Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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

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Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 69-74
0140-6566/84/1023-0069$18.50/0

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

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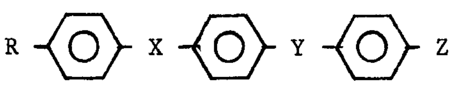
(Received for Publication March 7, 1984)

Six homologues of the new series 4-[4'-nitrobenzyloxy] benzylidene-4"-alkoxyaniline are presented. The reentrant sequence I N S_A N_{re} S_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 I S_A N S_C S_1.

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 $S_{\tilde{C}}$ [1] smectic modifications and a reentrant phenomenon such as the polar compounds having the general formulae [2] :



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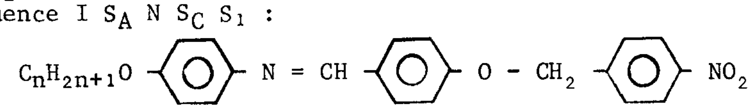
where Z = CN or NO_2

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

R = $C_nH_{2n+1}O$-

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 S_A N_{re} S_C S_1 S_2 and the dodecyloxy derivative presents the inverted sequence I S_A N S_C S_1 :



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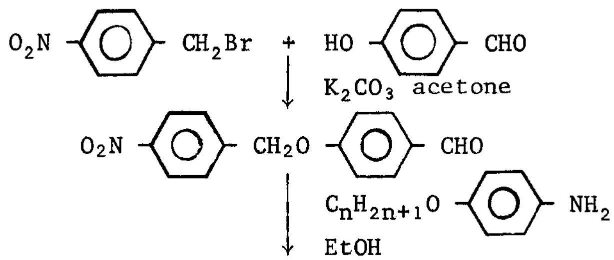
with $n = 8 \rightarrow 13$

RESULTS AND DISCUSSION

The substances were synthesized according to the scheme below :



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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	S_2	S_1	S_C	N_{re}	S_A	N	I
8	. 86	. 109	-	. 120.5	-	-	. 183	.
9	. 98	. 110	-	. 121.8	-	-	. 181	.
10	. 99	. 107	-	. 120	-	-	. 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 ;

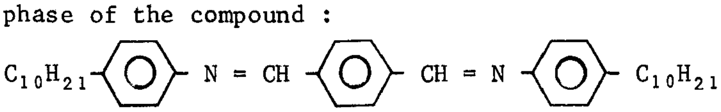
. : the phase exists ; - : the phase is not observed.

TABLE II : Transition enthalpies and entropies of compounds **2**

(ΔH in $Kcal.mol^{-1}$ and ΔS in $cal.mol^{-1}\ K^{-1}$)

n		K	S_2	S_1	S_C	N_{re}	S_A	N	I
8	ΔH	. 6.68	. 0.71	-	. 0.09	-	-	. 0.40	.
	ΔS	*18.6*	*1.86*		*0.23*			*0.88*	
9	ΔH	. 6.80	. 0.86	-	. 0.10	-	-	. 0.49	.
	ΔS	*18.3*	*2.24*		*0.25*			*1.08*	
10	ΔH	. 6.01	. 0.54	-	. 0.08	-	-	. 0.50	.
	ΔS	*16.2*	*1.42*		*0.20*			*1.1*	
11	ΔH	. 6.87	.	. 0.39	. 0.19	. 0.01	. 0.11	. 0.63	.
	ΔS	*18.2*		*1.03*	*0.49*	*0.03*	*0.24*	*1.4*	
12	ΔH	. 8.30	.	(. 0.36)	. 0.05	. 0.03	. 1.18	-	.
	ΔS	*22.*		*0.96*	*0.13*	*0.08*	*2.6*		
13	ΔH	. 7.10	.	.	. 0.14	-	. 1.24	-	.
	ΔS	*18.8*	.		*0.37*		*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 = 8 - 10) exhibit three mesophases : N, S_C and S_2. The latter is uniaxial with a rather strong transition enthalpy S_2-S_C. ($\Delta H = 0.71\ Kcal.mol^{-1}$) and could be a S_B 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 N_{re} phase, the smectic S_C phase becomes visible through a schlieren or broken fan shaped texture. Below this S_C phase, a smectic S_1 phase appears with a mosaic texture which looks like those of the S_I phase of the compound :



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K 75 S_G 115 S_F 149 S_I 156 S_C 198 N 199 I

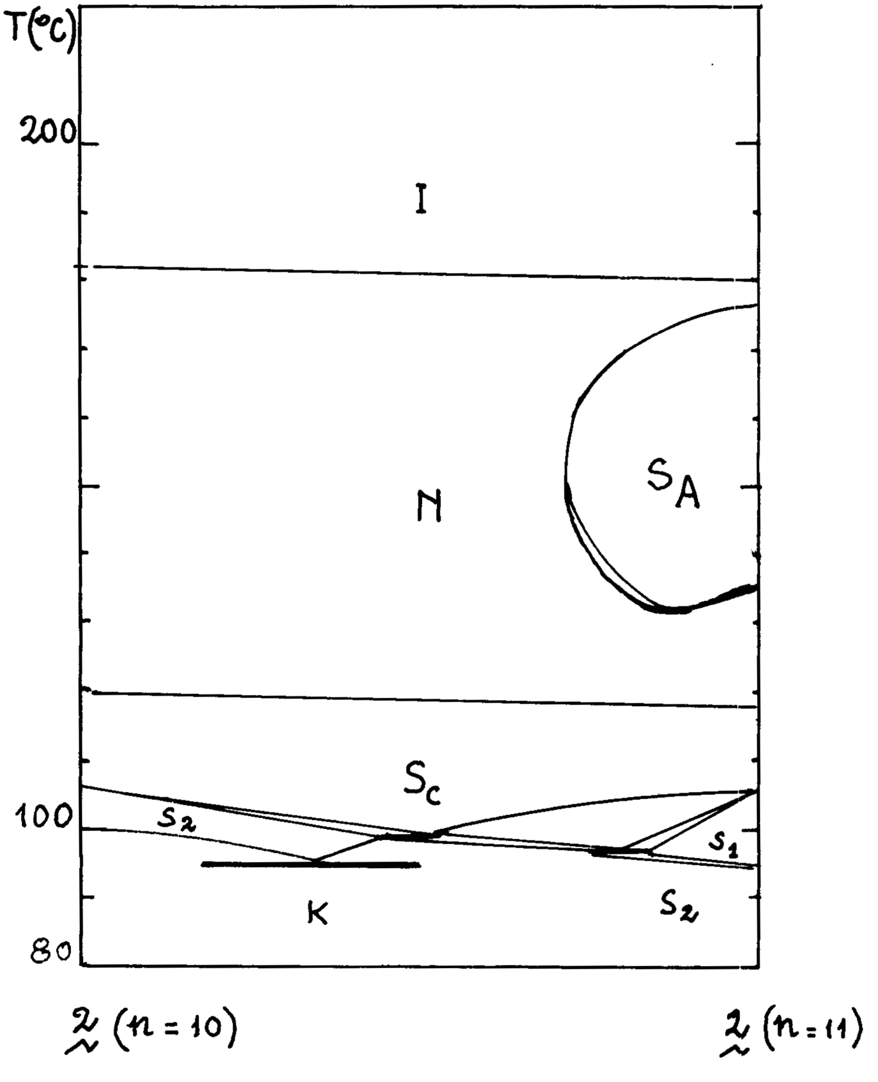

Fig. 1 Isobaric phase diagram

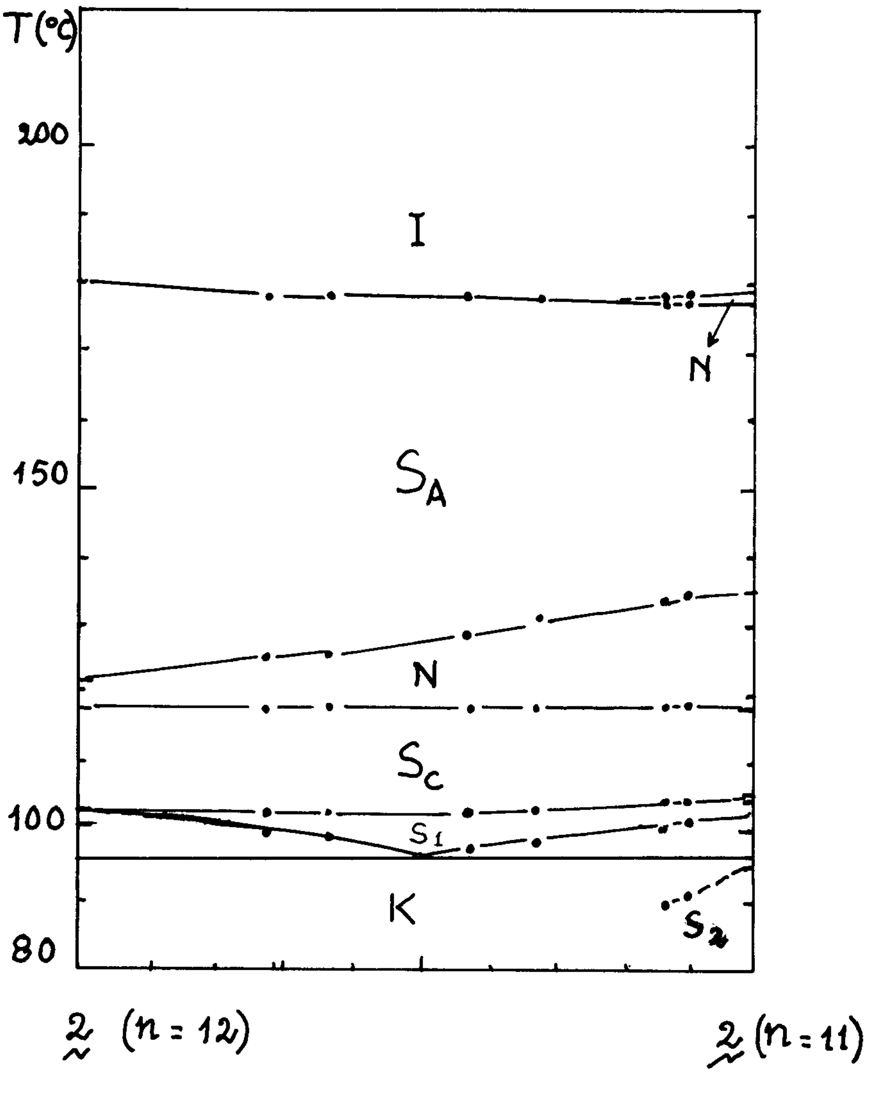

Fig. 2 Phase diagram of mixture

But these S_1 and S_I or S_F are not miscible. Despite this fact it is well known that S_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 :

$$I \quad S_A \quad N \quad S_C \quad S_1 \quad K$$

The sequence S_A N S_C was first observed by G. Pelzl et al.[4] 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[5] and by Heppke et al.[6]. 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 S_A N_{re} S_C S_1 S_2 and the inverted sequence I S_A N_{re} S_C S_1 were found for the first time in pure compounds. A more detailed study of these systems will be published elsewhere.

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