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New Liquid Crystals: 6-n-Alkoxy-3-Pyridinecarboxaldehyde Derivatives†

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Several members of a new mesogenic family of Schiff's bases: 6-n-alkoxy-3-pyridyl-methylene-4'-n-alkoxyanilines, were prepared and their mesomorphic properties studied.

Nematic mesomorphism was obtained when the alkoxy group in the carbocyclic ring was an ethoxy group, while the rest of the compounds studied showed smectic polymorphism (A, C, and B types). Comparative studies with the corresponding 4-n-alkoxybenzylidene-4'-n-alkoxyanilines and 4-n-alkoxybenzylidene-2'-n-alkoxy-5'-aminopyridines were carried out.

INTRODUCTION

The mesogenic properties of many series of Schiff's bases derived from benzenoid systems have been reported in literature up to now.

However, there have been comparatively few systematic studies of Schiff's bases derived from heterocyclic materials. This is fundamentally due to the scarcity of suitably substituted, commercially available precursors, and this makes their synthesis complicated.

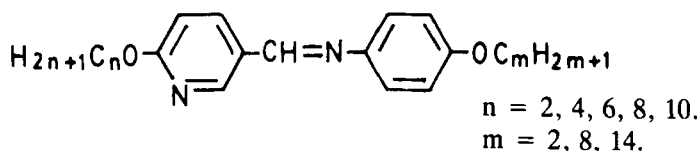
As is already known, the advantage of substituting a pyridine ring for a benzene ring is that a permanent dipole moment is introduced into the molecules without increasing molecular breadth. At the same time, the axial molecular electronic polarizability increases owing to

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the delocalization of the lone pair of electrons of the hetero-atom.¹

In this paper, the synthesis and mesogenic properties of a new series of heterocyclic Schiff's bases are described: these are the 6-*n*-alkoxy-3-pyridylmethylen-4'-*n*-alkoxyanilines (Sketch 1), derived from 6-*n*-alkoxy-3-pyridinecarboxaldehyde, the synthesis of which has been described in a previous paper.²

A comparative study with the corresponding 4-*n*-alkoxybenzylidene-4'-*n*-alkoxyanilines and with the 4-*n*-alkoxybenzylidene-2'-*n*-alkoxy-5'-aminopyridines is also made when possible.



RESULTS AND DISCUSSION

The transition temperatures, enthalpies and derived entropies, and the mesophase types of the synthesized compounds are listed in Table I.

As can be observed, the nematic mesophase appears only in cases where the terminal chain of the carbocyclic ring is an ethoxy group. The rest of the compounds studied show smectic polymorphism (see Figure 1).

This smectic behaviour was only to be expected, bearing in mind that the existence of a hetero-atom in position 3 in the pyridine ring originates a dipole moment transverse to the molecular axis, which favours the lateral intermolecular forces of attraction more than the terminal forces of attraction, this being a necessary requirement for the formation of smectic mesophases.⁵

However, it is noticeable that when the short chain ($\text{R} = \text{C}_2\text{H}_5$) is on the side of the benzene ring, the mesophase that appears is a nematic phase (irrespective of the length of the terminal chain attached to the pyridine ring).

On the other hand when the short chain ($\text{R} = \text{C}_2\text{H}_5$) is on the pyridine ring, smectic mesophases appear.

The largest mesophase ranges are obtained for compounds with an octyloxy group as a terminal chain on the carbocyclic ring as we can see in Figure 1.

TABLE I

Transition temperatures, enthalpies, and derived entropies
for the 6-alkoxy(n)-3-pyridylmethylene-4'-alkoxy(m)-anilines.*

n	m	Transition	Temperature°C	ΔH Kcal/mol	ΔS cal/mol.K
2	2	C - I	91.0	8.42	23.13
		I - N ^a	91.0	—	—
		C' - C''	80.2	0.36	1.01
		C'' - N	84.0	7.91	22.14
		N - I	90.8	0.37	1.01
2	8	C - I	91.2	8.32	22.84
		I - S _A ^a	88.7	—	—
2	14	C - I	90.4	15.91	43.75
		I - S _A ^a	88.6	—	—
4	2	C - C'	79.2	0.76	2.17
		C' - I	87.9	6.38	17.67
		I - N ^a	84.4	—	—
		C'' - I	85.0	7.31	20.42
		C - S _A	79.3	4.75	13.49
4	8	S _A - I	92.6	1.54	4.22
		C - S _A	88.6	13.53	37.40
		S _A - I	91.0	2.37	6.52
		S _A -S _B ^a	78.8	—	—
		C - I	90.5	13.99	38.46
6	2	I - N ^a	86.8	—	—
		C - S _B	61.0	4.91	14.70
		S _B - S _C	68.8	0.80	2.34
		S _C - S _A	80.5	—	—
		S _A - I	93.0	1.84	5.01
6	14	C - S _A	82.2	14.00	39.40
		S _A - I	91.5	2.63	7.22
		S _A - S _C ^a	81.9	—	—
		S _C - S _B ^a	79.4	—	—
		C - N	76.5	10.38	29.68
8	2	N - I	83.1	0.32	0.89
		C - S _B	63.7	8.67	25.72
		S _B - S _C	68.4	0.80	2.34
		S _C - S _A	84.0	—	—
		S _A - I	93.0	2.04	5.56
8	14	C - S _C	85.2	14.19	39.59
		S _C - I	92.6	2.76	7.54
		S _C - S _B ^a	83.4	—	—
		C - N	80.3	11.70	33.10
		N - I	81.9		
10	2	C - S _C	69.0	12.06	35.23
		S _C - S _A	84.0	—	—
		S _A - I	92.4	2.32	6.35
		S _C - S _B ^a	69.3	—	—
		C - S _C	86.3	16.37	45.53
10	14	S _C - I	92.4	3.47	9.49
		S _C - S _B ^a	86.2	—	—

^aMonotropic transition.

*where the S_B phase derives on cooling from a S_C phase, the S_B phase is tilted and therefore S_G is type.

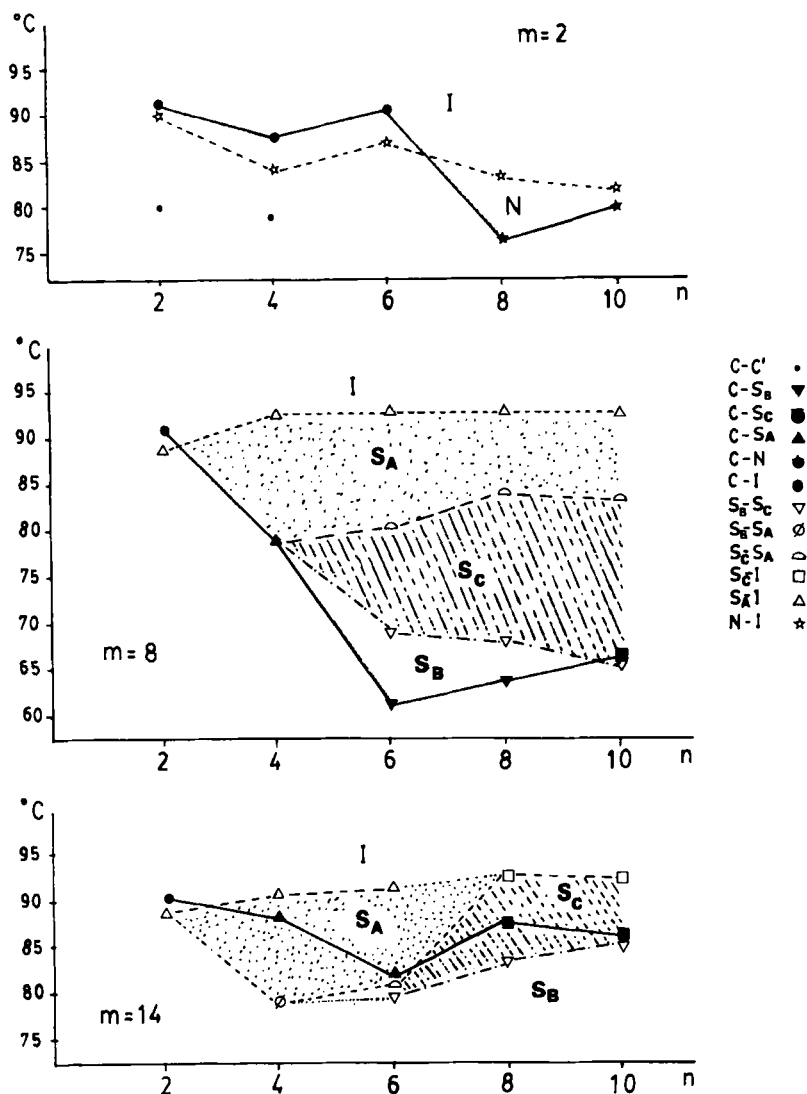


FIGURE 1 Transition temperatures as a function of alkoxy chain length for 6-alkoxy(n)-3-pyridylmethylene-4'-alkoxy(m)-anilines.

The smectic polymorphism detected was of the A, C, and B type. The latter only appears when the total number of carbon atoms in the terminal chains is high (≥ 14 carbon atoms). It is necessary to indicate here that when the S_B phase appears after a S_A phase in the cooling process (for example: $n=4$, $m=14$), the S_B mesophase is an

enthoagonal smectic B, and pseudoisotropic textures can be observed using an optical microscope by mechanical displacement of the sample.

When it appears after a S_C phase, the S_B mesophase is a tilted smectic B, i.e., smectic G. This was identified by the appearance of schlieren textures and the fact that it was impossible to obtain pseudoisotropic textures by mechanical displacement.

Some of the compounds studied ($n=2$, $m=2$; $n=4$, $m=2$) show polymorphism in the solid state.

As could be foreseen, the transition temperatures of the 6-alkoxy-pyridylmethylene-4'-alkoxyanilines were found to be lower than those of the corresponding benzene homologues,⁶ in those cases that can be compared, (see Table II).

This is due to the fact that the pyridine Schiff's bases show a lower degree of symmetry than the benzenoid derivatives, and this makes the melting points decrease⁷. This structural effect seems much more important than the introduction, due to the existence of the heteroatom, of a permanent dipole moment into the molecules.

A decrease in the intermolecular forces of attraction was also expected because of the repulsion between the lone pair of electrons of the pyridine nitrogen atom in one molecule and those of the oxygen atom of the alkoxy groups in another nearby molecule, an effect

TABLE II

Thermal data for some 6-alkoxy(n)-3-pyridylmethylene-4'-alkoxy(m)-anilines and the analogous 4-alkoxy(n)-benzylidene-4'-alkoxy(m)-anilines.

n	m	Transition	Temperature°C	Transition	Temperature°C
2	2	C - I	91.0	C - I	149.0
		I - N ^a	91.0	I - N ^a	143.0
		C' - C''	80.2		
		C'' - N	84.0		
		N - I	90.8		
4	2	C - C'	79.2	C - N	105.5
		C' - I	87.9	N - I	129.5
		I - N ^a	84.4		
		C'' - I	85.0		
		C - S _A	79.3	C - N	101.0
4	8	S _A - I	92.6	N - I	116.5
		C - I	90.5	C - N	97.5
6	2	I - N ^a	86.8	N - I	122.5
		C - N	76.5	C - N	99.0
8	2	N - I	83.1	N - I	119.0

^aMonotropic transition.

which makes the maintenance of order in the mesomorphic state difficult.¹

As can be observed in Table II, the greater the length of the terminal chains, the smaller this effect. This could be due to an increase in the intermolecular distances produced by the volume increase of the terminal chains, which would mask the effect of the nitrogen in the pyridine ring.

We make a comparison between the thermal data for the compounds synthesized by us and those of the homologous 4-alkoxybenzylidene-2'-alkoxy-5'-aminopyridines synthesized by Oh,⁸ in order to determine the effect of the inversion of the imine central linkage.

This was only possible in cases where the benzene ring carries an ethoxy chain.

It can be seen that the melting temperatures are higher in the compounds synthesized by us (Table III).

This suggests the existence of stronger interaction forces among the molecules in the solid state when the carbon atom of the imine linkage is next to the pyridine ring than when this atom is next to the benzene ring.

It can also be observed that the 4-ethoxybenzylidene-2'-alkoxy-5'-aminopyridines show enantiotropic polymorphism in the mesomorphic state, while the 6-alkoxy-3-pyridylmethylene-4'-ethoxyanilines only show monotropic nematic mesomorphism.

The lower nematic stabilities of our compounds compared with

TABLE III

Thermal data for some 6-alkoxy(n)-3-pyridylmethylene-4'-alkoxy(m)-anilines and the analogous 4-alkoxy(m)-benzylidene-2'-alkoxy(n)-5'-aminopyridines.

n	m	Transition	Temperature°C	Transition	Temperature°C
2	2	C - I	91.0	C - N	84.0
		I - N ^a	91.0	N - I	87.0
		C' - C''	80.0		
		C'' - N	84.0		
		N - I	90.8		
4	2	C - C'	79.2	C - N	76.0
		C - I	87.9	N - I	84.0
		I - N ^a	84.4	N - S _A ^a	65.0
		C'' - I	85.0		
		C - I	90.5	C - S _A	56.0
6	2	I - N ^a	86.8	S _A - N	69.0
				N - I	82.0
				S _A - S _B	48.0

^aMonotropic transition.

those synthesized by Oh seem to be due to the different contributions to the total dipole moment. While in the 4-alkoxybenzylidene-2'-alkoxy-5'-aminopyridines, the dipole moment originated by the pyridine nitrogen and the central linkage atoms reinforce, in the compounds studied by us, these contributions oppose and the resultant dipole moment decreases; this results in lower terminal cohesive forces.

However, it should be pointed out that the compounds synthesized by us, with an ethoxy terminal chain in the benzene ring, show a special nematic behaviour, as mentioned above.

Due to the scarcity of comparable data, this aspect is still being studied.

CONCLUSIONS

A new family of heterocyclic Schiff bases has been synthesized, i.e., the 6-n-alkoxy-3-pyridylmethylene-4'-n-alkoxyanilines. These compounds show nematic and A, C, and B smectic mesophases. The hydrocarbon chains on the pyridinecarboxaldehyde or aniline side of the Schiff's bases affect the mesomorphic behaviour differently. Short chains in the carbocyclic ring lead to nematic mesomorphism, and the large chains to smectic mesomorphism. However, smectic mesomorphism also occurs with short chains in the pyridine ring.

Transition temperatures are in all cases lower than those of the corresponding carbocyclic Schiff bases, due to the higher geometric anisotropy.

Making a comparison with the results obtained by Oh in his study of heterocyclic Schiff bases, we can conclude that the mesogenic behaviour of this type of compound is due to the presence of a permanent dipole moment, originated by the ring nitrogen atom, and not to the possible contribution of the imine linkage.

EXPERIMENTAL

Synthesis

6-n-alkoxy-3-pyridinecarboxaldehydes:

These compounds were prepared by the interaction of 6-chloronicotinic acid with the appropriate sodium alcoholate followed by reduction *via* the acyl chloride.³ The experimental details are described in a paper recently submitted to *Mol. Cryst. Liq. Cryst.*²

6-n-alkoxy-3-pyridylmethylene-4'-hydroxyanilines:

A solution of 6-n-alkoxy-3-pyridinecarboxaldehyde (10 mmole) and *p*-aminophenol (10 mmole) in 25 ml of tetrahydrofuran was heated under reflux for 12 h. After removing the solvent, the residue was dissolved in ethanol, precipitated by the addition of water, collected and recrystallized from carbon tetrachloride (50-70% yield).

6-n-alkoxy-3-pyridylmethylene-4'-n-alkoxyanilines:

6-n-alkoxy-3-pyridylmethylene-4'-hydroxyaniline (1mmole), *n*-alkyl bromide (1mmole), potassium carbonate (1mmole), and 10 ml of dried acetone were heated under reflux for 48 h. The warm solution was filtered, the solvent removed and the crude product recrystallized several times from an appropriate solvent (methanol, acetonitrile, ethyl acetate). Yield (recrystallized pure product) 50-60%.

Textures Observed

The mesophase textures were observed using thin films of the samples (mounted between a glass slide and a cover slip) and a polarizing microscope.

The nematic and the smectic mesophases of types A, B, and C were identified because of their similarities to the textures portrayed by Demus and Richter.⁴

Techniques

The melting points, transition temperatures, and enthalpies were determined using a PERKIN-ELMER DSC-2 Differential Scanning Calorimeter. The apparatus was calibrated by measuring the known melting points and fusion enthalpies of benzoic acid (121.2 °C, 33.9 cal/g) and indium (156.6 °C, 6.80 cal/g).

The optical observations were made using a REICHERT-THERMOVAR HT1-B11 polarizing microscope equipped with a heating stage.

The identification of products was carried out by the usual spectroscopic methods: UV (PERKIN-ELMER 200), IR (PERKIN-ELMER 283), NMR (PERKIN-ELMER R-12-B) and mass spectrometry (HEWLETT-PACKARD 5943A).

The purity of all products was checked using the above-mentioned techniques.

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