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INFLUENCE OF RIGID CORE STRUCTURE ON THE ABILITY TO INDUCE THE SMECTIC A_d PHASE IN POLAR SYSTEMS

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Abstract The binary mixtures of polar compounds where one component is 4-cyanobiphenyl-4'-yl 4'-heptylbiphenyl-4-carboxylate (7CBB) and another one is a cyano derivative with the same alkyl chain length and different core structure were tested. Their phase diagrams obtained by thermomicroscopy are presented. The induced A_d phase appears in all presented mixtures. Molecules with short cores and with low lateral interactions cause the strongest induction of the A_d phase.

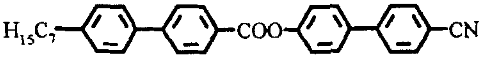
INTRODUCTION

The induction of the smectic A_d phase appearing on the phase diagrams in the form of an 'island' surrounded by a nematic phase was previously reported.[1] The smectic A_d phase induces in the binary mixtures of nematic polar compounds which contain as the first component the three or four ring compound and it belongs to the homologous series which longer members have a nematic, smectic A_d and reentrant nematic phases. Most of such compounds belong to the series reported by Nguyen.[2] The second component of these mixtures is two ring cyano nematogen and it has dimeric structure.

The influence of the alkyl chain length and the steric hindrances on the A_d phase induction was described.[3,4] The aim of this work was to test the influence of the rigid core structure on the smectic A_d phase induction.

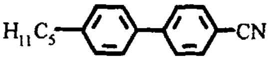
EXPERIMENTAL

To test the influence of the rigid core structure on the smectic A_d phase induction phenomenon the 7CBB compound:



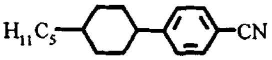
7CBB Cr 123 S_{A1} 136 N 350 I

was mixed with two and three ring cyano derivatives with the same alkyl chain length (n=5) and different cores:

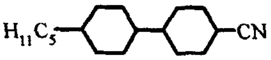


(5CB) Cr 22.5 N 35 I

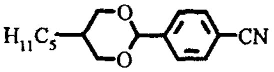
(5OCB) Cr 50 N 69 I



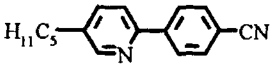
(5PCH) Cr 30 N 55 I



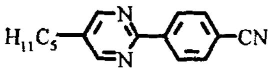
(5CCH) Cr 63.4 S_X 49.9 S_B 50.9 N 85.7 I



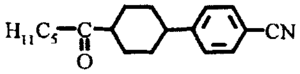
(5PD) Cr 57 (N 48) I



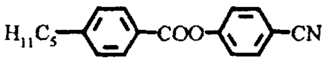
(5PP) Cr 32 N 44 I



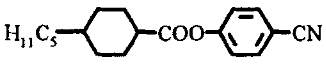
(5PPM) Cr 71 (N 52) I



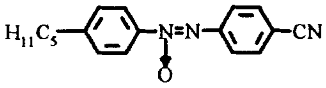
(5KPCH) Cr 42 (N 21) I



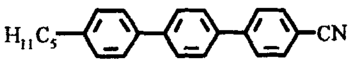
(5.CN) Cr 61.1 (N 57.8) I



(5PCHP) Cr 48.1 N 78.3 I



(5PAP) Cr 96 N 130 I



(5CT) Cr 60 N 79 I

The pyrimidine derivatives were obtained from ROLIC Ltd, Basel.

The results of investigations are summarized in phase diagrams where the phase transition temperatures are plotted vs. molar concentration. The phase diagrams were obtained by the single concentration method.

The phase transition temperatures of single compounds and their mixtures were measured by the thermomicroscopy using the polarizing microscope (BIOLAR) and the Linkam TMS 91 hot stage unit. In the phase transition region the heating ratio was 1deg min^{-1}.

RESULTS AND DISCUSSION

The 7CBB has a smectic A_1 phase and a virtual smectic A_d phase. The hypothetical phase transition temperature $T_{N\text{-}Ad}$ was estimated to be equal to 330°C.[5] The virtual smectic A_d phase is observed in the mixtures of 7CBB with short nematic polar compounds of different structures, see Figure 1. These compounds form better conditions for the dimerization of 7CBB than pure 7CBB.[6] The A_1 phase of 7CBB depresses in the mixture and the A_d phase appears in the form of a semi-island in the central part of phase diagram. Only in the case of 7CBB-5OCB (Figure 1i) it was possible to observe the closed contour of the smectic A_d island. In all other cases the temperatures of N_{re}-A_d phase transition are too low and it was not possible to overcool the samples to measure the transition temperatures. The shape of the island is more elongated in the direction parallel to the temperature axis, e.g. the induction is possible in broad temperature range. In some cases the injected A_d phase joins the A_1 phase of the compound 7CBB (7CBB-5PP, Figure 1h, and 7CBB-5PPM, Figure 1j) the same as it was observed in mixtures of 6CBB with short members of nCB, n=4÷0 (co. Figure 1 in Ref. 5).

The sequence of phase diagrams of bicomponent mixtures in Figure 1a-l relates to the decrease of the existence area of the induced A_d phase. The strongest induction is observed in the case of compounds which the rigid core comprises directly connected two cyclohexane rings, then for the cyclohexane and benzene core, and then for the core comprising two benzene rings. The induction of the A_d phase decreases when rings with heteroatoms (dioxane, pyridine, pyrimidine) or polar bridging groups are introduced. The

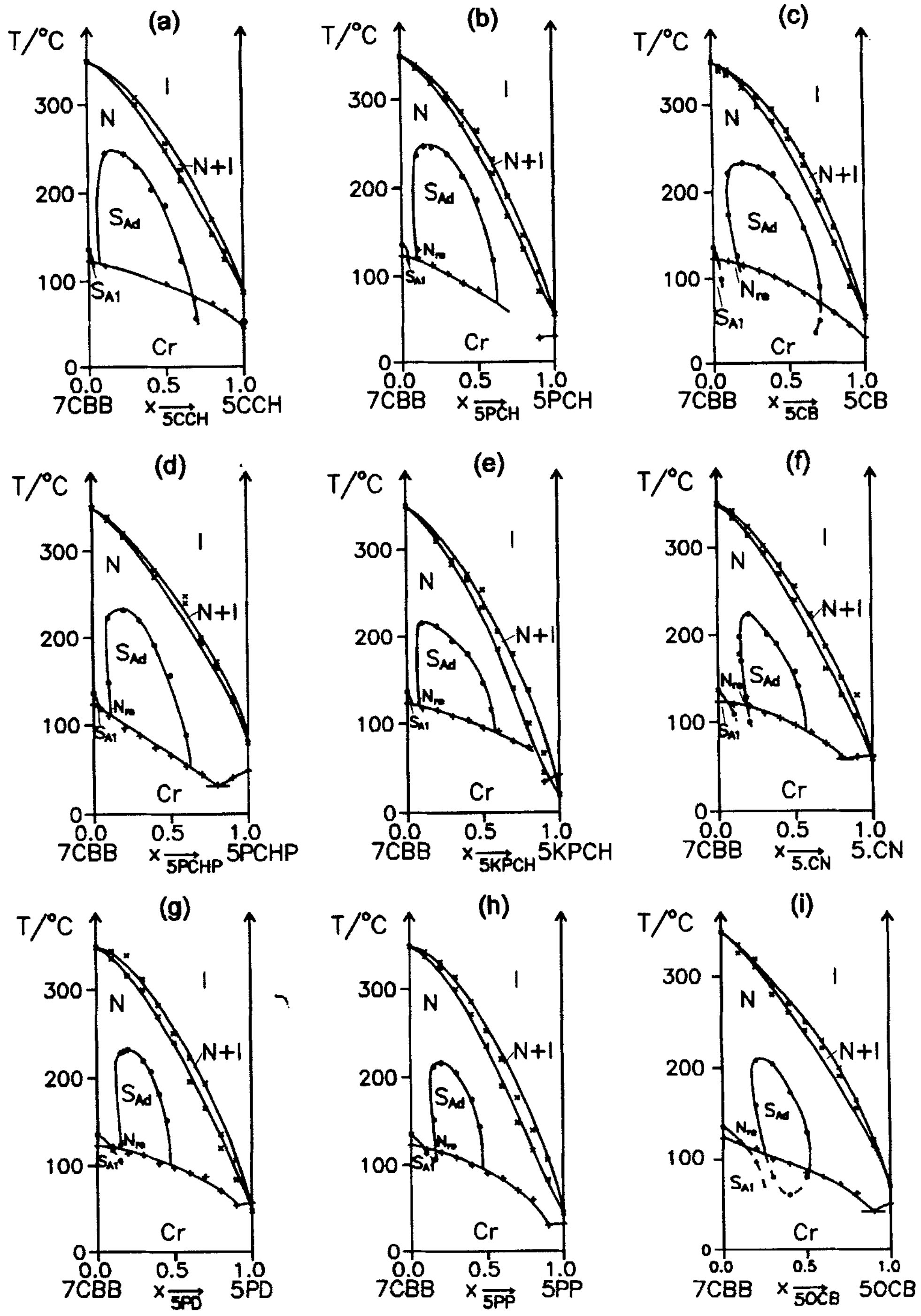


FIGURE 1 Phase diagrams of 7CBB with different cyano derivatives.

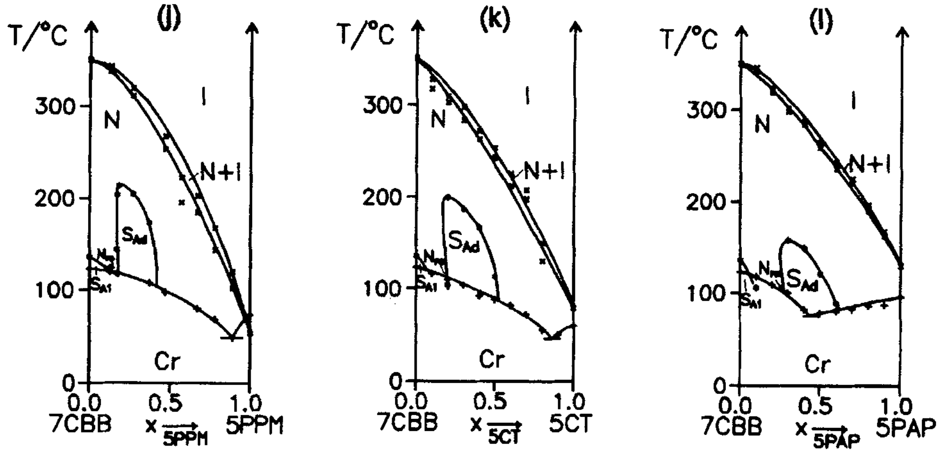


FIGURE 1 continued.

separation of cyclohexane and benzene rings or two benzene rings by the carboxylic group (-COO-) decreases the ability to the induction of an A_d phase, and the azoxy group (-NON-) causes even weaker induction. The insertion of another polar group such as -CO- or -O- at the end of the rigid core causes that the molecules behave similarly as these in which the polar group is placed in the central part of the molecule.

Testing the influence of the core structure on the induction phenomenon we have found the systems when A_d joins A_1 and the system when the A_d is isolated and surrounded by the nematic phase. Higher polarity of compounds mixed with 7CBB favors the situation that injected A_d phase is closer to the A_1 phase. It results probably from the fact that the A_1 phase is less depressed in the case when the compounds with higher polarity are introduced. A_1 phase is also less depressed by shorter molecules than longer molecules. There are cases that the induced A_d joins the A_d of two and three ring compound (7CBB-8OCB, co. Figure 1 in Ref. 1). Thus in the systems with the induced A_d phase there is a transformation from the situation when induced A_d phase joins A_d phase of the two ring component of the mixture to the situation when the induced A_d phase joins the A_1 phase of the four ring component.

The length of molecular cores influences the A_d phase induction. Taking into account compounds with similar structure it is seen that biphenyl molecules cause stronger induction than terphenyl molecules, see Figure 1c and 1k.

The rigidity of the molecular core is rather less important parameter. The compound with two cyclohexane rings which cause the strongest induction is rather flexible due to the many possible conformations, but the compound with rigid biphenyl core has higher ability to induce the A_d phase than more flexible compounds in which the rings are separated by linking groups.

The polarity seems to be the most important factor. The increase of the perpendicular and parallel components of the dipole moment causes the decrease of the smectic A_d induction. It is due to the decrease of dimerization. The A_d phase formation is strongly correlated with dimer concentration and the equilibrium monomer-dimer influence appearance or disappearance of the A_d phase. Two ring cyano compounds containing cyclohexane rings are stronger associated than the compounds with benzene, pyrimidine or pyridine rings. Replacing the cyclohexane ring with the benzene or heterocyclic ring decreases the dimer formation and depresses the A_d phase induction. It is also due to the increase of $\Delta\varepsilon$.[7] Lower polarity of the medium cause better conditions for antiparallel ordering of 7CBB molecules. Decreasing polarity of the systems by insertion unpolar rings to the molecular core gives the similar effect as the increase of the alkyl chain length.[1,3]

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