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Reentrant Phases in New Polar Cyclohexane Series†

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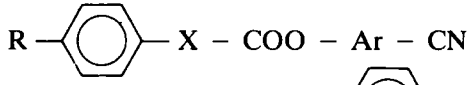
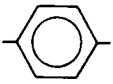
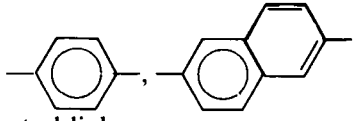
A homologous series of 4′-alkoxyphenyl 4″-cyanophenyl, 1,4-cyclohexanedicarboxylates in which the alkoxy group is $C_1 \rightarrow C_{12}$ has been prepared. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot stage microscopy. The nonyloxy compound is the first cyclohexane derivative to exhibit the reentrant phenomenon with the sequence K—$S_{C_{re}}$—N_{re}—S_C—S_A—N—I. A reentrant nematic phase is also observed in the binary mixture of the octyloxy and decyloxy derivatives. A plot of the nematic-isotropic transition temperatures against the number of carbon atoms in the alkoxy chain shows the usual odd-even effect. The behaviour of this new series is compared with that of the corresponding benzenic homologues.

INTRODUCTION

It is well known that strongly polar molecules with three benzene rings constitute the optimal condition for obtaining the reentrant phases at atmospheric pressure[1–3] with the general formula:

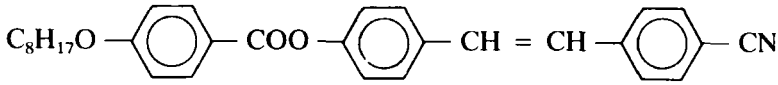


where X = single bond, —CH = CH—, 

Ar =  , two benzene rings with different central linkages.

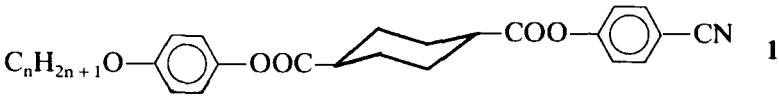
†Presented at the 10th International Liquid Crystal Conference, York, United Kingdom, July (1984).

Let us recall that the first example of pure reentrant compound at atmospheric pressure is:



K $\underrightarrow{96}$ (S_A $\underrightarrow{\underrightarrow{95}}$) N_{re} $\underrightarrow{\underrightarrow{138}}$ S_A $\underrightarrow{\underrightarrow{248}}$ N $\underrightarrow{\underrightarrow{283}}$ I^4

Here we report a new polar cyclohexane series with the general formula:

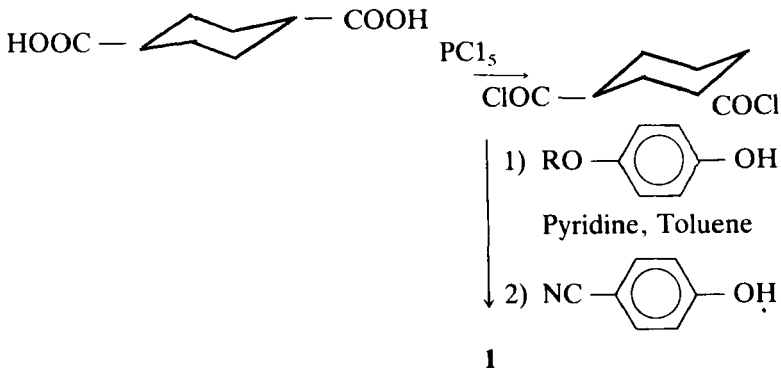


1

where n = 1 → 12

RESULTS AND DISCUSSION

The cyclohexane derivatives **1** were synthesized following the scheme:



1

This method gives a mixture of three compounds: bis(alkoxyphenyl) 1,4-cyclohexane dicarboxylate, bis (cyanophenyl) 1,4-cyclohexane dicarboxylate and the desired compound **1**.

The compounds **1** were purified by chromatography on silica gel with toluene as eluent and recrystallized with ethanol. The purity of the final product was checked by thin layer chromatography. All the compounds gave satisfactory elemental analyses. The transition temperatures are given in Table I.

TABLE I

Transition temperatures (°C) of compounds **1**.

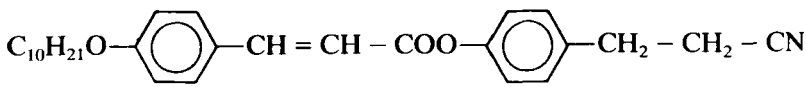
n	K	S_C	N_{re}	S_C	S_A	N	I
1	• 123	—	—	—	—	• 248	•
2	• 120	—	—	—	—	• 243	•
3	• 108	—	—	—	—	• 230	•
4	• 99	—	—	—	—	• 222	•
5	• 99	—	—	—	—	• 210	•
6	• 95.5	—	—	—	—	• 204	•
7	• 86	—	—	—	—	• 194	•
8	• 88	—	—	—	—	• 193	•
9	• 86	(• 59)	(• 71)	(• 78)	• 135	• 186	•
10	• 86	—	—	(• 79)	• 164	• 184	•
11	• 86	—	—	(• 81)	• 173	• 181	•
12	• 87	—	—	(• 86)	• 178	• 180	•

The meanings of the signs used in this table and in the following are:
K : crystalline phase ; N : nematic phase
S : smectic phase ; S_A, S_C : smectic phases A, C
I : isotropic phase ; • : the phase exists
— : the phase does not exist; ( ) : metastable transition

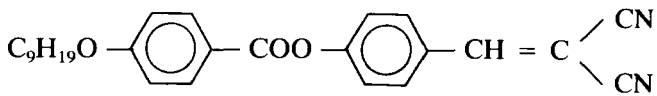
The first eight compounds (n = 1 → 8) exhibit only nematic phases with a wide temperature range (> 100°) but the nonyloxy derivative shows the remarkable reentrant sequence:

$$I—N—S_A—S_C—N_{re}—S_{C_{re}}$$

It is the first pure compound giving this sequence, although a similar behaviour had been observed for a binary mixture[5] of:



and



The three longest derivatives (n = 10 → 12) exhibit the three mesophases: nematic, smectic S_A, S_C phases.

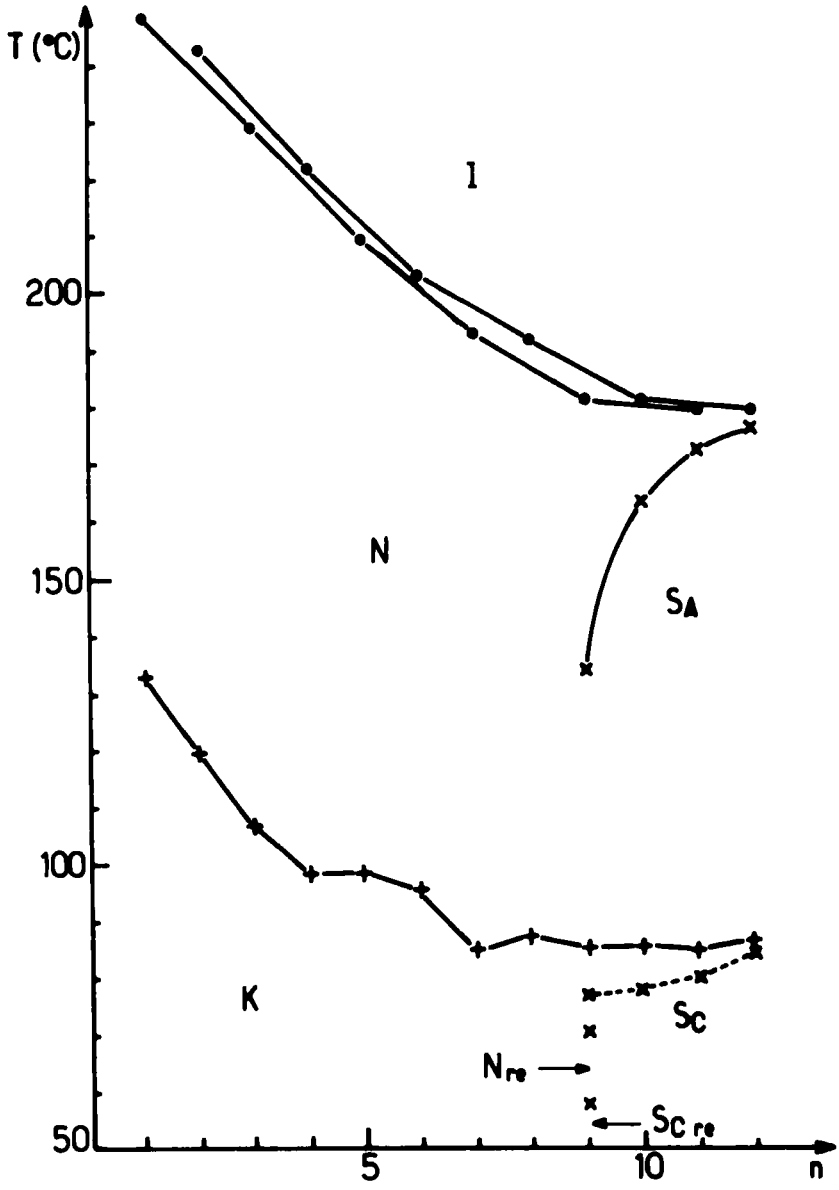


FIGURE 1 Plot of transition temperatures against n, the number of carbon atoms in the alkoxy chain of **1**.

Figure 1 shows the plot of transition temperatures as a function of the number of carbon atoms in the alkoxy chain of **1**. The nematic isotropic transition temperatures show the usual odd-even behavior.

The reentrant sequence of the nonyloxy derivative was first identified by optical texture observations. On cooling the isotropic liquid of this compound one can observe the nematic phase with a classical thread-like or marbled texture. Below this nematic phase, the smectic A phase with a focal conic or homeotropic texture appears. On further

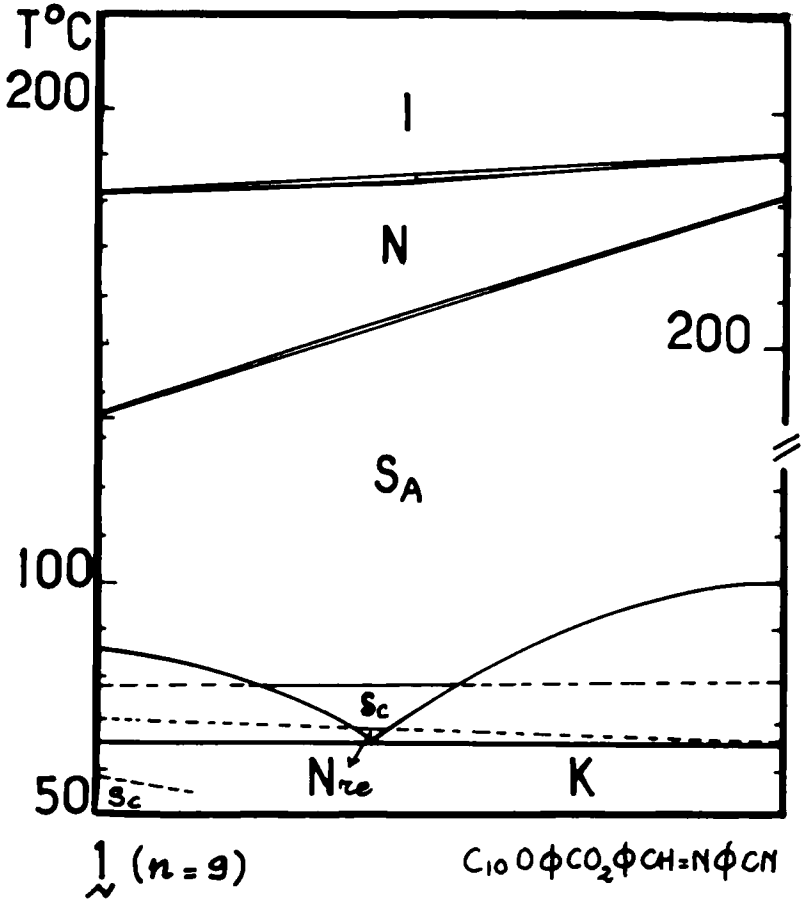


FIGURE 2 Diagram of isobaric state of the mixture of **1**, n = 9 (on the left) and $C_{10}H_{21}O$—⬡—COO—⬡—CH = N—⬡—CN (on the right).

cooling, the smectic C phase becomes visible with a schlieren texture arising in the previous homotropic domains and with a broken fan-shaped texture in the other areas of the sample. On cooling the S_C phase, the reentrant nematic phase shows a thread-like texture or a paramorphic fan texture. Below this N_{re} phase another S_C phase appears. Then the identification of the $N—S_A—S_C—N_{re}$ sequence of the nonyloxy derivative has been obtained by the miscibility method, with the well known: n-decyloxybenzoyloxy-benzylidene-N-4-cyanoaniline[6] as the reference substance. Figure 2 shows the perfect miscibility of these corresponding phases for the sequence $N—S_A—S_C—N_{re}$. We have not achieved the identification of the $S_{C_{re}}$

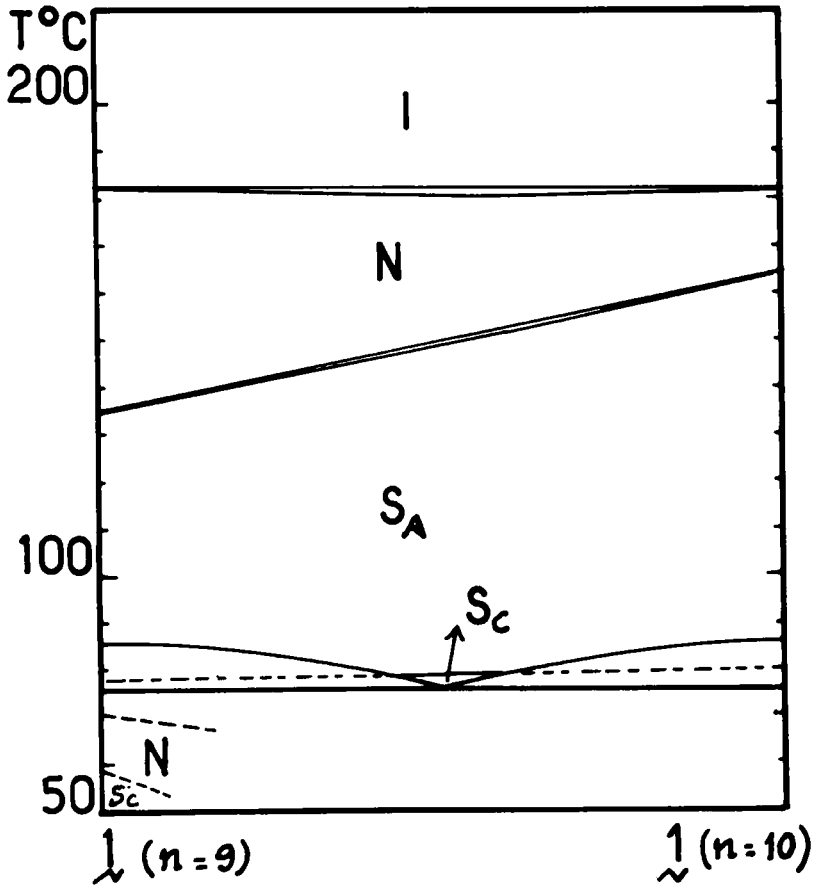


FIGURE 3 Diagram of isobaric state of the mixture of **1**, n = 9 (on the left) and **1**, n = 10 (on the right).

reentrant phase because it is very metastable. We have also obtained the miscibility of two S_C smectic C phases of the two compounds **1** (n = 9 and 10) in Figure 3. The reentrant nematic phase was observed in different concentrations between n = 8 and n = 10 derivatives

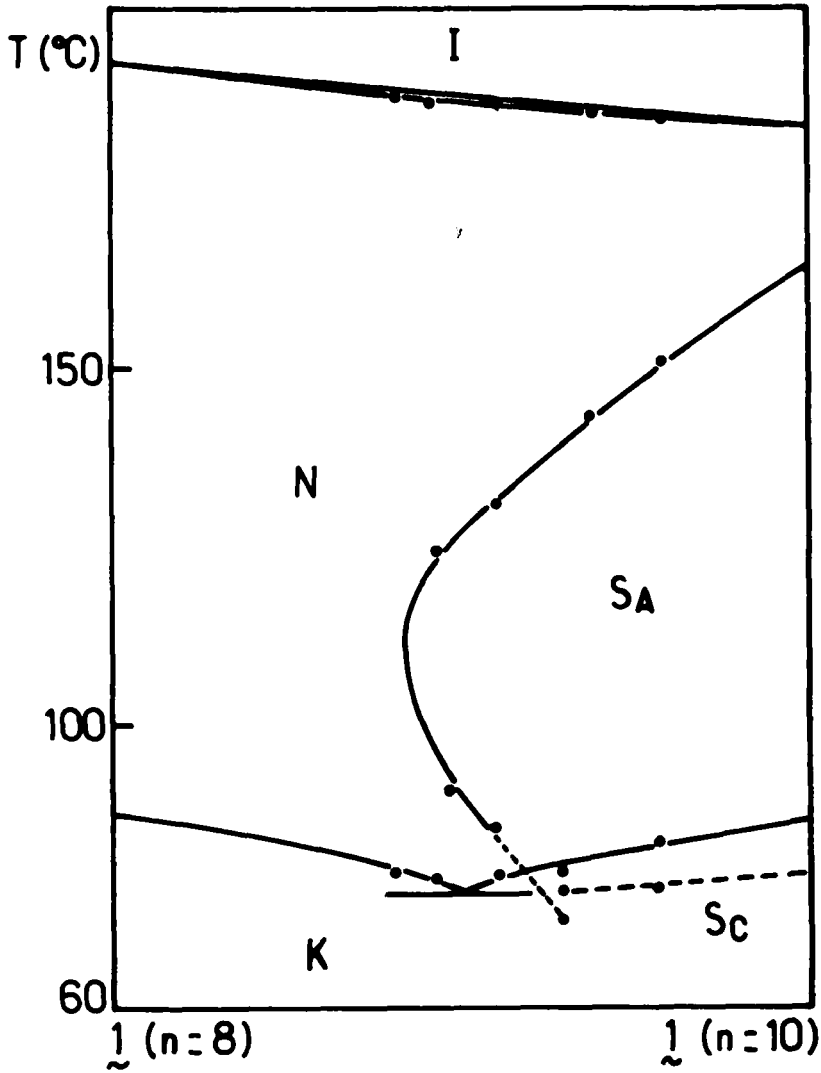


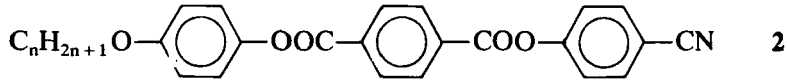
FIGURE 4 Diagram of isobaric state of the mixture of **1**, n = 8 (on the left) and **1**, n = 10 (on the right).

(Figure 4) with two following sequences:

$$K—N_{re}—S_A—N—I$$

$$K—N_{re}—S_C—S_A—N—I$$

This behaviour was not observed in pure compound in the homologue benzenic series.



2

The transition temperatures of these compounds are given in Table II.

A comparison of the data of compounds **2** which possess nematic and smectic A properties with that for the analogous cyclohexane derivatives **1** shows that the replacement of the central benzene ring in this system with a cyclohexane ring favors formation of smectic C phase even though the transition temperatures are very lower. These known relationships between molecular structure and mesomorphic properties have been extensively discussed by Gray and others.[7-9]

CONCLUSION

A large number of new substances exhibiting reentrant nematic phases have been synthesized during the last five years. These substances generally possess three benzene rings in the general formula. A new series with a cyclohexane central ring is described and showed for the first time the sequence: $S_{C_{re}}—N_{re}—S_C—S_A—N—I$ in a pure pure compound.

Acknowledgment

The author is indebted to Dr. C. Destrade for discussions and helpful comments.

TABLE II

Transition temperatures (°C) of compounds **2**.

n	K		S_A		N		I
7	▪	151	—		▪	236	▪
8	▪	148	▪	158	▪	233	▪
9	▪	143	▪	202	▪	226	▪

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