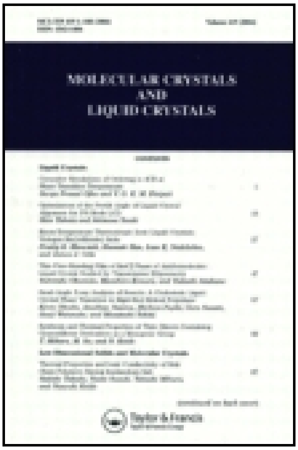

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Liquid Crystals with a New Central Core: 5,5′-Dialkoxy-2,2′-Pyridoins

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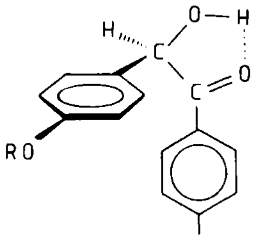
A series of 5,5′-dialkoxy-2,2′-pyridoins was synthesized by benzoin condensation of 5-alkoxy-2-pyridinecarboxaldehydes, and their mesomorphic behavior studied by optical microscopy and differential scanning calorimetry. Several compounds of the series showed enantiotropic mesophases of the nematic and smectic C type.

A spectroscopic study of two model molecules was made and the mesogenicity of the compounds interpreted in terms of intramolecular hydrogen bonding, geometry and degree of electronic conjugation.

INTRODUCTION

Mesomorphic compounds containing the acyloin group have not been described up to the present date. Some authors[1,2] have reported the preparation of 4,4′-dialkoxybenzoins as precursors of mesomorphic 4,4′-dialkoxybenzoinylidene-*p*-alkoxyanilines. However, liquid crystal properties are not mentioned by these authors for the 4,4′-dialkoxybenzoins. The absence of mesomorphism in these compounds is most probably due to hydrogen bonding, either inter- or intramolecular. Intermolecular hydrogen bonding, in general, is known to be unfavorable to mesomorphism, as it favors a nonlinear molecular arrangement which is incompatible with mesophase formation.[3] Intramolecular hydrogen bonding would cause an angular conformation, which would prevent the molecule from being linear and would therefore not allow the parallel arrangement typical of the mesophase[4]:



We have previously described the liquid crystal properties of some series of compounds derived from alkoxypyridinecarboxaldehydes.[5,6,7] We now wish to report the mesomorphic behavior of some 5,5′-dialkoxy-2,2′-pyridoins, which result from benzoin condensation of 5-alkoxy-2-pyridinecarboxaldehydes.

RESULTS AND DISCUSSION

The results of the microscopical and DSC studies of the compounds are gathered in Table I (see also Figs. 1 and 2).

Four of the five compounds studied were mesomorphic. Those with butoxy and hexoxy groups showed a nematic phase, while those with octoxy and decoxy groups showed both nematic and smectic C phases. In all cases the mesophases were enantiotropic. The ethoxy homologue was not mesomorphic.

The mesogenicity of these compounds with an acyloin group is not surprising if we take into account the fact that 2,2′-pyridoins exist predominantly in the (E)-enediol tautomeric form, where stabilization by intramolecular hydrogen bonding occurs[8,9] (see Figure 2).

Tautomer I presents two intramolecular hydrogen bonds in six-membered chelate rings. Conformations IIa and IIb of the hydroxycarbonyl tautomer could only have one intramolecular hydrogen bond, which, in the case of conformation IIb, would form a geometrically disfavored five-membered chelate ring.[10]

In Structure I the parallel conformation and the approximately lath-like shape of the molecule enable a mesomorphic arrangement to take place. On the other hand, Structures IIa and IIb would deviate appreciably from linearity, and would not favor mesomorphism.

In the course of the microscopic study of the compounds belonging to this series, gradual degradation was observed as the products were subjected to successive

TABLE I

Transition temperatures and enthalpies for the compounds in the series (see Figure 2).

n	Transition	T(°C)	ΔH(KJ/mol)
2	C_1–C_2	138.6	11.4
	C_2–I	190.2	31.5
4	C–N	157.5	49.9
	N–I	172.0	2.0
6	C–N	132.4	55.9
	N–I	160.3	2.9
8	C_1–C_2	69.0	9.2
	C_2–C_3	100.8	11.1
	C_3–S_C	110.5	19.2
	S_C–N	123.6	1.9
	N–I	155.4	2.8
10	C–S_C	104.3	55.9
	S_C–N	137.2	3.6
	N–I	146.2	2.7

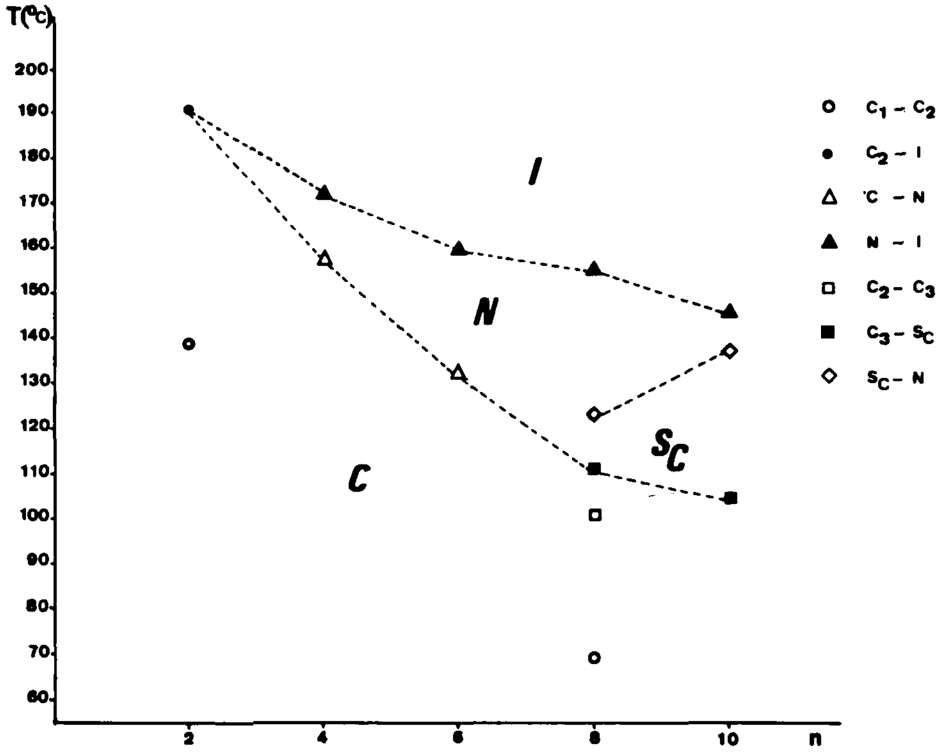


FIGURE 1 Transition temperatures as a function of the length of the terminal chain in the 5,5'-dialkoxy-2,2'-pyridoins.

heating processes. This degradation gradually led to a decrease in the melting points and finally also to the disappearance of mesomorphism. The phenomenon was caused by the oxidation of the pyridoins to pyridils by the effect of atmospheric oxygen at high temperatures (see Figure 2).

On the other hand, sharp peaks were generally registered on the DSC study under a nitrogen atmosphere and reappeared when the study was repeated. After several runs, however, a certain broadening of some high temperature peaks was detected.

The disappearance of mesomorphic properties as oxidation progresses in the course of the microscopic study is noteworthy. In order to find a reasonable explanation for the absence of mesomorphism in the oxidized products, we made a study of pyridoins and pyridils. To this end, we prepared and studied by spectroscopic techniques 2,2'-pyridoin and 2,2'-pyridil, which can be considered as models for the analogous substituted compounds.

2,2'-Pyridoin was synthesized by benzoin condensation from 2-pyridinecarboxaldehyde. 2,2'-Pyridil was prepared by oxidation of 2,2'-pyridoin with concentrated nitric acid. IR, ^{1}H-NMR and UV spectroscopic data for 2,2'-pyridoin and 2,2'-pyridil are gathered in Table II.

IR and ^{1}H-NMR spectra revealed that 2,2'-pyridoin only exists in the enediol form. Thus, in the NMR spectrum the only OH peak appeared at $\delta = 12.2$ ppm,

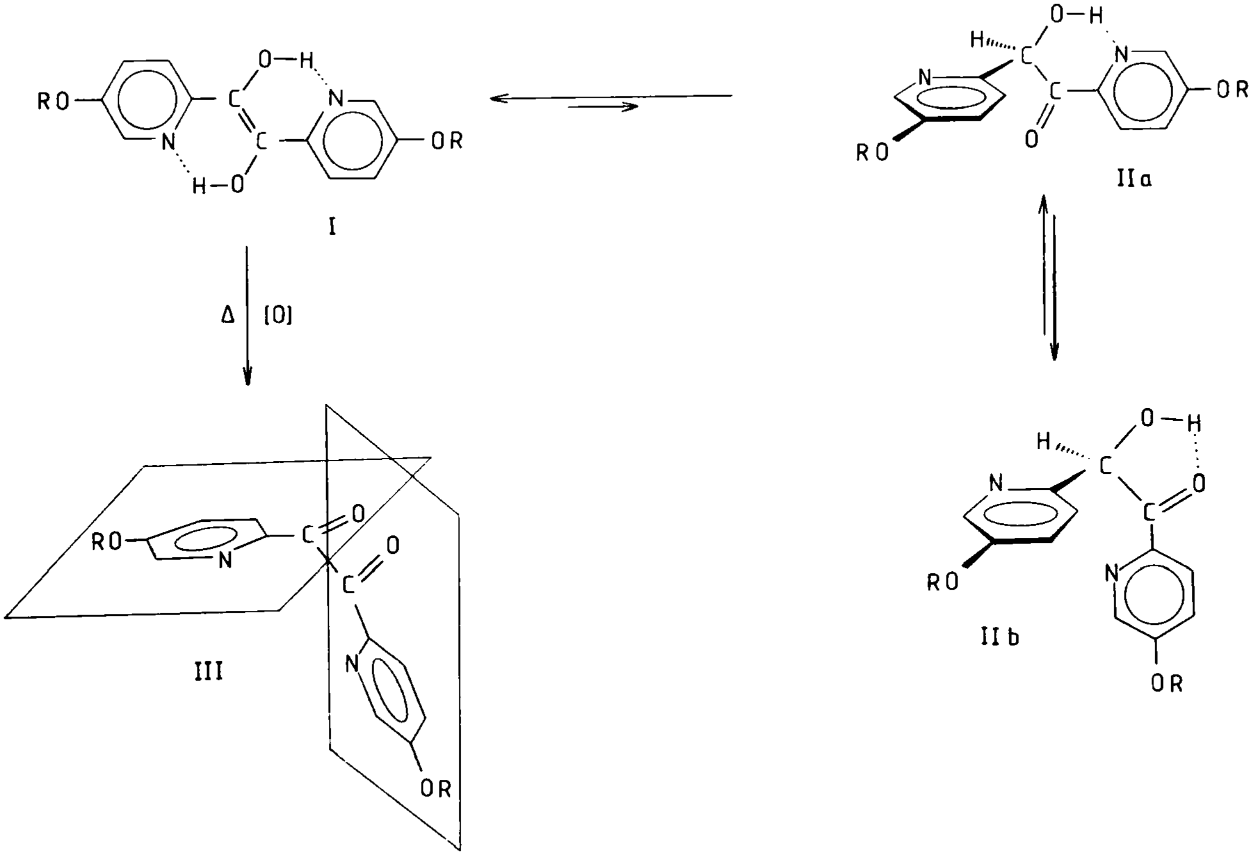


FIGURE 2 Structures of the 5,5′-dialkoxy-2,2′-pyridoins (I, IIa and IIb) and 5,5′-dialkoxy-2,2′-pyridils (III).

TABLE II

^{1}H-NMR, IR and UV data for 2,2'-pyridoin and 2,2'-pyridil

		^{1}H-NMR (in $CDCl_3$ solution) δ(ppm)			
Compound					
2,2'-pyridoin	12.18 (s, wide, 2H)	8.40 (dd, 2H)	7.85 (dd, 2H)	7.77 (m, 2H)	7.12 (m, 2H)
2,2'-pyridil		8.50 (dd, 2H)	8.13 (dd, 2H)	7.85 (m, 2H)	7.42 (m, 2H)
		IR (in solid state)			
Compound	νO—H (cm^{-1})	νC—H (cm^{-1})	νC=O (cm^{-1})	νC—C (cm^{-1})	νC—O (cm^{-1})
2,2'-pyridoin	—	—	—	1595, 1565	1260
2,2'-pyridil	—	3060	1715–1695	1590	—
		IR (in $CHCl_3$ solution)			
Compound	νO—H (cm^{-1})	νC—H (cm^{-1})	νC=O (cm^{-1})	νC—C (cm^{-1})	νC—O (cm^{-1})
2,2'-pyridoin	—	3010	—	1595, 1565	1270
2,2'-pyridil	—	—	1720–1700	1590	—
		UV (in cyclohexane solution)			
Compound	λ_1 nm (log ε)	λ_2 nm (log ε)			
2,2'-pyridoin	248 (3.91)	387 (4.28)			
2,2'-pyridil	232 (4.22)	268 (3.91)			

this high value being indicative of the existence of a strong intramolecular hydrogen bond. At the same time the non-existence of the hydroxycarbonyl tautomer was also confirmed by the absence of a peak corresponding to the acyloin CH proton.

The IR results lead us to the same conclusion. Carbonyl absorption was not observed for 2,2'-pyridoin, either in the solid state or in $CHCl_3$ solution, and this rules out the hydroxycarbonyl structure. Furthermore, a clearly defined O—H absorption was not observed, this absence being typical of hydroxy groups forming strong intramolecular hydrogen bonds.

The UV spectra showed two absorption maxima for each compound. For 2,2'-pyridoin the absorption maxima were at wavelengths of $\lambda_1 = 248$ nm and $\lambda_2 = 387$ nm. For 2,2'-pyridil, the absorptions were at $\lambda_1 = 232$ nm and $\lambda_2 = 268$ nm. The fact that 2,2'-pyridoin registers absorption of ultraviolet light at higher wavelength values than 2,2'-pyridil indicates a higher degree of electron conjugation. This was to be expected, taking into account the fact that the presence of the carbon–carbon double bond in 2,2'-pyridoin allows conjugation between the two aromatic rings, which is not the case in 2,2'-pyridil.

The electron-like features of the molecule have an effect on its geometrical features. Thus, both intramolecular hydrogen bonding and the extent of conjugation cause the molecule of 2,2'-pyridoin to be coplanar. On the other hand, the lesser degree of conjugation between the two aromatic rings prevents the molecule of 2,2'-pyridil from being planar and consequently from being linear. This is consistent with a skewed structure, like the benzil molecule, in which the two benzoyl units are known to lie in planes approximately perpendicular to each other, and the dicarbonyl system is not coplanar.[11,12] The lack of coplanarity and linearity and the restricted extent of conjugation must weaken the attractive intermolecular forces and undoubtedly account for the absence of mesomorphism in 2,2'-pyridil derivatives.

EXPERIMENTAL

Synthesis

5-Alkoxy-2-pyridinecarboxaldehydes. The synthesis of the aldehydes was carried out by O-alkylation of 5-hydroxy-2-picoline, followed by oxidation of the methyl group to carbonyl, according to a procedure described previously.[7]

5,5'-Dialkoxy-2,2'-pyridoins. A solution of potassium cyanide (0.25 g) in water (2 ml) was added to a solution of 5-alkoxy-2-pyridinecarboxaldehyde (4 mmole) in 96% ethanol (8 ml). The resulting solution was stirred for 3 h at room temperature. The yellow precipitate was collected by filtration, washed with 96% ethanol and crystallized from acetone (55–75% yield).

2,2'-Pyridoin. A solution of potassium cyanide (2.5 g) in water (20 ml) was added to a solution of 2-pyridinecarboxaldehyde (3.96 g, 0.04 mol) in 96% ethanol (80 ml). The resulting solution was heated under reflux for 1 h. After cooling, the orange precipitate was collected by filtration and crystallized from 96% ethanol (80% yield).

2,2'-Pyridil. A mixture of 2,2'-pyridoin (1.98 g, 0.01 mol) and concentrated nitric acid (10 ml) was heated in a boiling-water bath for 1 h. After cooling, the mixture was carefully neutralized with 10% aqueous sodium carbonate. The white precipitate was collected by filtration, washed with water and crystallized from 96% ethanol (75% yield).

Techniques

The transition temperatures and enthalpies were determined using a Perkin-Elmer DSC-2 instrument. The apparatus was calibrated by measuring the known melting points and heats of fusion of indium (156.6°C, 6.8 cal/g) and tin (231.9°C, 14.45 cal/g).

Optical observations were made using a Meiji polarizing microscope equipped with a Mettler FP-82 heating stage and an FP-80 central processor.

^{1}H-NMR spectra were registered with a Bruker WP-80-CW instrument using $CDCl_3$ solutions and TMS as an internal reference.

IR spectra were obtained with a Perkin-Elmer 783 spectrophotometer using KBr mulls and $CHCl_3$ solutions with a concentration of 5 mg/ml.

UV spectra were registered with a Perkin-Elmer 200 instrument.

The purity of all products was checked by the above-mentioned techniques and by elemental analysis using a Perkin-Elmer 240-C microanalyzer.

CONCLUSIONS

Mesomorphism in 5,5'-dialkoxy-2,2'-pyridoins is due to the fact that they exist only in the (E)-enediol form. This structure contains two intramolecular N······H bonds, which preserve the parallel conformation and the coplanarity of the molecule, and allow conjugation between the two aromatic rings.

These compounds are unstable when heated in air because slow oxidation to the corresponding pyridils occurs. The oxidized products are not mesomorphic due to their skew-structure, which prevents the molecules from being linear and coplanar, and obstructs electronic conjugation between the two pyridine rings.

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