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LIQUID CRYSTALLINE PROPERTIES OF 4-CHLOROBENZYLIDENE-4-ALKYLANILINES

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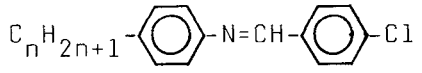
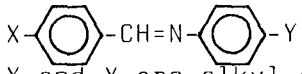
Abstract A new group of Schiff bases containing a polar terminal group was synthesized:



The alkyl was changed from n=1 to n=12. Based on calorimetric (DSC) studies and on observations of textures the phase situation was characterized.

INTRODUCTION

The Shiff bases have been extensively studied liquid crystalline compounds from the scientific as well as practical point of view. Special attention was paid to compounds of the general formula:



where X and Y are alkyl and alkoxy chains. In these materials a variety of different smectic phases were found. It seemed of interest to investigate the influence of the interchange of one of the alkyl or alkoxy groups with a strongly polar group (halogen or nitro group). Up to now all 4-alkoxybenzylidene derivatives were described in literature [1]. In these materials only the nematic, smectic A and smectic B phase were found. In case

of the 4-alkoxyaniline and 4-alkylaniline derivatives only a few series of compounds were described. The aim of this work was the synthesis and investigation of liquid crystalline properties of 4-chlorobenzylidene-4-alkylaniline, where the length of the alkyl chain was changed from 1 to 12.

PHYSICAL MEASUREMENTS

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

SYNTHESIS

4-Ethylaniline was prepared from the 4-ethyl-nitrobenzene following the method of Dąbrowski [2].

4-Propylaniline was prepared in the series of six reactions following the scheme [3]:

$$C_2H_5COOH \xrightarrow{SOCl_2} C_2H_5COCl \xrightarrow[\text{benzene}]{AlCl_3} C_2H_5CO\text{-}C_6H_5$$

$$\xrightarrow[\text{glycol}]{N_2H_4} C_3H_7\text{-}C_6H_5 \xrightarrow[CH_3COCl]{AlCl_3} C_3H_7\text{-}C_6H_5\text{-}COCH_3 \xrightarrow[H_2SO_4]{NaN_3}$$

$$C_3H_7\text{-}C_6H_4\text{-}NH\text{-}COCH_3 \xrightarrow{NaOH} C_3H_7\text{-}C_6H_4\text{-}NH_2$$

4-Alkylaniline (from butyl to dodecyl) were prepared from aniline and the corresponding alcohol following the method of Dąbrowski [4].

All anilines were purified by vacum distillations. The boiling points were in good agreement with literature data.

4-Chlorobenzylidene-4-alkylanilines were prepared by refluxing of the equimolar mixture of the 4-chlorobenzaldehyde and appropriate aniline in absolute ethanol for 2 hours. After cooling white precipitates were obtained. So prepared compounds were crystallized several times from absolute ethanol up till constant melting point. These Shiff bases were dried with help of P_2O_5. The correctness of the synthesis was proved by NMR spectroscopy.

CALORIMETRIC PROPERTIES

A different influence of the chain length on the phase situation of the studied systems was detected. The methyl, ethyl and propyl derivatives do not exhibit a mesophase; only a very short temperature hysteresis takes place (Fig. 1a). The highest melting point was found for the methyl derivative. The melting temperature of the other ones decreases with the length of the alkyl chain. The butyl and pentyl derivatives show one monotropic mesophase, of an existence range shifted considerably below the melting point. The pentyl derivative has additionally a phase transition in the solid state (Fig. 1b). Higher derivatives (from hexyl to nonyl) exhibit the existence of one enantiotropic mesophase, which was strongly super-

cooling (ca 30 deg) (Fig. 1c) The heptyl and nonyl derivatives show a different behaviour during the first heating run; the first melting was accompanied by a considerably higher heat effect and started at higher temperature.

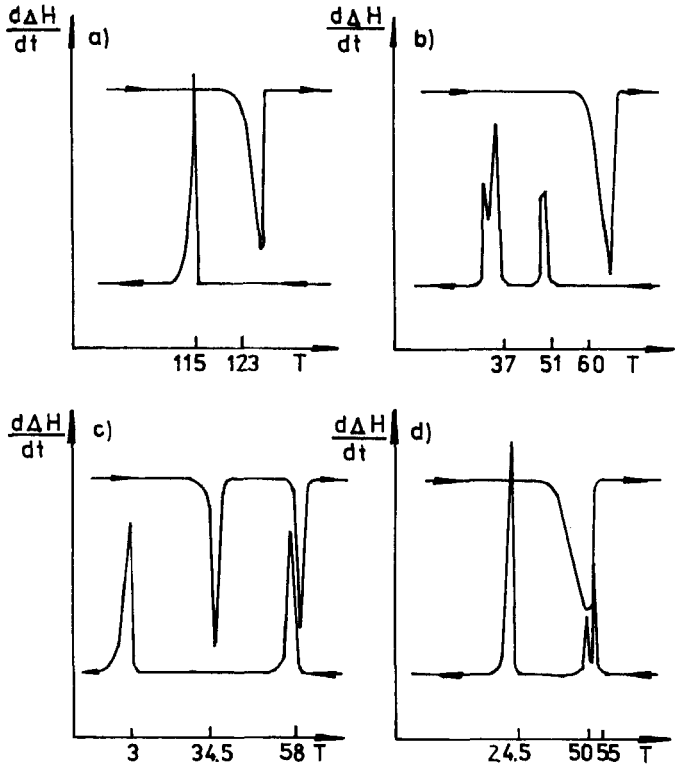


FIGURE 1. DSC thermograms for 4-chlorobenzylidene-4-alkylanilines. Scan rate 10 K/min a) methyl derivative, b) amyl derivative, c) heptyl derivative, d) undecyl derivative.

The decyl, undecyl and dodecyl derivatives exhibited one broad melting transmition and showed during cooling two mesophase (Fig. 1d). During very

slow heating (2.5 K/min) one mesophase was found for the undecyl derivative, in contrary to the decyl and dodecyl ones. A slower temperature scan caused a faster transition into the solid. The temperatures of all detected phase transitions are given in Table 1.

OBSERVATIONS OF TEXTURES

In all studied compounds the existence of 2 characteristic textures was observed (Fig. 2, Fig. 3). The first (mosaic texture) was characteristic for derivatives from butyl to octyl. This texture is typical for the smectic B phase. The nonyl and higher derivatives exhibited fan-shaped textures, which are characteristic for smectic A mesophases. All observed phase transitions exhibited the same sequences as in DSC method. During the very slow heating the undecyl derivative exhibited an enantiotropic fan-shaped texture. It was not possible to recognize the first mesophases during slow cooling of the decyl and higher derivatives, because recrystallization process appears faster.

CONCLUSIONS

On the base of the obtained data it was possible to build the phase diagram of the series of 4-chlorobenzylidene-4-alkylanilines which is presented in Fig. 4. The found mesophases were the same as in the similar Shiff bases with inverted central group. It means that strong dipole moments disturb the formation of a nematic and more exotic

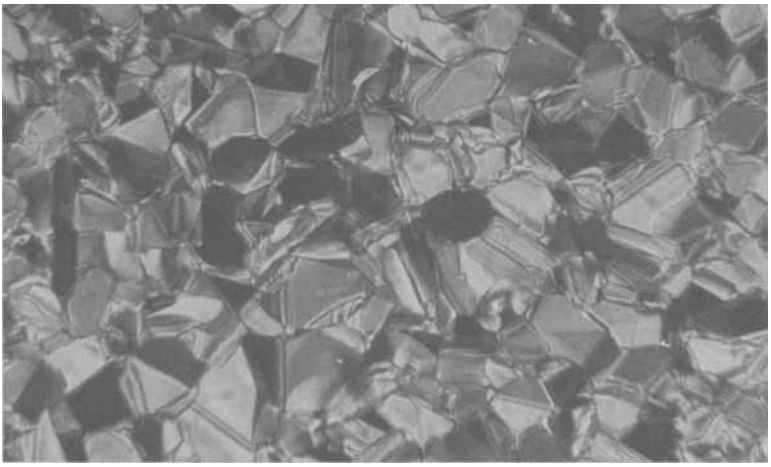


FIGURE 2. 4-Chlorobenzylidene-4-pentylaniline. Smectic B, mosaic texture, 45°C, x 120.

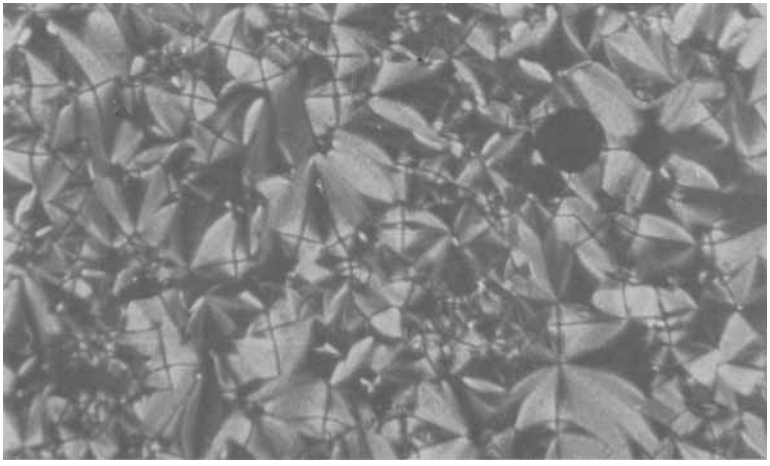


FIGURE 3. 4-chlorobenzylidene-4-nonylaniline. Smectic A, fan-shaped texture, 40°C, x 120.

TABLE I. Transition temperatures of the 4-chlorobenzylidene-4-alkylanilines.

n	Recrystallization	C → S_B	C → S_A	S_3 → I	C(S) → I
1	115.5	-	-	-	123
2	78	-	-	-	81
3	53	-	-	-	69
4	49	(53)	-	-	62
5	37	(51)	-	-	60
6	- 9	32	-	-	55
7	3	34.5	-	-	59
8	- 7	35.5	-	-	55
9	1	-	38	-	51.5
10	24.5	-	(49)	(50)	50
11	24.5	-	(50)	(55)	55
12	38	-	(46.5)	(54)	60

C = crystal, S_A = smectic A, S_B = smectic B, S_3 = unidentified phase, I = isotropic.

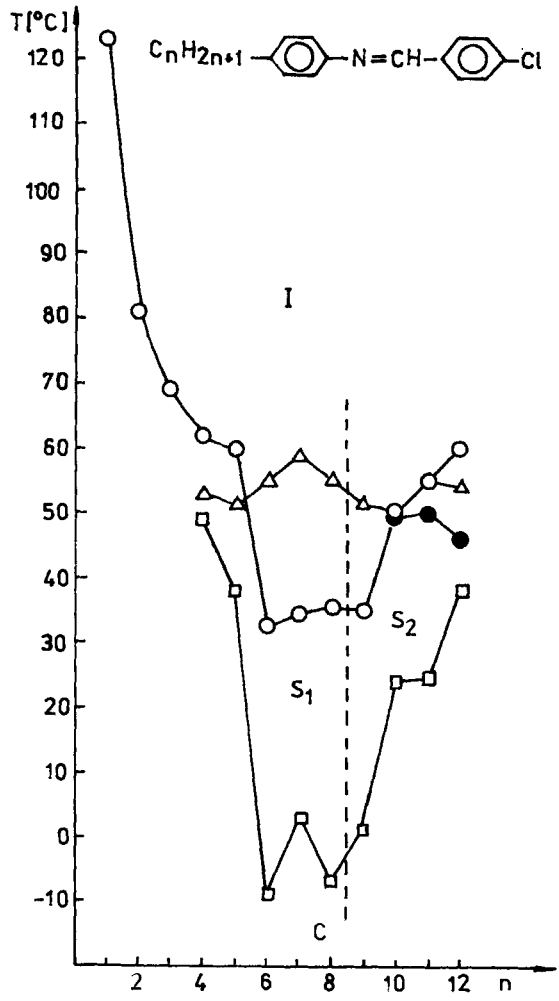


FIGURE 4. Plot of liquid crystal transition temperatures against the number of carbons in the alkyl chain in the 4-chlorobenzylidene-4-alkylanilines (o - melting, □ - recrystallization, Δ = I → Smectic, ● - S_2 - S_3)

mesophases, and mainly the smectic A and smectic B mesophases appear.

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