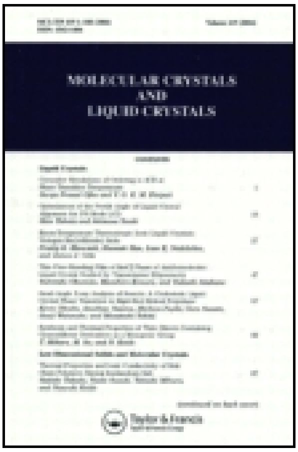

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LIQUID CRYSTALS FROM NON-MESOGENIC ANILS INDUCED THROUGH HYDROGEN BONDING

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Abstract The interaction of N-(p-methoxy-o-hydroxybenzylidene)-p-aminopyridine (I) and N-(p-methoxy-o-hydroxybenzylidene)-m-aminopyridine (II) with certain p-alkoxybenzoic acids results in the formation of liquid crystals. Specifically, as established by optical microscopy, DSC and X-ray diffraction studies, complexes of I with short-chain acids afford nematic phases while smectic and nematic phases are induced with acids of long alkyl chain. In the complexes derived from anil II only the acids with long alkyl chains induce the formation of nematic and smectic phases.

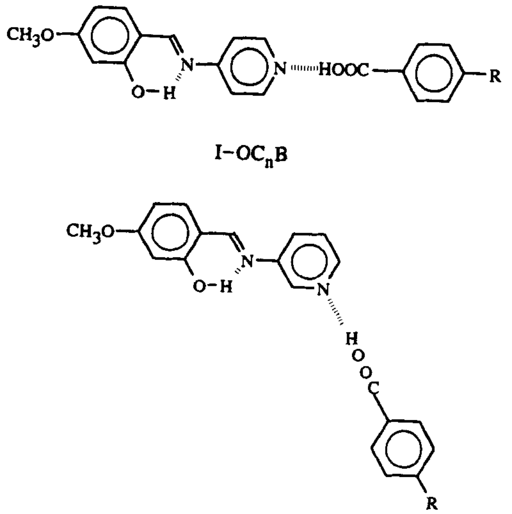
INTRODUCTION

The role of hydrogen bonding in the formation of liquid crystals had not been greatly appreciated, primarily in the early years of liquid crystalline research, and only recently a number of publications and reviews[1-30] deal with the subject. This may be attributed to the fact that common hydrogen bonded compounds, such as phenols and amines, are not generally mesomorphic.

The first class of compounds found to exhibit liquid crystalline behavior induced by hydrogen-bonding was that of aromatic acids.[1,2] These molecules dimerize through intermolecular hydrogen bonding, leading to a long rigid-rod complex, inducing in turn liquid crystallinity. The pair of acceptor-donor molecules used for the formation of the complex may or may not be mesomorphic. In both cases however, and primarily for non-mesomorphic molecules, hydrogen bonding is responsible for the modification or induction of liquid crystalline formation. Other compounds that form liquid crystals by hydrogen bonding include amphiphilic carbohydrates[5,6] multihydroxy amphiphilic compounds[7-9] and bolaamphiphilic molecules,[10] certain troponoid based derivatives[11] or dissimilar complementary molecules[12,13] of amphiphilic or rigid-rod type which form liquid crystalline complexes. The subject on hydrogen bonded liquid crystals has been reviewed quite recently.[14,15]

Mesogenic or non-mesogenic molecules bearing pyridyl and carboxylic moieties have been proven very useful for the formation of monomeric[16-24] and polymeric[25-30] liquid crystals by hydrogen bonding. Among the most popular molecules employed as acceptors were stilbazole, 4-pyridine derivatives and 4,4'-bipyridine. As donors were used various aliphatic and aromatic acids.

In the present study, two new compounds bearing the pyridyl group are used as acceptors i.e. N-(p-methoxy-o-hydroxybenzylidene)-p-aminopyridine (I) and N-(p-methoxy-o-hydroxybenzylidene)-m-aminopyridine (II). These molecules were interacted in the melt with short and long chain p-n-alkoxybenzoic acids and the complexes obtained were investigated as far as the exhibition of liquid crystalline character is concerned. It has to be noted that compound II and the complexes resulting from this angular anil and alkoxybenzoic acids do not possess at first sight the appropriate geometry for the formation of liquid crystalline phases. Compound II was however employed as acceptor in order to check whether the chevron-type complexes obtained are able to induce the formation of liquid crystals. The structures of the materials that will be investigated in this work are shown in the Scheme below, the two classes of complexes abbreviated as: I-OC$_n$B and II-OC$_n$B where n = 1,2,3,4,5,10 and 12.



I-OC$_n$B

II-OC$_n$B

Scheme

EXPERIMENTAL

Synthesis of Anils.

To 0.006 mol of p-methoxy-o-hydroxybenzaldehyde, dissolved in benzene, is added an equimolar quantity of 4-aminopyridine or 3-aminopyridine and the dispersion obtained is refluxed for several hours (about 30 hours) employing a Dean-Stark condenser. The reaction mixture was allowed to reach room temperature, then filtered. Benzene of the filtrate is distilled-off and the remaining material is recrystallized from hexane. The anils were pure as established by elemental analysis and NMR spectra.

Formation of Complexes.

Equimolar quantities of each anil with the corresponding p-n-alkoxybenzoic acid derivative were thoroughly mixed and subsequently allowed to remain at approximately 120 °C for a few minutes. The material obtained after cooling was used for liquid crystalline characterization.

Characterization.

Optical microscopy studies were performed with a Reichert polarizing microscope equipped with a Linkam TMS 91 controller and a hot-stage. For DSC studies a Perkin Elmer DSC-7 calorimeter coupled with TAC 7/3 controller was employed. The thermograms were obtained at a heating-cooling rate 10 °C/min. FT-IR were obtained by a Perkin Elmer 1600 spectrometer with resolution 2 cm^{-1}. X-ray diffraction patterns were recorded with a Guinier focusing camera ($CuK_{\alpha 1}$).

RESULTS AND DISCUSSION

In the search of new complementary components for hydrogen bonding interaction it was considered that anils with pyridyl group at the para position could be potential acceptors for interacting with carboxylic acids to afford liquid crystals. The facile hydrolysis of anils prohibits in general their use when employed for long-term applications. The anils I and II however do not easily hydrolyze due to the ortho hydroxy group which interacts intramolecularly with the nitrogen of the C=N bond protecting them from hydrolysis.

Concerning the components employed for the formation of the complexes, anils are not mesomorphic with anil I melting at 125-128 °C and II at 121-124 °C. On the other hand, it was found[31] that p-methoxy and ethoxybenzoic acid do not exhibit liquid crystalline behavior, propoxy- to hexyloxybenzoic acids are nematic, while the higher members exhibit both smectic and nematic phases. It was of interest therefore to see whether the formation of complexes by the interaction of anils with the acids will induce the exhibition of liquid crystalline phases.

Complexation of anils with acids was established with FTIR spectra. Thus the peaks of OH at 2500 and 1923 cm^{-1} attributed to hydrogen bonding[22,32,33] appear in the spectra of the complexes. The carbonyl band at 1697 cm^{-1} is attributed to the "free", non-hydrogen bonded carbonyl group of the complex while the carbonyl peak of the dimeric acid is observed at 1681 cm^{-1}.

Optical microscopy experiments showed that complexes I-OC_nB with n = 1-5 i.e. the methoxy, ethoxy, propoxy, butoxy and pentyloxy derivatives exhibited enantiotropic nematic phases. The decyloxy derivative exhibits on cooling a nematic phase, transformed at about 121 °C to a primarily homoetropic smectic phase. The dodecyloxy derivative exhibited smectic and nematic mesophases. In Figure 1 a typical nematic texture for I-OC_5B,

FIGURE 1 A typical nematic texture for the I-OC_5B complex
See Color Plate I.

and in Figure 2 a characteristic smectic texture for I-$OC_{12}B$ complex are shown. The presence of nematic and smectic phases was clearly confirmed by X-ray diffraction.

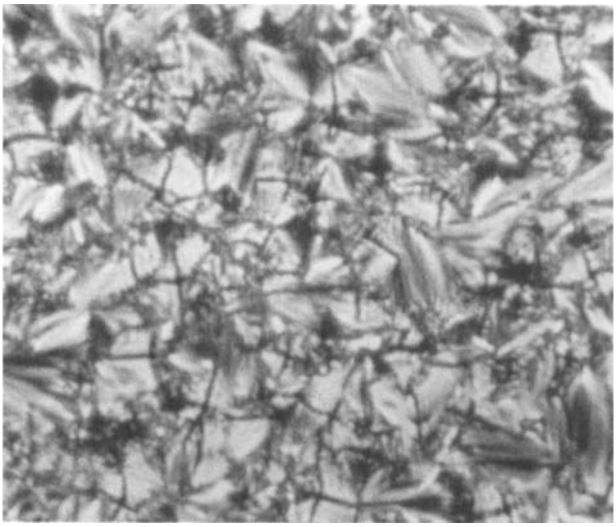


FIGURE 2 A smectic texture for the I-$OC_{12}B$ complex
See Color Plate II.

Concerning the complexes originating from the angular anil, the decyloxy derivative exhibited enantiotropic nematic and smectic phases while the dodecyloxy complex exhibited on cooling a monotropic nematic phase (droplet texture), then a smectic phase quickly crystallizing. It has thus been shown that long aliphatic chains promote organization leading to liquid crystals even for these unfavorable angular complexes.

The thermotropic behavior of these complexes was also established by DSC. A typical DSC thermogram for a nematic liquid crystalline complex i.e. I-OC_5B is shown in Figure 3. Distinct phase transitions were in general observed on cooling and together with the corresponding enthalpies of the complexes are shown in Table I.

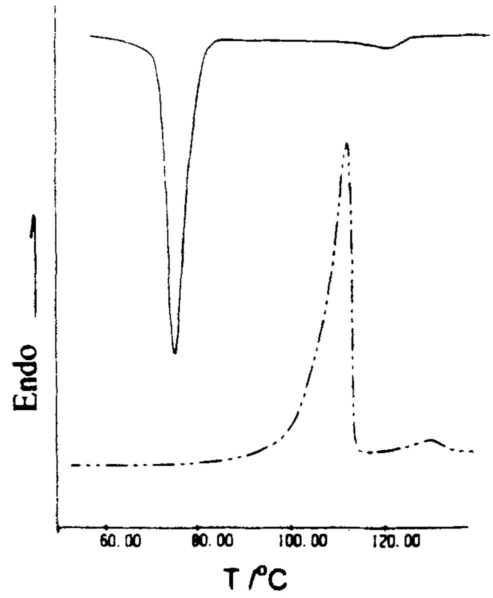


FIGURE 3 A typical DSC trace for I-OC$_5$B complex

TABLE I Phase transitions and corresponding enthalpies of the complexes I-OC$_n$B and II-OC$_n$B.

Compound		T /°C		ΔH /KJ.mole^{-1}
I-OC$_1$B	I	119.0	N	0.38
	N	104.0	K	4.51
I-OC$_2$B	I	140.7	N	2.00
	N	77.8	N	23.60
	N	68.8	K	2.54
I-OC$_3$B	I	102.2	N	0.02
	N	100.3	K	35.13
I-OC$_4$B	I	133.0	N	2.85
	N	90.5	K	51.40
I-OC$_5$B	I	122.0	N	1.18
	N	76.1	K	41.63
I-OC$_{10}$B	I	123.6	N	1.62
	N	105.9	S	0.02
	S	62.0	K	38.86
I-OC$_{12}$B	I	143.0	N	0.35
	N	123.7	S	4.48
	S	65.7	K	49.84
II-OC$_{10}$B	I	81.1	N	4.39
	N	75.2	S	4.30
	S	47.8	K	39.10
II-OC$_{12}$B	I	81.1	N	4.39
	N	67.2	S	4.30
	S	49.6	K	33.73

CONCLUDING REMARKS

Hydrogen bonding interaction of p-n-alkoxybenzoic acids with non-mesomorphic anils I and II leads to the formation of hydrogen-bonded complexes the properties of which can be summarized in the following: a. Complexes of methoxy-, ethoxy-, propoxy-, butoxy-, pentyloxybenzoic acids with the linear anil I afford materials with nematic liquid crystalline structures, while decyloxy- and dodecyloxybenzoic acid with the same anil afford smectic and nematic phases. The phase transitions of the complexes are always at lower temperatures compared to the transitions of the corresponding dimeric acids. b. The interaction of angular anil II with the same alkoxybenzoic acids does not in general induce the formation of mesogenic complexes. Among the complexes tested only those obtained by the interaction of decyloxy- and dodecyloxybenzoic acids with anil II afford nematic phases coexisting at low temperatures with metastable smectic phases. Detailed study, including the complete homologous series of the acids (C_1 - C_{12}) is in progress.

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