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A PURE REENTRANT CHOLESTERIC PHASE

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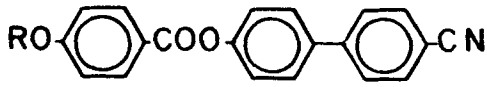
Abstract : An optically active derivative of p-cyanobiphenyl exhibits a stable reentrant cholesteric phase with the sequence : K N^* S_A N^* I.

Introduction

The existence of a pure reentrant nematic phase is known for several years[1-4]. The recent publication of a reentrant cholesteric mixture[5] induced us to publish a part of our results in this field.

Several cores with the cyano group are known to be suitable for the appearance of the reentrant phenomenon at atmospheric pressure, among them p-cyanobiphenyl is one of the more stable and easily available. As a matter of fact the com-

pounds 1a and 1b exhibit a reentrant nematic phase[2]



1a R = C_8H_{17} K 97 N 120 S_A 201 N 240 I
1b R = C_9H_{19} K 96(N 71) S_A 217 N 232 I

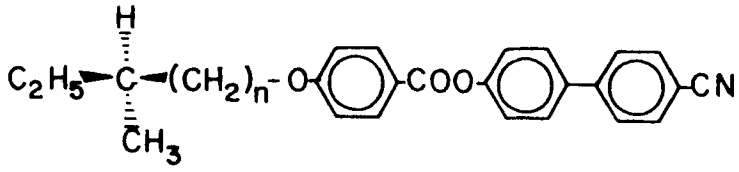
Generally, this phenomenon is only observed with one, two or three chain lengths in the same series, typically from C_8 to C_{10}[3,4]. On the other hand, the substitution of an hydrogen atom by a methyl group in the normal chain is known to destabilise the nematic phase when it is near the polar rigid core[6].

According to these observations, in order to prepare a pure p-cyanobiphenyl exhibiting a reentrant cholesteric phase, we have built up the chiral chain with a length nearly equivalent to those of 1 and a lateral methyl at its extremity.

Results

The compounds (S)-(+)-2a and (S)-(+)-2b were prepared by reaction of the corresponding optically active benzoyl chloride (obtained from (S)-(-)-2-methylbutanol) with 4-hydroxy-4'-cyanobiphenyl, and were purified by chromatography on silicagel. The purity was checked by elemental analysis and thin layer chromatography. Transition temperatures were determined by calorimetry using a DSC (Dupont 990). The textures were observed with a

polarizing microscope equipped with an heating and cooling stage (Mettler FP5).



(S)-(+)-2a, n=3 : K 74 N^* 99 S_A 178 N^* 231 I;
$[\alpha]^{25}_{578}$=+ 5.4° ($CHCl_3$, c∿ 1).
(S)-(+)-2b, n=5 : K 72(S_C^* 42)S_A 214 N^* 220 I;
$[\alpha]^{25}_{578}$=+ 3.7° ($CHCl_3$, c∿ 1).

A reentrant cholesteric phase could be observed with compound 2a and was entirely miscible with the reentrant nematic phase of 1a (Fig. 1). The presence of "finger prints" in 2a cholesteric phases allowed us to observe an increasing of the pitch only near the $N^* \rightarrow S_A$ transition on heating, a similar behaviour has been described in a binary mixture[5].

Discussion.

It is rather surprising that only 2a, with the relatively short C_6 branched chain, exhibits the reentrant phenomenon, when 2b with chain length corresponding to this of the reentrant nematogenic 1a is devoid of the expected properties. Furthermore, we must point out that 2b exhibits a metastable S_C^* smectic phase: it is the first example of a pure twisted S_C^* smectic liquid crystal with a strong longitudinal dipole moment.

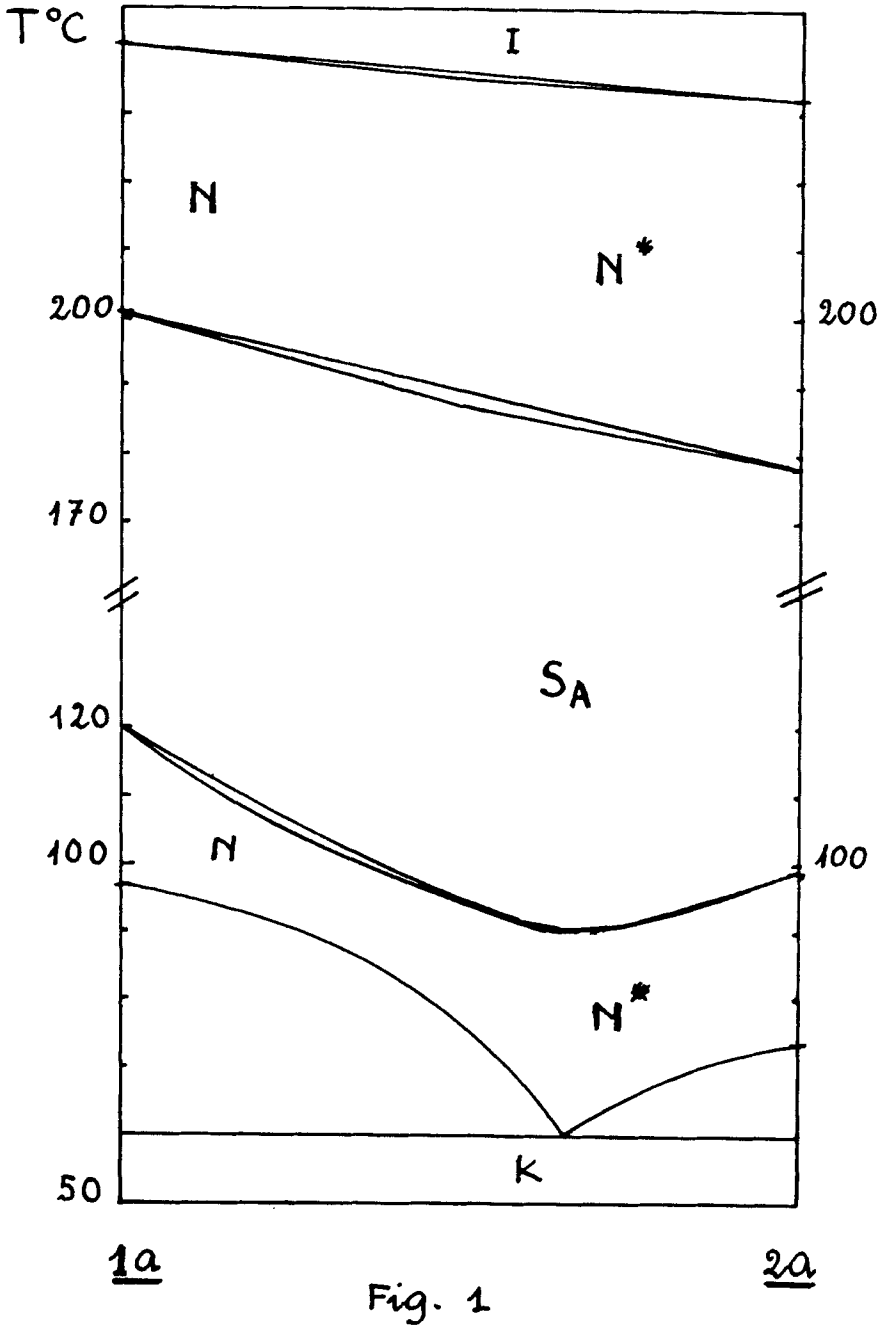


Fig. 1

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