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

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Version of record first published: 20 Apr 2011.

To cite this article: B. K. Sadashiva (1986): An Inverted Sequence of Transitions in a Mesogen, Molecular Crystals and Liquid Crystals, 132:1-2, 143-147

To link to this article: http://dx.doi.org/10.1080/00268948608079535

Mol. Cryst. Liq. Cryst., 1986, Vol. 132, pp. 143–147
0026-8941/86/1322–0143/$10.00/0

Printed in the United States of America

An Inverted Sequence of Transitions in a Mesogen

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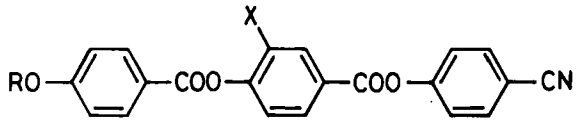
(*Received April 8, 1985*)

A number of derivatives of the homologous series of 4-cyanophenyl-4′-(4″-n-alkoxybenzoyloxy)benzoates are reported. Most of the derivatives exhibit a metastable reentrant nematic phase (N_R). The laterally unsubstituted dodecyloxy derivative exhibits phase sequence I S_A N K on cooling. The binary phase diagram of this compound with that of the octyloxy derivative confirms that the lower temperature phase is indeed nematic.

INTRODUCTION

In the last few years, the reentrant phenomenon has been observed in a large number of compounds belonging to different homologous series.[1–8] The occurrence of the reentrant nematic and smectic phases in relation to the chemical structure have been reasonably well understood.[9–11] However, the synthesis of new compounds have led to the observation of not only new phases but a number of interesting different sequences of phase transitions. Recently,[12] an example of an inverted sequence I S_A N S_C S_1 has been described. We report here the simplest case of an inverted sequence of phase transitions in a pure compound of the series 4-cyanophenyl-4′-(4″-n-alkoxybenzoyloxy)benzoate, represented by the general formula



(1)

Where $R = C_nH_{2n+1}$, X = H or CH_3.

RESULTS AND DISCUSSIONS

The compounds were all prepared by standard methods described elsewhere.[4] They were purified by several recrystallizations from suitable solvents. The mesophases and the transition temperatures were determined by means of a polarizing microscope equipped with a Mettler heating stage (FP52) and controller unit (FP5). These were confirmed from thermograms recorded using a differential scanning calorimeter (Perkin-Elmer Model DSC-2) with a heating rate of 5°/min.

The transition temperatures of the compounds synthesized are given in Table I. As can be readily seen compounds 2,3,4,5 and 7 exhibit a metastable reentrant nematic phase. However, compound 5 does not show any nematic phase above the smectic A phase and goes over to the isotropic liquid with a transition enthalpy of 0.83 K cals/mole. On cooling the smectic A phase, one can observe the thread like nematic phase appearing well below the melting point of this compound. It is however not possible to measure the enthalpy of this transition; it can at best be seen as a shift in the base line of the thermogram (suggesting a very weak first order transition). Figure 1 shows the relationship between the mesophase transition temperatures and the number of methylene units in the chain.

The introduction of a lateral methyl group reduces the mesophase isotropic transition temperature. Further, the unsubstituted derivative (compound 4) has a smectic A phase range of 109°C. The lateral methyl group (compound 6) has completely eliminated this phase. The dodecyloxy derivative (compound 5) has a phase sequence I S_A

TABLE I

Transition temperatures (°C) of the compounds with the general formula 1

No.	n	X	K		N_R		S_A		N		I
1	8	H	·	123	–		–		·	232.5	·
2	9	H	·	122	·	(117)	·	198.5	·	228.5	·
3	10	H	·	106[a]	·	(95)	·	208	·	221.0	·
4	11	H	·	103	·	(86)	·	212	·	217.0	·
5	12	H	·	102	·	(84)	·		–	215.0	·
6	11	CH_3	·	100.5	–		–		·	167.5	·
7	12	CH_3	·	101	·	(76)	·	146.5	·	162.0	·

K: crystal, N_R: reentrant nematic phase, S_A: smectic A phase,
N: nematic phase, I: isotropic phase. Temperature in parentheses indicate monotropic transition.

[a]There is a solid-solid transition at 101°C.

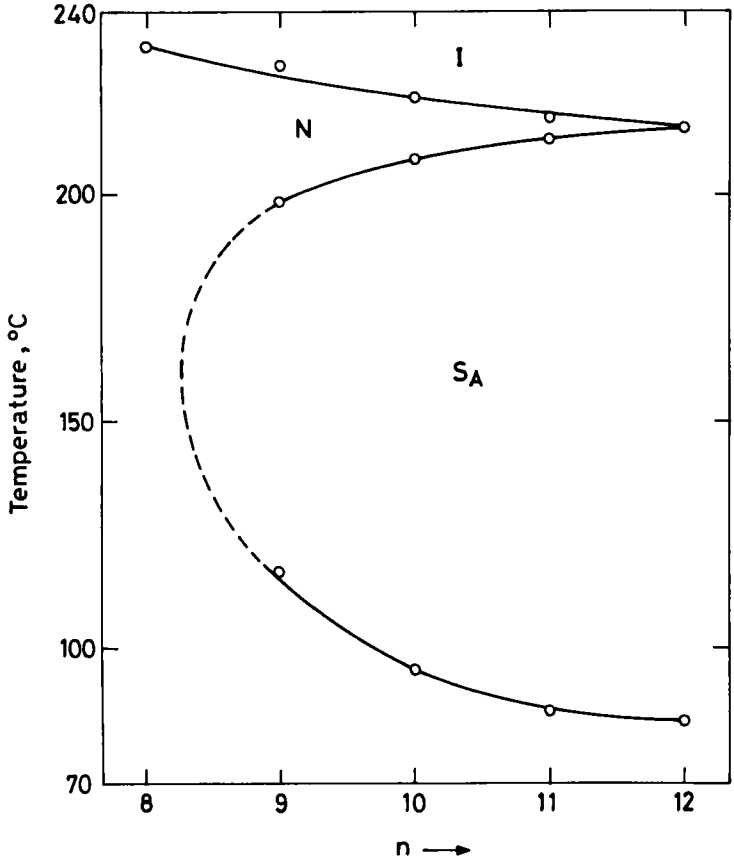


FIGURE 1. Smooth curve relationship of the N-S_A transition temperatures (on cooling) of the successive homologues of the 4-cyanophenyl-4′-(4″-n-alkoxybenzoyl-oxy)benzoates. The dotted line indicates the probable N-S_A phase boundary.

N K on cooling. The methyl group (compound 7) has altered this sequence to I N S_A N K in addition to reducing the mesophase ranges.

Figure 2 shows the binary phase diagram of a mixture of compounds 1 and 5. Compound 1 has only a nematic phase which has a range of about 110°, while compound 5 has only smectic A phase (on heating) with a range of 113°. It is clear from the diagram of state that the metastable phase of compound 5 is continuously miscible with the nematic phase of compound 1 confirming that it is nematic. Also, the mixture exhibits an enantiotropic reentrant nematic phase when compound 1 is present in the range of about 65 to 85 mole%.

In conclusion the dodecyloxy derivative of the homologous series

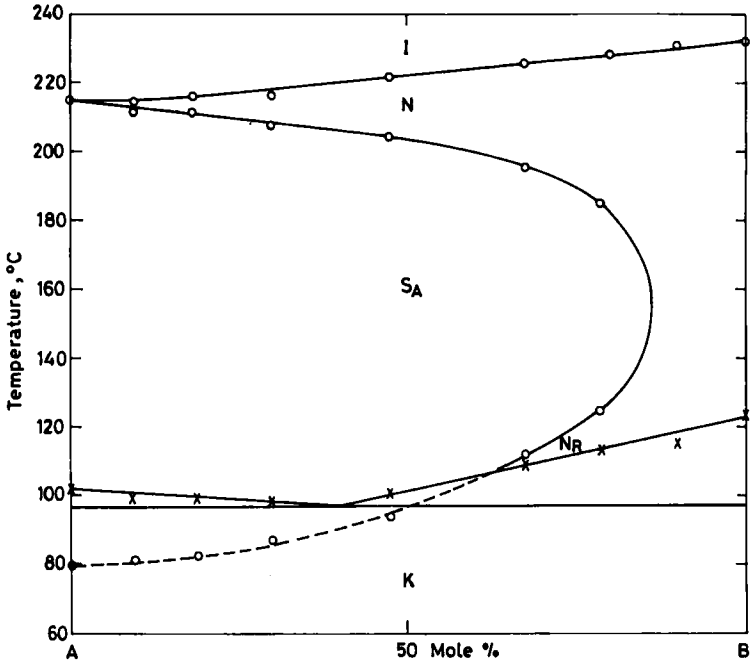


FIGURE 2. Diagram of state of a mixture of A: 4-cyanophenyl-4'-(4"-n-dodecyloxybenzoyloxy)benzoate; B:4-cyanophenyl-4'-(4"-n-octyloxybenzoyloxy)benzoate. The broken curve indicates phase transition in the supercooled state.

4-cyanophenyl 4'-(4"-n-alkoxybenzoyloxy)benzoates exhibits the interesting phase sequence I S_A N K on cooling at atmospheric pressure. This is the simplest case of such an inverted phase sequence.

Acknowledgments

I thank Professor S. Chandrasekhar for discussions and Mr. K. Subramanya for help in obtaining the DSC runs.

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