Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphic Properties of Some Series of 5-n-Alkoxy-2-Pyridinecarboxaldehyde Derivatives

Joaquín Barberá [a], Mercedes Marcos [a], Enrique Meléndez [a] & José Luis Serrano [a]
[a] Instituto de Ciencia de los Materiales de Aragón, Departamento de Quimica Organica, Facultad de Ciencias, Universidad de Zaragoza, 50009, Zaragoza, Spain
Version of record first published: 13 Dec 2006.

To cite this article: Joaquín Barberá , Mercedes Marcos , Enrique Meléndez & José Luis Serrano (1987): Mesomorphic Properties of Some Series of 5-n-Alkoxy-2-Pyridinecarboxaldehyde Derivatives, Molecular Crystals and Liquid Crystals, 148:1, 173-183

To link to this article: http://dx.doi.org/10.1080/00268948708071787

Mol. Cryst. Liq. Cryst., 1987, Vol. 148, pp. 173–183
Photocopying permitted by license only

Printed in the United States of America

Mesomorphic Properties of Some Series of 5-*n*-Alkoxy-2-Pyridinecarboxaldehyde Derivatives

JOAQUÍN BARBERÁ, MERCEDES MARCOS, ENRIQUE MELÉNDEZ and JOSÉ LUIS SERRANO

Instituto de Ciencia de los Materiales de Aragón, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

(*Received May 21, 1986*)

A new type of mesogen intermediate, the 5-*n*-alkoxy-2-pyridinecarboxaldehydes, has been synthesized. Three homologous series of derivatives were prepared and their mesomorphic properties studied: Schiff's monobases (5-*n*-alkoxy-2-pyridylmethylene-4′-*n*-alkoxyanilines), Schiff's dibases (bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines) and azines (bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines). These derivatives are all mesogenic. The principal phases formed are nematic but, to a lesser extent, smectic C phases occur also. In some cases smectic A, B, G and H phases were detected.

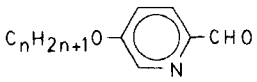
Keywords: nematic mesophases, mesogen synthesis, alkoxypyridinecarboxaldehydes

INTRODUCTION

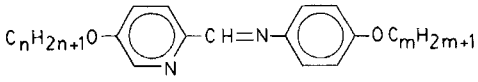
In two previous papers[1,2] we reported the synthesis and mesogenic properties of series of compounds derived from 6-*n*-alkoxy-3-pyridinecarboxaldehydes. Neither these aldehydes nor their isomeric 5-*n*-alkoxy-2-pyridinecarboxaldehydes had previously been reported as liquid crystal precursors in spite of their being of interest as intermediates in the synthesis of such potentially mesogenic compounds as Schiff's bases, azines and stilbenes.

In this paper we report a method of synthesis of the 5-*n*-alkoxy-2-pyridinecarboxaldehydes (I) and describe the properties of three

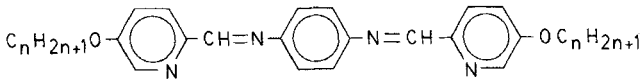
homologous series of derivatives expected to show mesomorphism: 5-*n*-alkoxy-2-pyridylmethylene-4′-*n*-alkoxyanilines (II), bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines (III) and bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines (IV).



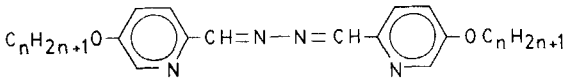
(I)



(II)



(III)



(IV)

n = 2, 4, 6, 8, 10 m = 2, 8, 14

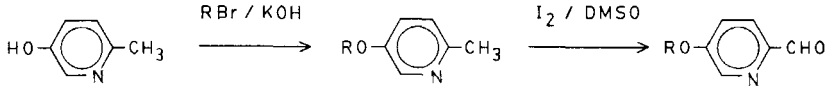
RESULTS AND DISCUSSION

I. Synthesis of the 5-*n*-alkoxy-2-pyridinecarboxaldehydes

The synthesis of the pyridinic aldehydes involves two steps:

1. O-alkylation of 5-hydroxy-2-methylpyridine.
2. Oxidation of the methyl group to carbonyl.

The scheme of reactions is as follows:



The reaction of O-alkylation was carried out using *n*-alkyl bromide as a reagent, potassium hydroxide as a base and ethanol as a solvent.

To oxidize the 5-*n*-alkoxy-2-methylpyridines to 5-*n*-alkoxy-2-pyridinecarboxaldehydes, we employed the method reported by Markovac and others,[3] oxidation being brought about by the attack of iodine and dimethylsufoxide.

The aldehydes obtained are unstable liquids at room temperature and decompose before reaching their boiling points. The melting points of their 2,4-dinitrophenylhydrazones are set out in Table I.

II. 5-*n*-alkoxy-2-pyridylmethylene-4'-*n*-alkoxyanilines

Fifteen homologues belonging to Series (II) (n = 2, 4, 6, 8, 10; m = 2, 8, 14) were prepared. Types of mesophase, as well as thermal and thermodynamic data for the different transitions are listed in Table II.

All the compounds studied show enantiotropic mesomorphism (see Figure 1). The derivatives with short alkoxy chains exhibit only a nematic mesophase, whereas the majority of those with long chains show both nematic and smectic C phases. Only the homologue with the longest chains (n = 10, m = 14) exhibits smectic C mesomorphism alone. The smectic A mesophase appears in only one case (n = 10, m = 2).

TABLE I

Melting points of 2,4-dinitrophenylhydrazone derivatives of 5-*n*-alkoxy-2-pyridinecarboxaldehydes (I)

n	Melting point °C
2	209.0
4	191.3
6	181.8
8	176.6
10	173.7

TABLE II

Transition temperatures and enthalpies for 5-*n*-alkoxy(n)-2-pyridyl-methylene-4′-*n*-alkoxy(m)-anilines (II)

n	m	Transition	Temperature°C	ΔH Kcal/mole
2	2	C–N	132.6	8.51
		N–I	139.2	0.53
4	2	C_1–C_2	78.4	2.78
		C_3–C_2	66.3	2.51
		C_2–N	89.5	5.77
		N–I	117.2	0.38
6	2	C–N	73.9	6.66
		N–I	112.2	0.45
8	2	C–N	53.6	8.84
		N–I	110.1	0.50
10	2	C–S_A	63.6	10.38
		S_A–N	79.4	0.15
		N–I	108.2	0.52
2	8	C–N	65.1	9.29
		N–I	108.9	0.47
4	8	C–N	62.8	13.51
		N–I	103.6	0.56
6	8	C–S_C	48.6	7.80
		S_C–N	61.5	0.23
		N–I	104.9	0.61
8	8	C–S_C	51.2	10.31
		S_C–N	87.7	0.27
		N–I	106.4	0.82
10	8	C–S_C	52.9	6.03
		S_C–N	99.5	0.61
		N–I	105.5	1.59
2	14	C–N	83.5	15.74
		N–I	99.6	0.59
4	14	C–N	61.8	13.51
		N–I	94.4	0.56
6	14	C–S_C	63.2	11.59
		S_C–N	76.6	0.14
		N–I	96.7	0.82
8	14	C–S_C	65.9	14.10
		S_C–N	94.2	0.41
		N–I	99.7	1.44
10	14	C_1–S_C	66.2	15.42
		C_2–S_C	50.2	7.57
		S_C–I	102.7	2.64

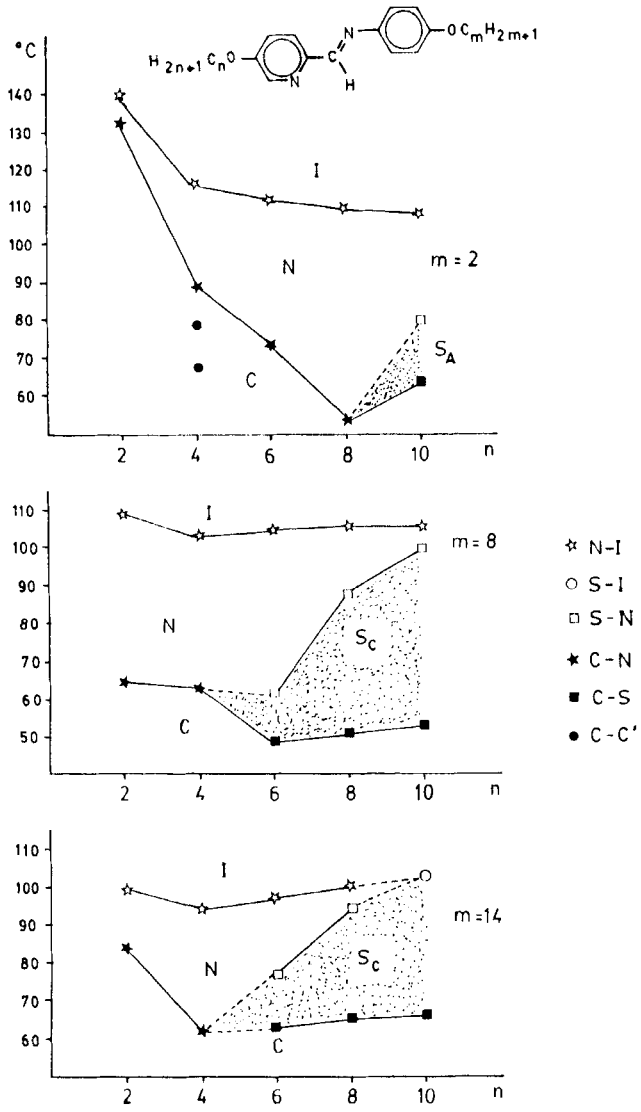


FIGURE 1 Transition temperatures as a function of alkoxy chain length for 5-*n*-alkoxy(n)-2-Pyridylmethylene-4′-n-alkoxy(m)-anilines (II).

In addition to mesomorphism, solid state polymorphism is observed in two compounds (n = 4, m = 2; n = 10, m = 14).

The lowest melting points and the widest mesomorphic ranges are obtained for compounds with an octyloxy group as a terminal chain on the benzene ring (m = 8).

Taking thermodynamic data into account, the high values of the molar enthalpy for nematic-isotropic transitions (0.38–1.54 Kcal/mole) as well as the comparatively low values for smectic-nematic transitions (0.14–0.41 Kcal/mole) are noticeable. This indicates a high degree of intermolecular order in the nematic state in the compounds of this series.

III. Bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines

Five homologues belonging to Series (III) (n = 2, 4, 6, 8, 10) were prepared. The phases formed and thermal and thermodynamic data for the different transitions are listed in Table III.

TABLE III

Transition temperatures and enthalpies for bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines (III)

n	Transition	Temperature°C	ΔH Kcal/mole
2	C_1-C_2	183.7	3.79
	C_3-C_2	181.8	3.73
	C_2-C_4	185.9	0.43
	C_4-N	188.4	7.04
	N–I	decomp.	—
4	C–N	153.3	10.03
	N–I	278.9	0.86
6	$C-S_B$	122.4	3.49
	S_B-N	132.6	2.70
	N–I	243.0	0.72
8	C_1-S_H	61.2	3.30
	C_2-S_H	55.2	—
	S_H-S_G	100.2	1.94
	S_G-S_C	121.2	2.15
	S_C-N	158.4	0.82
	N–I	223.1	0.71
10	C_1-C_2	62.8	—
	C_2-S_G	89.9	8.97
	S_G-S_C	95.5	2.25
	S_C-N	173.4	1.07
	N–I	202.1	0.84
	S_G-S_H[a]	87.2	—

[a]Monotropic transition.

All the homologues studied show enantiotropic mesomorphism (see Figure 2). All of them exhibit at least a nematic mesophase. The third member of the series (n = 6) forms a smectic B phase as well. The two highest homologues show four types of mesophase: nematic and smectic C, G and H.

In some derivatives (n = 2, 8, 10) solid state polymorphism is observed.

The mesophase-isotropic transition temperatures for this series are unusually high. The first member prepared has such a high clearing point (>310°C), that decomposition takes place before it is reached. In consequence, the mesophase ranges are considerable (≥115°C in all the cases studied). This heightening of mesomorphic stability can be attributed to the appreciable extension of the electronic conjugation due to the presence of an aromatic ring and an additional imine linkage in the central core of the molecule.

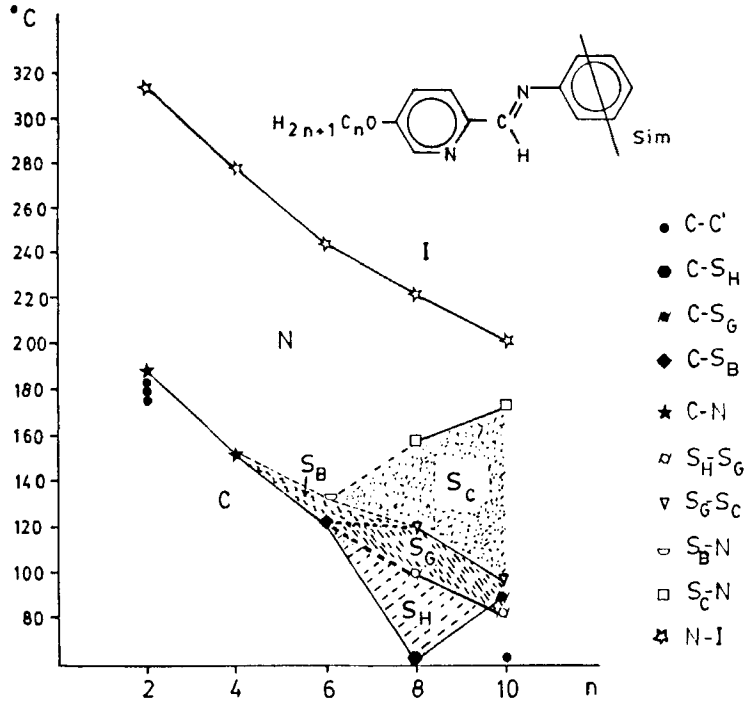


FIGURE 2 Transition temperatures as a function of alkoxy chain length for bis-(5'-*n*-alkoxy-2'-pyridylmethylene)-1,4-phenylenediamines (III).

TABLE IV

Transition temperatures and enthalpies for bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines (IV)

n	Transition	Temperature°C	ΔH Kcal/mole
2	C–N	163.0	10.56
	N–I	210.6	0.77
4	C–N	110.6	8.45
	N–I	175.2	0.71
6	C–N	103.9	9.68
	N–I	159.4	0.64
8	C_1–C_2	99.7	2.45
	C_3–C_2	98.1	2.26
	C_2–S_C	102.0	7.96
	S_C–N	109.2	0.64
	N–I	151.0	0.64
10	C_1–C_2	76.8	4.71
	C_3–C_2	68.6	7.02
	C_2–S_C	96.2	5.17
	S_C–N	125.0	0.89
	N–I	143.1	0.85

IV. Bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines

Five hydrazine derivatives belonging to Series (IV) (n = 2, 4, 6, 8, 10) were prepared. Phase types and transition temperatures and molar enthalpies are listed in Table IV.

All the members studied in the series exhibit enantiotropic mesomorphism and show nematic phases (see Figure 3). In addition, a smectic C mesophase is observed in the two highest homologues (n = 8, 10), which also show solid polymorphism.

Taking thermodynamic data into account, the value of the molar enthalpy for the C_3-C_2 transition in compound n = 10 (7.02 Kcal/mole) is noticeable. This value is unusually high for a crystal-crystal transition, even greater than that of the C_2-S_C transition (5.17 Kcal/mole). This points to the existence of a high degree of intermolecular order in the crystalline state C_3, far greater than in the crystalline state C_2.

EXPERIMENTAL

Techniques

Transition temperatures and enthalpies were determined using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. Optical obser-

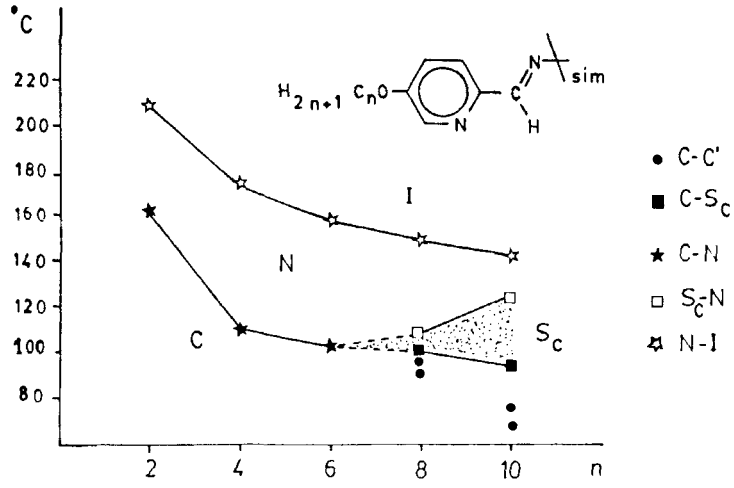


FIGURE 3 Transition temperatures as a function of alkoxy chain length for bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines (IV).

vations were made using a Reichert-Thermovar HT1 B11 polarizing microscope equipped with a heating stage. The characterization of products was carried out by the usual spectroscopic methods: UV (Perkin-Elmer 200), IR (Perkin-Elmer 283) and ^{1}H NMR (Brüker WP-80-CW). The purity of all products was checked by the above-mentioned techniques and by elemental analysis.

The mesophase textures were observed using thin films of the samples mounted between a glass slide and a cover slip in a polarizing microscope. The mesophase textures were identified because of their similarities to the textures portrayed by Demus and Richter[4] and by Gray and Goodby.[5]

SYNTHESIS

5-*n*-alkoxy-2-methylpyridines

A solution of *n*-alkyl bromide (0.2 mole) in ethanol (50 ml) was added to a solution of 5-hydroxy-2-methylpyridine (0.2 mole) and potassium hydroxide (14 g, 0.25 mole) in ethanol (150 ml). The mixture was refluxed for 6 h and then cooled at room temperature. The potassium salts were removed by filtration and the solvent was distilled using a rotovapor. The oily residue was dissolved in ether, washed several times with saturated aqueous sodium bicarbonate, once with water

and then dried over anhydrous calcium chloride. After removing the solvent, the product was purified by distillation at reduced pressure (40–65% yield).

5-*n*-alkoxy-2-pyridinecarboxaldehydes

A mixture of 5-*n*-alkoxy-2-methylpyridine (0.1 mole) and iodine (25.4 g, 0.1 mole) was stirred for 5 min at room temperature. Dimethylsufoxide (100 ml) was added and the resulting solution was heated at 160°C for 15 min. After cooling, the mixture was neutralized with saturated aqueous sodium bicarbonate and extracted with toluene. The organic layer was treated with dilute hydrochloric acid (1:1), and the aqueous acidic solution was carefully neutralized with solid sodium carbonate and extracted with hexane. After drying the organic layer over anhydrous calcium chloride and removing the solvent, the product was purified by column chromatography using hexane/ether (5:1) as an eluent. In some cases subsequent purification was carried out using the sodium bisulfite method (15–25% yield).†

5-*n*-alkoxy-2-pyridylmethylene-4′-n-alkoxyanilines

A solution of 5-*n*-alkoxy-2-pyridinecarboxaldehyde (1 mmole), 4-*n*-alkoxyaniline‡ (1 mmole) and a few drops of glacial acetic acid in ethanol (25 ml) was stirred at room temperature for 1 h. The resulting precipitate was collected, washed with ethanol and recrystallized several times from the appropriate solvent (50–80% yield).

Bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines

A solution of 5-*n*-alkoxy-2-pyridinecarboxaldehyde (2 mmole), 1,4-phenylenediamine (108 mg, 1 mmole) and a few drops of glacial acetic acid in ethanol (25 ml) was stirred at room temperature for 1 h. The resulting precipitate was collected, washed with ethanol and recrystallized several times from the appropriate solvent (55–75% yield).

---

†2,4-dinitrophenylhydrazones were prepared by refluxing for 1–2 min a solution of 5-*n*-alkoxy-2-pyridinecarboxaldehyde (1 mmole), 2,4-dinitrophenylhydrazine (198 mg, 1 mmole) and ten drops of concentrated hydrochloric acid in methanol (25 ml), followed by cooling and subsequent recrystallization of the resulting precipitate from acetonitrile.

‡4-*n*-alkoxyanilines were synthesized in accordance with the method described in Reference 6.

Bis-(5-*n*-alkoxy-2-pyridylmethylene)-hydrazines

A solution of 5-*n*-alkoxy-2-pyridinecarboxaldehyde (2 mmole), hydrazine hydrate (50 mg, 1 mmole) and a few drops of glacial acetic acid in ethanol (25 ml) was stirred at room temperature for 1 h. The resulting precipitate was collected, washed with ethanol and recrystallized several times from the appropriate solvent (45–65% yield).

Acknowledgments

The authors are grateful to Dr. Patrick Keller for his helpful collaboration with the microscopic study of some compounds. One of the authors would like to thank the Ministerio de Educación y Ciencia (Spain) for the award of a F.P.I. grant, which made this research possible.

References

1. J. Barberá, M. Marcos, E. Meléndez, B. Ros and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **123**, 159 (1985).
2. J. Barberá, E. Meléndez, P. Romero and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **126**, 259 (1985).
3. A. Markovac, C. L. Stevens, A. B. Ash and B. E. Hackley, *J. Org. Chem.*, **35**, 841 (1970).
4. D. Demus and L. Richter, "The Textures of Liquid Crystals," V.E.B. Deutscher Verlag für Grundstoffindustrie, Leipzig (1978).
5. G. W. Gray and J. W. G. Goodby, "Smectic Liquid Crystals," Leonard Hill, Glasgow (1984).
6. N. P. Buu-Hoi, M. Gautier and N. Dat Xuong, *Bull. Soc. Chim. Fr.*, **2154** (1962).