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# On the First Example of an Inverted Sequence $S_A$ N $S_C$ in a Pure Polar Compound

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ON THE FIRST EXAMPLE OF AN INVERTED SEQUENCE  $S_A$  N  $S_C$  IN A PURE POLAR COMPOUND.

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Six homologues of the new series 4-[4'-nitrobenzyloxy] benzylidene-4"-alkoxyaniline are presented. The reentrant sequence I N  $_{\rm N}$   $_{\rm N}$   $_{\rm C}$  was found for the first

time in the pure compound : 4-[4'-nitrobenzyloxy] benzylidene-4"-undecyloxyaniline, while the dodecyloxy derivative presents the inverted sequence ISANSCS<sub>1</sub>.

#### INTRODUCTION

As reported in earlier paper the benzyloxy derivatives with three phenyl rings give a rather rich polymorphism with the so-called  $S_{A_1},\ S_{A_d},\ S_{A_2}$  and  $S_C^{\sim 1}$  smectic modifications and a reentrant phenomenon such as the polar compounds having the general formulae  $^2$ :

$$R \stackrel{\frown}{\longrightarrow} X \stackrel{\frown}{\longrightarrow} Y \stackrel{\frown}{\longrightarrow} Z \qquad \qquad 1$$

where Z = CN or  $NO_2$ 

$$X = -COO-, -CH = N-, ...$$

$$R = C_n H_{2n+1} O -$$

Furthermore these different interesting smectic phases are available at rather low temperature. Now we present six homologues of the new series 4-[4'-nitrobenzyloxy] benzylidene-4"-alkoxyaniline 2 in which the undecyloxy derivative exhibits the enantiotropic reentrant sequence N  $\rm S_A$   $\rm N_{re}$  SC  $\rm S_1$   $\rm S_2$  and the dodecyloxy derivative presents the inverted sequence I  $\rm S_A$  N  $\rm S_C$  S $_1$ :

$$C_nH_{2n+1}O \xrightarrow{} N = CH \xrightarrow{} O - CH_2 \xrightarrow{} NO_2 \overset{2}{\sim}$$
with  $n = 8 \rightarrow 13$ 

# RESULTS AND DISCUSSION

The substances were synthesized according to the scheme below:

They were purified by repeated recrystallization from ethanol. Phase transitions were studied both by polarization microscopy (equipped with a Mettler FP5) and differential scanning calorimetry (Dupont 990). The transition temperatures and types of mesophases are listed in Table I. Their transition enthalpies and entropies are given in Table II.

TABLE I: Transition temperatures (°C) of compounds 2

n	K	S2	$S_1$	sc	Nre	e S <sub>A</sub>	N	I
8	•	86 .	109 -		120.5 -	-	"	183 .
9	•	98 .	110 -	•	121.8 -	-		181 .
10	-	99 .	107 -	•	-120 -	-	u	180 .
11		105 (.	95) •	106 .	118 .	135 -	177	179 .
12		103 -	(.	101) .	118 .	121.5 .	178.3	
13		104 -	(.	94) .	108.5 -		178	•

K : crystal phase ;  $S_A$ ,  $S_C$ , S ... smectic A, C ... phases

N : nematic phase ;  $N_{re}$  : reentrant nematic phase ;

I : isotropic phase ; ( ) : monotropic transition ;

. : the phase exists ; - : the phase is not observed.

TABLE II: Transition enthalpies and entropies of compounds 2 ( $\Delta H$  in Kcal.mol<sup>-1</sup> and  $\Delta S$  in cal.mol<sup>-1</sup> K<sup>-1</sup>)

n	K	;	S <sub>2</sub>	<b>S</b> <sub>1</sub>		sc	1	۱re	•	SA		N		I
8			. 0.71 1.86	-		_	0.09 0.23			-			0.40 0.88	
9			. 0.86 2.24	_			0.10 0.25			-		•	0.49 1.08	
10			. 0.54 1.42				0.08 0.20			-		•	0.50 1.1	•
11		6.87 18.2		•	0.39 1.03									•
12		8.30 22.			0.36) 0.96							-		•
13		7.10 18.8		•			0.14 0.37			_	1.24 2.75			•

At first, we must point out that the all presented derivatives exhibit a smectic C phase. This fact is uncommon in polar rod-like molecules. This  $S_{C}$  phase presents a maximum stability temperature with n = 9. The three compounds (n = 9) 8-10) exhibit three mesophases: N, SC and S2. The latter is uniaxial with a rather strong transition enthalpy S2-SC.  $(\Delta H = 0.71 \text{ Kcal.mol}^{-1})$  and could be a S<sub>B</sub> phase. The undecyloxy derivative presents for the first time the reentrant sequence N  $S_A$   $N_{re}$   $S_C$   $S_1$   $S_2$ . On cooling the isotropic liquid of this compound one can observe the nematic phase with a thread like or marbled texture. Below this nematic phase the smectic A phase with focal conic and homeotropic textures appears. On further cooling, one can observe the reentrant nematic phase with a thread like or paramorphic fan shaped texture. On cooling the  $\rm N_{re}$  phase, the smectic  $\rm S_{\rm C}$  phase becomes visible through a schlieren or broken fan shaped texture. Below this Sc phase, a smectic S1 phase appears with a mosaic texture which looks like those of the SI phase of the compound:

$$C_{10}H_{21}$$
  $\longrightarrow$  N = CH  $\longrightarrow$  CH = N  $\longrightarrow$   $C_{10}H_{21}$   
K 75 S<sub>G</sub> 115 S<sub>F</sub> 149 S<sub>I</sub> 156 S<sub>C</sub> 198 N 199 I  $\longrightarrow$ 

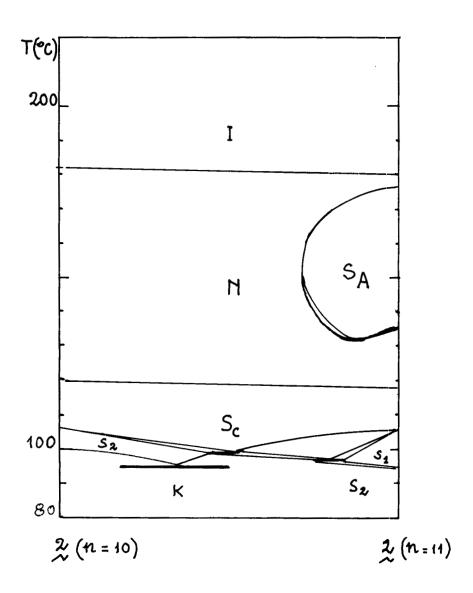


Fig. 1 Isobaric phase diagram

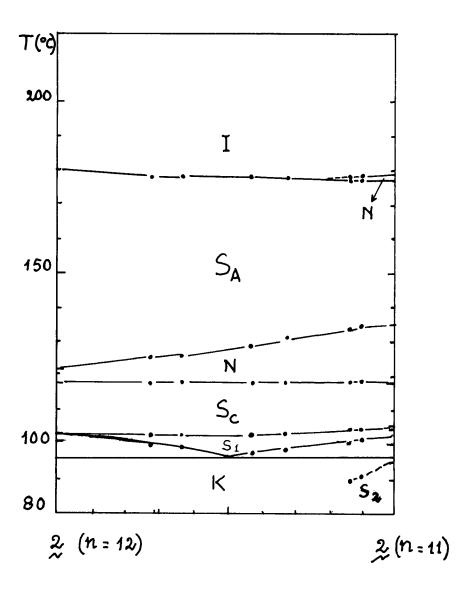


Fig. 2 Phase diagram of mixture

But these  $S_1$  and  $S_{\bar{1}}$  or  $S_{\bar{F}}$  are not miscible. Despite this fact it is well known that  $S_{\bar{A}}$  phases of polar and nonpolar compounds are often immiscible, so that there is an evident need for X-ray investigation on this  $S_1$  phase. On cooling the  $S_1$  phase, the  $S_2$  phase appears with large homeotropic domains. The  $S_2$  phases of two compounds n=10 and n=11 are miscible (Fig. 1). The more interesting compound is the dodecyloxy derivative which exhibits the inverted sequence:

The sequence  $S_A$  N  $S_C$  was first observed by G. Pelzl et al. in binary systems. The existence of a nematic phase below  $S_A$  phase without a nematic at high temperature was already predicted by J. Prost and by Heppke et al. The above sequence was also observed in the binary diagram between n = 11 and n = 12 derivatives (Fig. 2) or between n = 11 and n = 13 derivatives.

This N phase below the  $S_A$  phase totally disappears from n = 13.

# CONCLUSION

We have prepared a new series 4-[4'-nitrobenzyloxy] benzylidene-4"-alkoxyaniline. The reentrant sequence I N SA Nre SC S1 S2 and the inverted sequence I SA Nre SC S1 were found for the first time in pure compounds. A more detailed study of these systems will be published elsewhere.

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