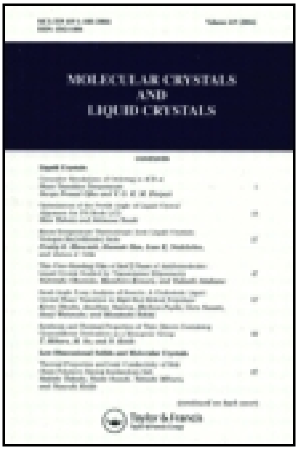

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Liquid Crystalline Properties of 4-Alkoxy-Aniline-4′-Alkoxy-Anilines

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LIQUID CRYSTALLINE PROPERTIES OF 4-HALOGENOBENZYLIDENE-4'-ALKOXYANILINES

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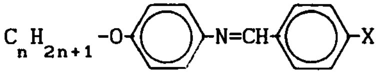
Abstract Liquid crystalline properties of the four families with the general formula:



where X = NO_2, Cl, Br, F, have been investigated.

Among these compounds nematic, smectic A and smectic B mesophases were found. These phase situations are compared with the isomeric families with the reversed -N=CH- central group.

INTRODUCTION

The popularity of Schiff bases began in 1970 from the Kelker publication [1] about methoxybenzylidene-butylaniline (MBBA). Now MBBA is a standard in liquid crystal science.

Schiff bases are very interesting because of their rich polymorphism [2,3,4,5] and convenience due to low temperatures of phase transitions. Their disadvantage is a very high sensitivity onto moisture. Compounds with high dielectric anisotropy are important, when applications are considered. Such compounds were prepared by introducing groups with strong dipole moment (-F,-Cl,-Br,-NO_2) on the one end. This increases De but reduces the number of mesophases.

The investigation of such compounds with high, positive dielectric anisotropy started in the end of seventies.

For the first time the family with the nitro group was partly described in 1976 by Malthete et al. [6] and fully by Vora et al. in 1980 [7]. Calorimetric properties were presented in series of papers [8,9,10], and very recently their dielectric properties were published [11,12,13]. The isomeric family was only partly described in 1976 by Malthete et al. [6].

The family with the chloro group was as well partly described in 1976 by Malthete et al. [6] and fully lately by the author in [14]. The properties of the isomeric family was partly described in 1976 by Malthete et al. [6] and more fully by Sakagami et al. in 1980 [15] and by Suerin et al. in 1981 [16].

The bromo family was presented in 1990 at the ILCC in Vancouver as a poster [17] with information about phase situations, but a full description was done lately by the author [18], the results of which generally agree with [17]. Properties of the isomeric family were described in 1980 by Sakagami et al. [15] and in 1980 by Vora [19].

The fluoro family was published in patent form [20] and its liquid crystalline properties were presented in the book of Demus et al.[3]. These results do not agree with ours which will be presented here.

The aim of this paper is to present the proper phase diagram for the described families and discuss the nature of phase transition, taking into account the enthalpy of the phase transitions. These phase situations are compared with those of their isomers.

4-NITROBENZYLIDENE-4-ALKOXYANILINES

The phase situation in this family and in the isomers is presented in Fig. 1. They have two mesophases: nematic and smectic A. The phase sequence is typical. There are no mesophases for the shorter chains.

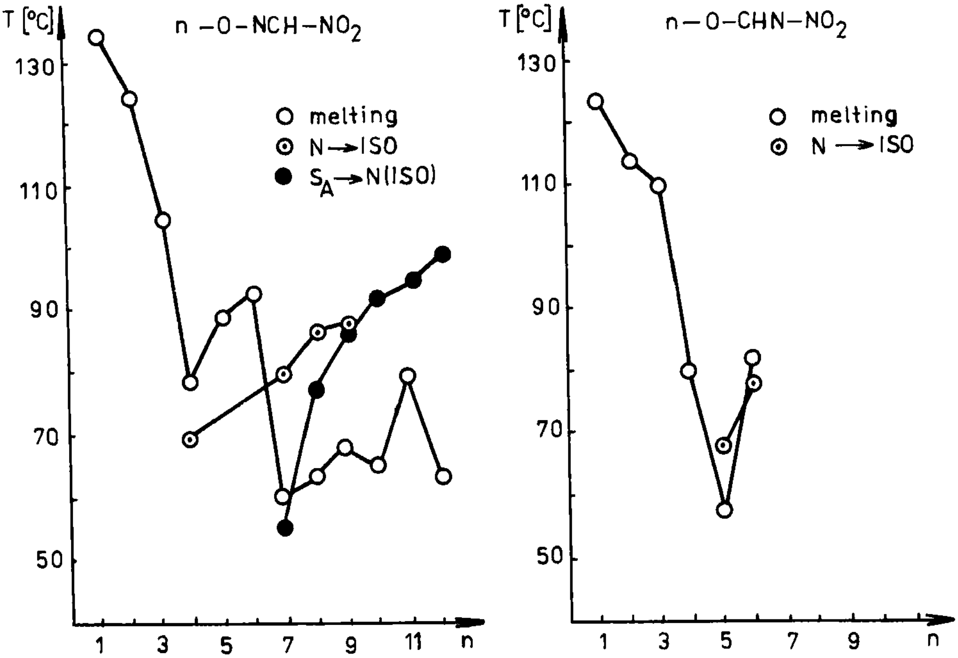


FIGURE 1 Phase diagram of the 4-nitrobenzylidene-4'-alkoxyanilines (left) and 4-alkoxybenzylidene-4'-nitroanilines (right).

With the chain's length increasing firstly appears the nematic phase, next the smectic A and in the end the nematic disappears. It is interesting that first nematic (monotropic) appears in the butyl derivative and next in the heptyl as an enantiotropic mesophase. In this family a large dipole moment (connected with two groups: -NO_2,-NCH-) exists, and introduces strong dipole interactions. This is the reason of higher energy of lattice and higher melting temperatures in comparison with the Schiff's bases with alkyl chains on both ends [2,3,4].

The enthalpy of phase transitions [10] depends slightly on the chain's length. It was found that $\Delta H \cong 35 \pm 5$ kJ/mol for melting and only for undecyl and dodecyl the ΔH values are 20% higher. The enthalpy of smectic A → isotropic transition is small ($\Delta H \cong 2.5 \pm 0.5$ kJ/mol) and it decreases to 0,2 kJ/mol when the nematic is present. Enthalpy of nematic's clearing is very small (on the border of accuracy) and has been found $\cong 0.2 \pm 0.1$ kJ/mol.

4-CHLOROBENZYLIDENE-4-ALKOXYANILINES

The phase situation in this family and in the isomers is presented in Figure 2. Both families have two mesophases: smectic A and smectic B only. The first three members of the family are nonmesomorphic.

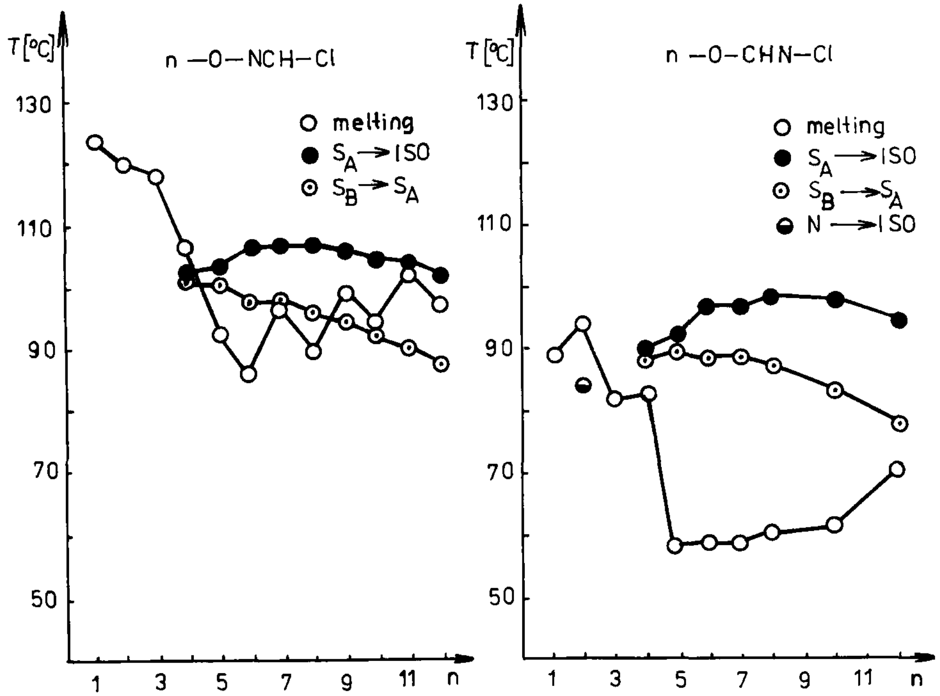


FIGURE 2 Phase diagram of the 4-chlorobenzylidene-4'-alkoxy anilines (left) and 4-alkoxybenzylidene-4'-chloroanilines (right).

Mesophases first appear in the butyl derivative (monotropic smectic A and smectic B). All the next members have the same phase sequence: crystal - smectic B - smectic A - isotropic. There is a very strong even-odd effect in melting curve. The clearing temperatures and temperatures of the smectic B - smectic A transitions depend very weakly on the chain's length. The isomeric family has the same phase topology, but all temperatures of phase transitions are lower.

For this family the melting enthalpy is as large as for nitro family 30 kJ/mol but stronger dependence on the chain's length [18] was found. Enthalpy of the smectic B - smectic A phase transition is 3.0 kJ/mol and depends very weakly on chain's length. The enthalpy of clearing (smectic A - isotropic) equals to 6.5 kJ/mol. The isomeric family has almost the same enthalpies of phase transitions [15]. For clearing there was found ΔH≅5.5kJ/mol and 3.2 kJ/mol for the smectic B → smectic A phase transitions.

4-BROMOBENZYLIDENE-4-ALKOXYANILINES

The phase situation of this family and its isomers is presented in Figure 3. The topology of phase sequence is very similar to the chloro families (Fig.2). The same mesophases for the same alkyl chains were found. Only for the butyl and pentyl derivatives one mesophase was found: smectic B. In the isomeric family the propyl derivative has a monotropic smectic B phase and the butyl derivative an enantiotropic smectic A phase. All next derivatives have both mesophases, smectic A and smectic B. Lower melting temperatures and almost the same temperatures of phase transition between mesophases were found as well.

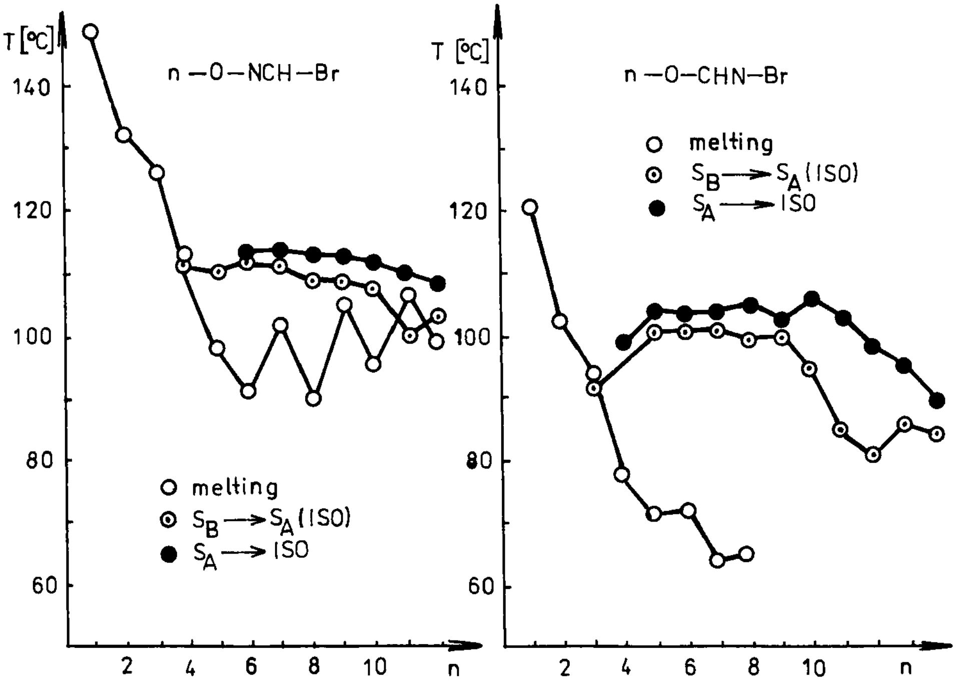


FIGURE 3 Phase diagram of the 4-bromobenzylidene-4'-alkoxyanilines (left) and 4-alkoxybenzylidene-4'-bromoanilines (right).

The enthalpy of melting for the bromo family was higher than that one in the chloro family and has a value of 30 kJ/mol and it strongly depends on the alkyl chain's length. The smectic B - smectic A phase transition has an enthalpy of 3.5±0.5 kJ/mol and the enthalpy is constant for the rest of family members. The clearing enthalpy (smectic A → isotropic) equals for all members 7.5±0.5 kJ/mol. For the butyl and pentyl derivative, where only one mesophase exists, clearing enthalpies 11.0±0.5 kJ/mol were found, which is the strict sum of the phase transitions: smectic B → smectic A and smectic A → isotropic.For the isomeric family enthalpies of phase transitions are the same for smectic B → smectic A (3.5±0.5 kJ/mol)and for clearing 7.2±0.5 kJ/mol [15].

4-FLUOROBENZYLIDENE-4-ALKOXYANILINES

The phase sequences for this family and their isomers are presented in Fig.4. In this family mesomorphism was not found. The melting temperatures are high for the first three members. All next derivatives melt 15°C lower.These observations do not agree with the literature [20,3], where data were presented for the pentyl, hexyl and heptyl derivatives. For these three compounds enantiotropic nematics with a range from 10°C to 30°C was presented. The purity of our compounds was confirmed by NMR spectroscopy on the each step of synthesis. The same procedures were applied for other families, where the disagreements do not exist.

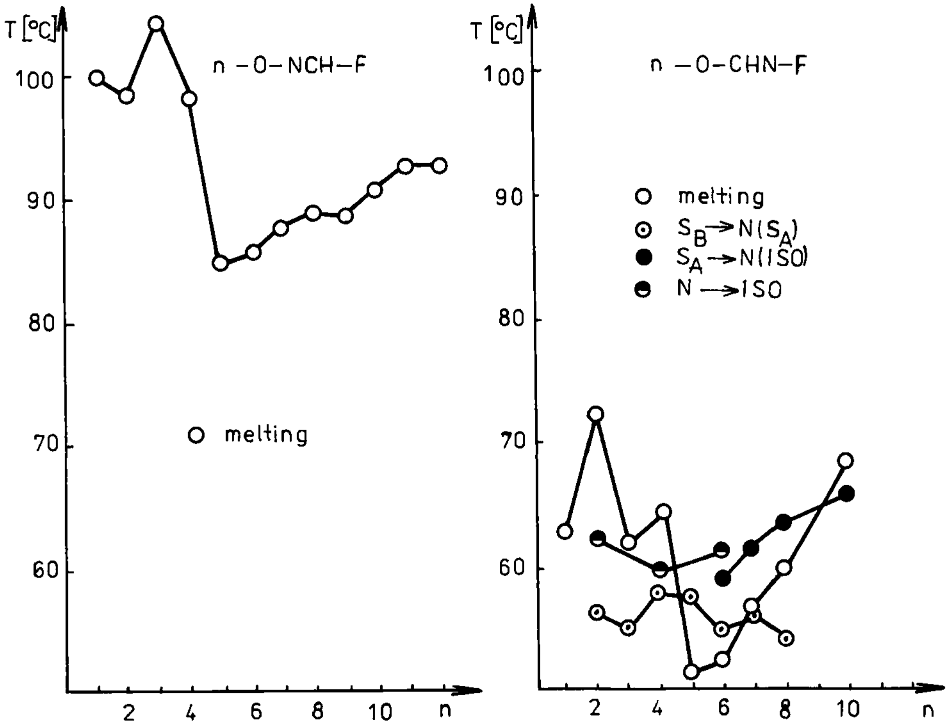


FIGURE 4 Phase diagram of the 4-fluorobenzylidene-4'-alkoxyanilines (left) and 4-alkoxybenzylidene-4'-fluoroanilines (right).

For the isomeric family the biggest polymorphism was found; i.e. for the hexyl derivatives three mesophases (nematic, smectic A, smectic B) were found. The melting temperatures are 30°C lower than for the first family. All phase transitions behavior is typical. For the first members there is a nematic phase which disappears for the longest alkyl chain. Smectic B phase exists in all mesomorphic derivatives, except decyl derivative, and smectic A appears for the longest alkyl chain when nematic starts to disappear.

The enthalpies of phase transitions agree with the values presented for the other families and for isomeric family for hexyl derivative there are: melting - 22 kJ/mol, smectic B → smectic A 2.5 kJ/mol, smectic A → nematic 3.2 kJ/mol and clearing 0.6 kJ/mol. When the nematic does not exist, the enthalpy of smectic A clearing is higher.

CONCLUSIONS

1. Temperatures of melting depend very weakly on the kind of halogen atom on the end.
2. The inversion of central group does not change phase transition type between mesophases, but changes melting temperatures.
3. The increase of dipole moment of molecules causes increasing stability of lattice and melting temperatures.
4. Families with nitro group have bigger dependence of phase transitions temperatures on the alkyl chain's length.
5. The enthalpy of intermesophase phase transitions is very weakly dependent on the central group inversion and kind of substitutents on the end.
6. In the homologous series there is additivity of the enthalpies of phase transitions between mesophases.

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