermal stabilities. It is interesting to compare the group of Schiff bases derived from 5-amino-2-*n*-butoxypyridines with those of *p*-alkoxybenzylidene-*p'*-*n*-butoxyanilines. Dave and Patel(18) studied a series of *p*-alkoxybenzylidene-*p'*-alkoxyanilines in which the alkoxy group of the aniline portion of the Schiff base was *n*-propoxy, *n*-butoxy or *n*-pentyloxy. The corresponding plots of the transition temperatures against the number of carbon atoms of the alkoxy group in the aldehyde portion showed the well known type of odd–even effect. The curves connecting nematic–isotropic points coalesced smoothly with those of the smectic–isotropic points (Fig. 5). In contrast, all of the transition temperatures in pyridine analogs were lower. The lower crystal–mesomorphic transition temperatures are indicative of less symmetry in the pyridine compounds compared to the benzene analogs: In both classes of compounds, the Schiff bases with *p*-ethoxybenzaldehyde showed the highest nematic–isotropic transition temperature. The nematic thermal stabilities of the higher homolgs in the series of benzene analogs decreased sharply while the increase in smectic thermal stabilities was less distinct. In the pyridine analogs, a nematic phase appeared only in the Schiff bases of *p*-ethoxybenzaldehyde or anisaldehyde, the former having higher thermal stability. A further elongation of the chain in the aldehyde portion resulted in only smectic mesomorphism. This rapid increase

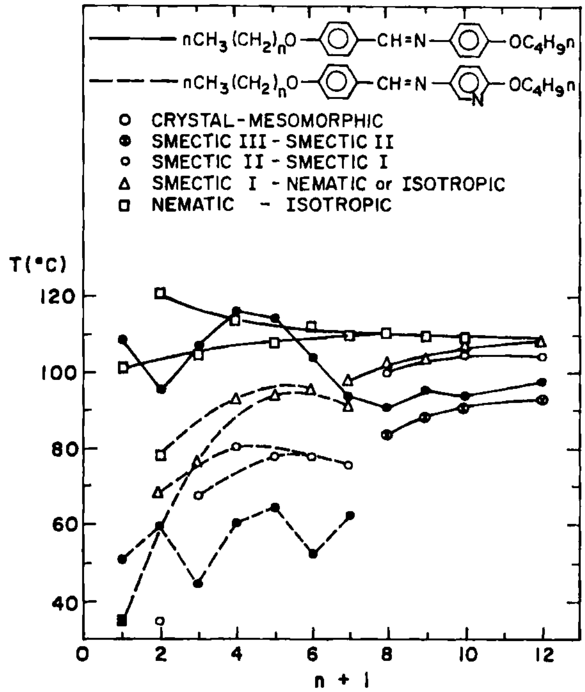


Figure 5. Comparison of the odd–even effect between the pyridine Schiff bases and the benzene analogs.

in smectic thermal stability would appear to indicate that the ratio of lateral to terminal attractive forces which are present in the benzene analogs is greatly increased in the pyridine compounds. This increase is due almost exclusively to the presence of the nitrogen atom. It is difficult to draw any conclusion from the concave shape of the curves since the series does not extend beyond seven carbon atoms. Gray(1) has observed similar concave curves for the smectic III → smectic II transitions (maximum thermal stability at dodecyl ether) in the series of 4-*n*-alkoxy-3-nitrobiphenyl-4′-carboxylic acids, but his only comment on the significance of this behavior is that some fundamental modification of the molecular order, which remains to be determined, occurs in the smectic mesophase.

As pointed out earlier, the nematic–isotropic transition temperatures of 4-ethoxybenzylidene-2′-alkoxy-5′-aminopyridines showed the classical odd–even effects and the nematic phase persisted throughout the series. The smectic thermal stabilities did not show sharp increases relative to the decrease of nematic thermal stabilities, and thus the curves showed the classical shape. This indicates that the terminal groups of the aldehyde and the aminopyridine portions of the molecule produce drastically different effects on the mesomorphic thermal stabilities of these compounds.

This behavior may be explained in the following way. While the hydrocarbon chain of the aldehyde portion " shielded " the terminal oxygen atom and thus increased the ratio of lateral to terminal attractive forces, the hydrocarbon chain of the pyridine portion has little effect on the terminal attractive and cohesive forces between neighbors. The nitrogen atom in the pyridine ring and the imine linkage have overall dipoles towards the side of the pyridine ring. Thus the major lateral and terminal attractive forces are already determined by those two moieties, and any additional alteration on the pyridine ring portion of the molecule (e.g. by an alkoxy group) caused minor changes. On the other hand, the alkoxy group in the aldehyde portion of the molecule has a dipole counteracting those of the pyridine ring portion. Hence a minor change in the polarizability of the aldehyde portion (e.g. by extension of the chain in the alkoxy group) caused a drastic change in the overall terminal attractive force of the molecule. An increase of the side chain length by one carbon (e.g. from ethoxy to *n*-propoxy) in the aldehyde portion reduced the terminal attractive force of the oxygen atom. The result of this is a predominance of lateral attractive forces due to the pyridine ring which yields pure smectic behavior. It is, however, incorrect to conclude that this difference is entirely attributable to the presence of a heterocyclic nitrogen atom, because changes in the anisotropy of the molecules due to the imine linkage must not be excluded in the absence of comparable data on the corresponding benzene analogs.

4. Conclusion

Liquid crystals were obtained by condensation of 4-alkoxybenzaldehyde with 2-alkoxy-5-aminopyridines. Nematic mesomorphism was obtained only when the alkoxy group of the aldehyde portion of the Schiff base was methoxy or ethoxy. The higher homolog yielded polymorphic smectic liquid crystals. The higher and lower temperature smectic phases were identified as smectic A and B respectively based on their texture and heats of transition. All the transition temperatures of the pyridine anils were lower than those of the corresponding benzene analogs. The lower crystal–mesomorphic transition temperatures indicated a lower degree of symmetry in the pyridine anils as compared to the benzene analogs. The increased smectic properties of the pyridine anils is undoubtedly due to the presence of heterocyclic nitrogen.

The hydrocarbon side chains of the benzaldehyde and aminopyridine of the Schiff bases modified the mesomorphic behavior differently. The nematic phase disappeared completely when the alkoxy chain of the aldehyde portion was changed from ethoxy to *n*-propoxy and smectic thermal stabilities increased sharply. On the other hand, increases in the side chain length in the pyridine portion of 4-ethoxybenzylidene-2′-alkoxy-5′-aminopyridines did not produce sharp increases in the smectic thermal stabilities. Although these effects may be due to the presence of a permanent lateral dipole introduced by the ring nitrogen atom, a possible contribution from the imine linkage could not be ruled out.

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