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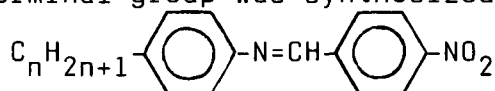
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LIQUID CRYSTALLINE PROPERTIES OF 4-NITROBENZYLIDENE 4-ALKYLANILINES

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Abstract A new group of Schiff's bases containing a polar terminal group was synthesized:



The phase situation was characterized on the basis of the calorimetric (DSC) studies and the textures observations.

INTRODUCTION

The Schiff's bases are a group of liquid crystalline compounds which have been extensively studied both from practical and scientific point of view^{1,2}. The most interesting are the compounds with the alkyl and alkoxy chains at the both ends of them. Less known are compounds with one alkyl or alkoxy chain and a strong dipole group on the other side. In spite of simplicity of these compounds not all families of such asymmetric Schiff's bases are described in the literature so far.

The aim of this paper is to describe the synthesis and the phase situations of a family of the liquid crystalline compounds: 4-nitrobenzyliden-4-alkylanilines.

COMPOUNDS PRESENTATIONS

The Schiff's bases were synthesized by condensing in

ethanol equimolecular quantities of freshly prepared 4-alkylanilines with the appropriate 4-nitrobenzaldehyd³. The products were crystallized from ethanol to constant transition temperatures. Structural identification of the compounds was based on the NMR spectra.

PHYSICAL MEASUREMENTS

The calorimetric measurements have been performed using a differential scanning calorimeter RIGAKU and the textures observations have been made with the help of the AMPLIVAPOL polarizing microscope equipped with heating stage (Boetius type) and a camera. The NMR spectra have been recorded with a TESLA BS 567 A spectrometer.

CALORIMETRIC PROPERTIES

A different influence of the chain length on the phase situation of the studied systems was detected. The derivatives from methyl to hexyl do not exhibit a mesophase; only a short temperature hysteresis take place. The derivatives from heptyl to dodecyl exhibit liquid crystalline properties, but only two of them, nonyl and undecyl exhibit enantiotropic liquid crystalline properties. All the phase transitions are presented in Figure 1. The heptyl, decyl and dodecyl derivatives exhibit one monotropic phase transition, the first-one with very small heat during the isotropic liquid - mesophase phase transition. The octyl derivative shows two monotropic phase transitions. The nonyl derivative exhibits two mesophases, one of them enantiotropic whereas the undecyl derivative has one enantiotropic mesophase. Temperatures and heats of all phase transitions for the studied compounds are listed on Table 1.

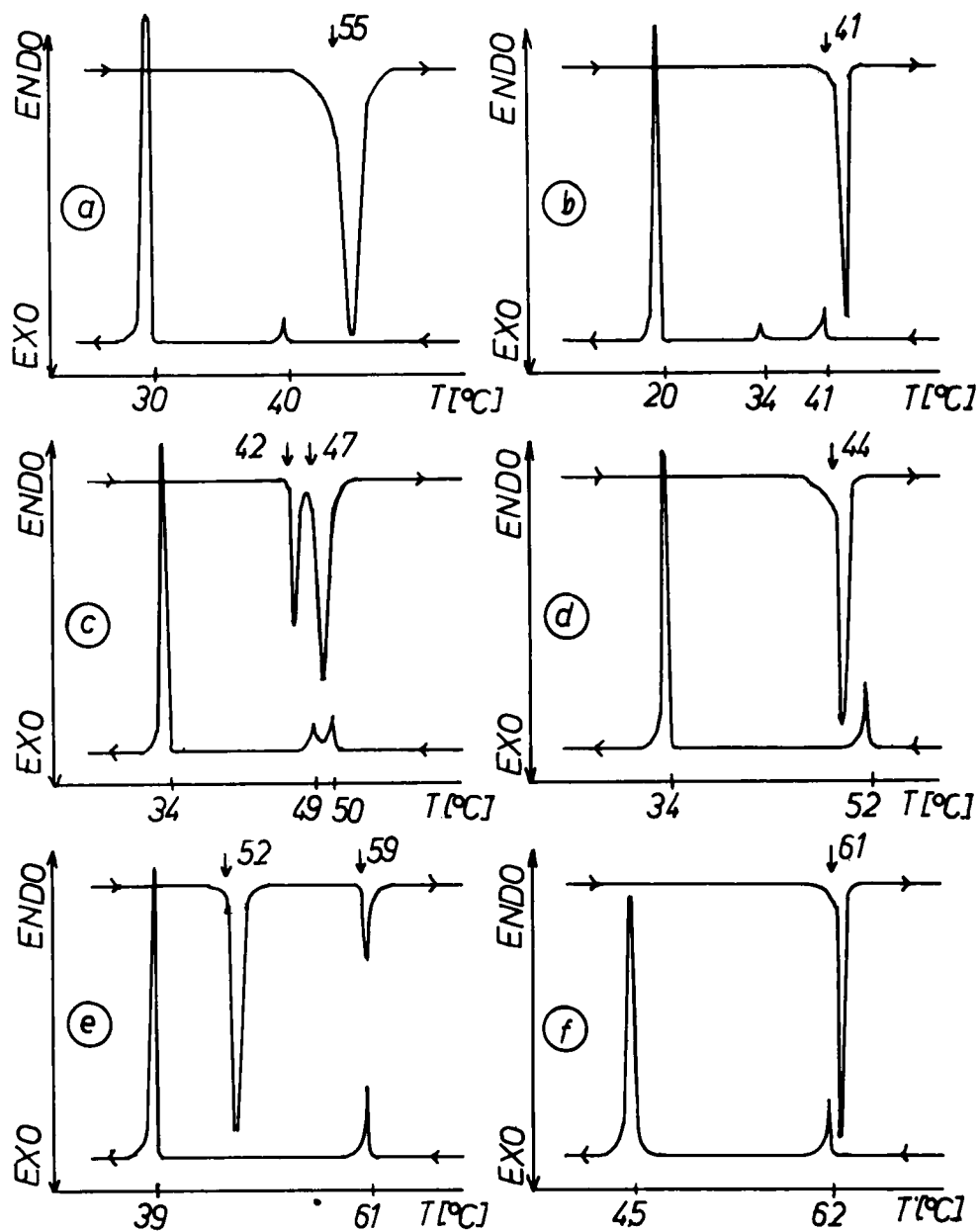
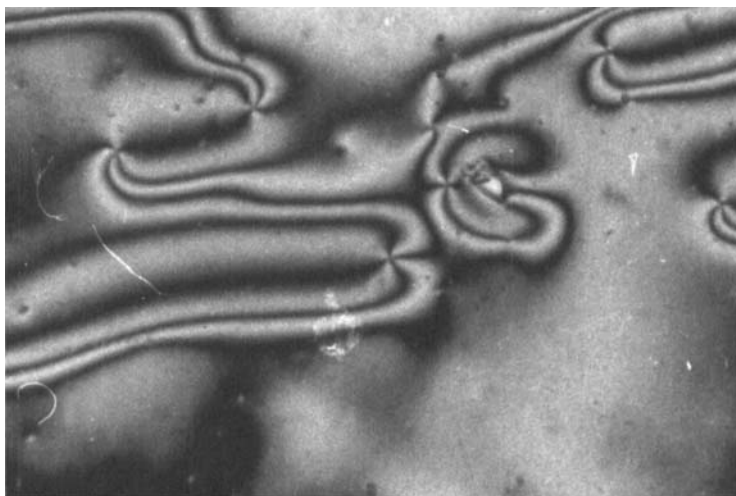


FIGURE 1 DSC thermograms for 4-nitrobenzylidene-4-alkylanilines. Scan rate 10 K/min. a) heptyl, b) octyl, c) nonyl, d) decyl, e) undecyl, f) dodecyl derivatives.

TABLE I Transition temperatures and enthalpies of 4-nitrobenzylidene-4-alkylanilines.

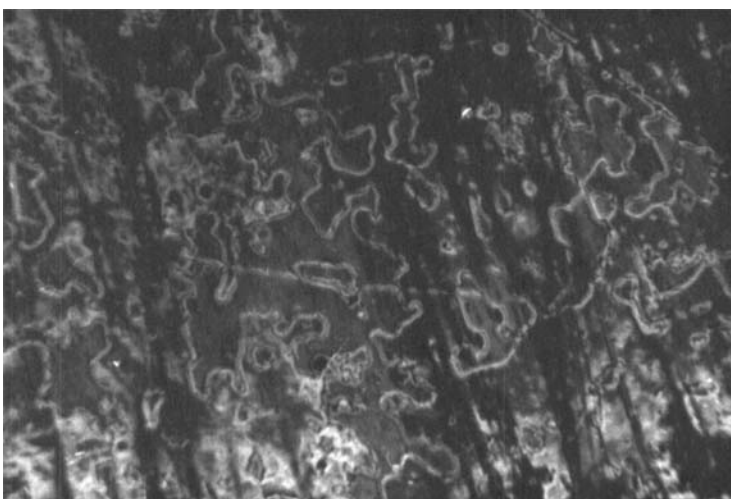
n	melting point	C	S _A	N	I
1	116 (5.69)	-	-	-	-
2	86 (3.72)	-	-	-	-
3	75 (4.52)	-	-	-	-
4	57 (3.11)	-	-	-	-
5	54 (5.48)	-	-	-	-
6	54 (5.48)	-	-	-	-
7	56 (4.44)	-	(30)(4.05)	41 (0.104)	-
8	43 (5.68)	(27)(5.14)	(35)(0.03)	41 (0.106)	-
9	46 (1.80)	(33)(4.63)	50 (0.10)	52 (2.810)	-
10	52 (8.32)	(38)(7.00)	-	54 (0.410)	-
11	52 (3.81)	37 (4.00)	-	61 (0.261)	-
12	62 (8.94)	(47)(8.16)	-	63 (0.525)	-

H (in round brackets) in kcal/mol.



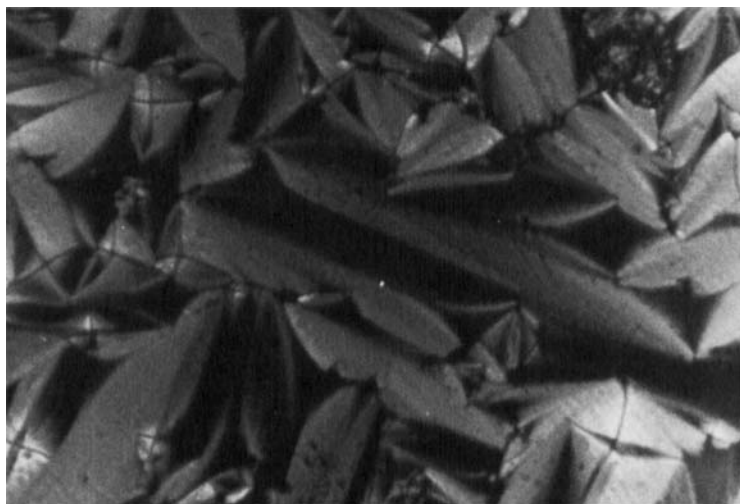
See Color Plate I

FIGURE 2 Microscopic texture (120x, crossed polarizers) for 4-nitrobenzylidene-4-octylaniline, 38°C schlieren texture of nematic.



See Color Plate II

FIGURE 3 Microscopic texture (120x, crossed polarizers) for 4-nitrobenzylidene-4-nonylaniline, 49°C , marbled texture of nematic.



See Color Plate III

FIGURE 4 Microscopic texture (200x, crossed polarizers) for 4-nitrobenzylidene-4-dodecylaniline, 59°C, focal-conic texture for S_A .

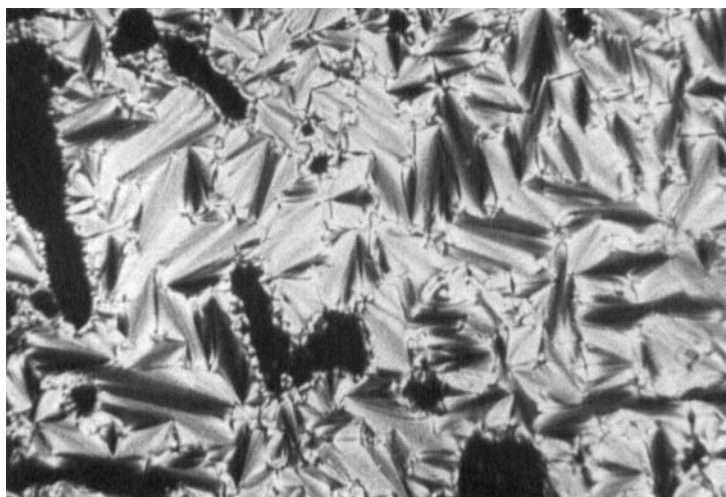


FIGURE 5 Microscopic texture (120x, crossed polarizers) for 4-nitrobenzyliden-4-decylaniline, 49°C, fan shaped texture of S_A .

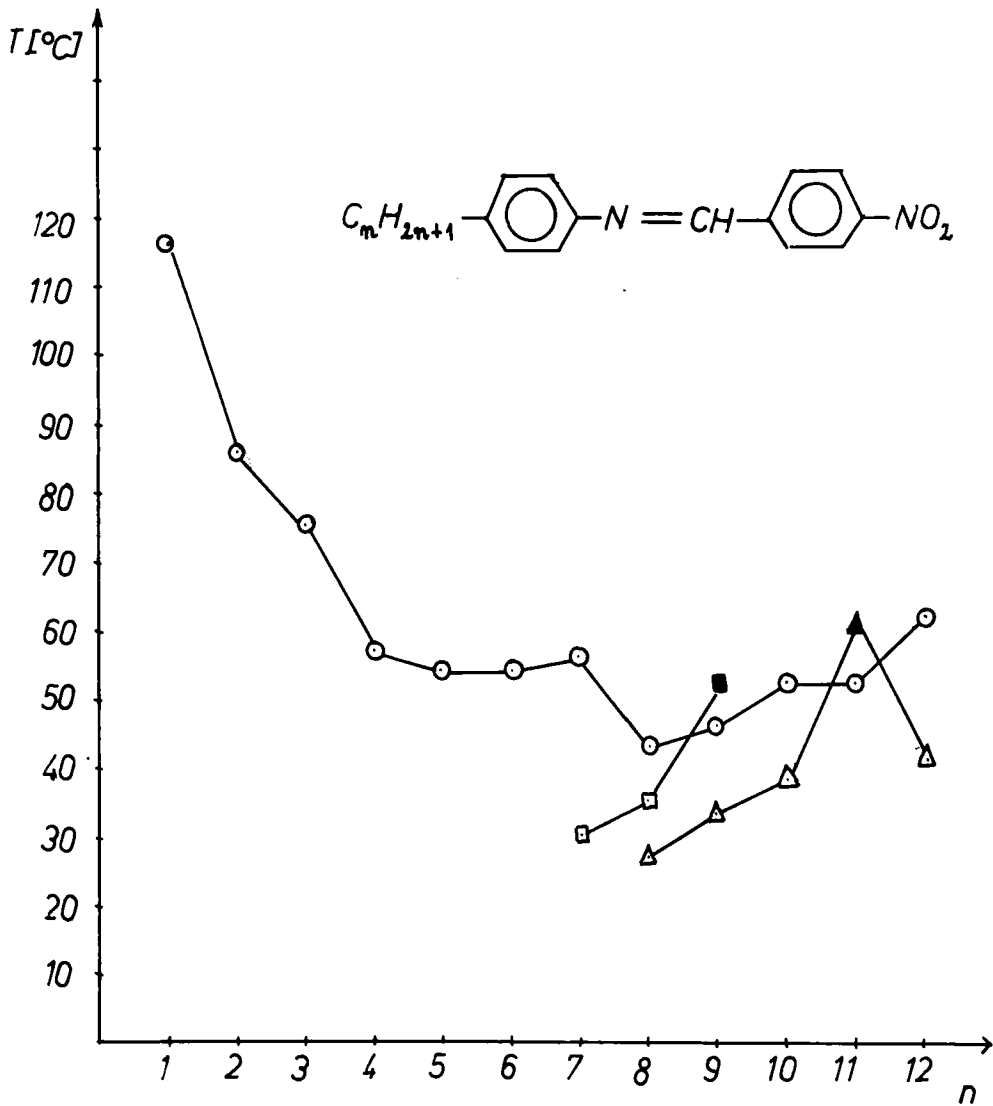


FIGURE 6 Plot of liquid crystal transition temperatures against the number of carbons in the alkyl chain in the 4-nitrobenzylidene-4-alkylanilines (o - melting, \square - N - Iso, \triangle - S_A - Iso (N)).

OBSERVATIONS OF TEXTURES

In all studied compounds textures characteristic for the nematic and S_A phases were observed (Fig 2,3,4,5). In the heptyl, octyl and nonyl derivatives schlieren and marbled textures were found (Fig 2,3), which are characteristic for nematics.

For the derivatives from the octyl to dodecyl the fan-shaped and focal-conic textures (Fig 4,5), characteristic for S_A , were observed. For the octyl and nonyl derivatives we have observed two liquid crystalline textures. All photos presented here were taken during the decreasing run.

CONCLUSIONS

On the basis of the data obtained it was possible to build the phase diagram of the series of the 4-nitrobenzylidene-4-alkylanilines, which is presented in Fig 6. The mesophases found were the same as in the similar Schiff's bases with alkoxy chains^{4,5,6}. It means that the nematic and S_A mesophases are characteristic for the molecules with the $CH=N$, NO_2 and alkyl (alkoxy) groups.

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