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Induction of the smectic A_d phase in polar systems
II. Role of steric effects in the smectic A_d phase induction

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Binary mixtures in which one component is *n*CBB or its chiral analogue, and the second component is *n*CB, *n*OCB, *n*.CN, or one of their chiral analogues are studied by thermomicroscopy. The branched compounds induce the smectic A_d phase more strongly than unbranched compounds with the same alkyl chain length. The observed behaviour is discussed from the point of view of dimer formation. In all chiral systems, the TGB_A phase appears.

1. Introduction

The induction of the smectic A_d phase in bi- and multi-component mixtures of polar nematic or smectic compounds is possible [1, 2]. Such a case in which the induction of the smectic A_d phase is in the form of a 'smectic island' surrounded by nematic phase was described recently [3, 4]. The appearance of smectic A_d phase is due to a change in the monomer$\rightleftharpoons$dimer equilibrium in mixtures in comparison to that existing in the single compounds. The induction of the smectic A_d phase is observed in polar systems in which one component has a virtual smectic A_d phase. It occurs in homologous series where long members may have the smectic A_d phase at high temperatures, while the short members have the smectic A_1 at low temperatures; the re-entrant nematic phase can sometimes exist in these series [5]. The second component had to be a polar compound exhibiting the nematic phase.

It is well known that introducing a lateral substituent into pure mesogens suppresses their nematic and smectic A mesophases [6–17]. Sometimes the S_A–I or S_A–N phase transition temperatures are more strongly decreased than the N–I phase transition temperature [9], and sometimes the reverse is true. It depends on the position of the lateral substituent in the rigid core or in the alkyl chain, and on the structure of the whole molecule (e.g. the length of the alkyl chain, and the kind of substituents, bridging groups and rings). Usually, the upper temperature limit of the smectic A (A_1 or A_d) phase existence is depressed more strongly than that of the nematic when a lateral substituent (e.g. methyl group or fluorine atom) is placed in the central part of the rigid core of the molecule (in the 2-position) or in the 1-position of the alkyl chain [6–8, 12, 13, 15–17]. When the lateral substituent is shifted towards the terminal position in the rigid core (from the 2 to 3-position) or is shifted towards the end of the alkyl chain (from 1 to 2, 3 or 4-position), the smectic phase is depressed less than the nematic [6, 10, 11, 13]. Sometimes, compounds with lateral substituents possess only smectic phases [6, 10] and their temperature range may be slightly broader than in the case of corresponding unbranched analogues with the same alkyl chain length [10].

In the case of polar–non-polar bicomponent mixtures (donor–acceptor systems), in which induction of monolayer smectic phases is observed, branching of the alkyl chain reduces the thermal stability of the induced mesophase [14].

In bicomponent systems containing non-polar compounds, it was observed that molecules involving steric hindrance, arising from lateral substituents or bulky swallow-tailed chains, can also feature the induction of the smectic A phase (the so called 'filled smectic A phase') when short molecules are added [18–20]. These steric interactions cause a cage effect to develop for short molecules; steric effects prohibit the close packing of the host molecules and cause the existence of cavities in the host structure, which may be filled by short molecules of guest compounds. A favourable dense packing leads in turn to stabilization of the smectic A phase.

One should note that steric effects on the one hand can stabilize the smectic layering, because they do not allow molecules freely to permeate between the layers, but on the other hand, they can decrease the stability of a smectic phase because they disturb close packing in the smectic layers.

It was suggested that formation of the antiferroelectric structure is due to the presence of dimeric molecular

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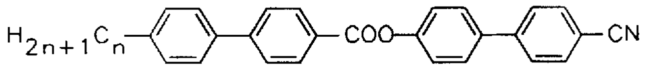
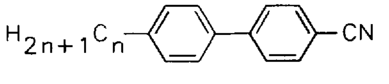
entities [21]. Steric hindrance on one side of a molecule favours their antiparallel alignment and is therefore responsible for creating the antiferroelectric $S_{C_A}^*$ phase. Longer branching groups (e.g. ethyl instead of methyl) also favours the $S_{C_A}^*$ phase [22]. The present work shows that steric hindrance can strongly influence the induction of the smectic A_d phase, and modification of the molecular structure has been carried out by branching the alkyl chain in different ways.

2. Experimental

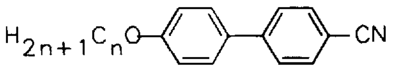
The compounds investigated had the following structures:



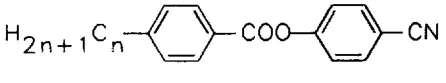
*n*CBB, *n* = 7, 6, 5, 4, 5*



*n*CB, *n* = 5*



*n*OCB, *n* = 7, 6, 4, 5*, 8*



n.CN, *n* = 9, 6, 4, 5*

where 5* and 8* denotes branched aliphatic chains—the 2-methylbutyl and 1-methylheptyloxy chains of a chiral molecule, respectively.

Phase diagrams were studied for the following mixtures: non-chiral *n*CBB – non-chiral two-ring compound, chiral *n*CBB – non-chiral two-ring compound, non-chiral *n*CBB – chiral two-ring compound, and chiral *n*CBB chiral two-ring compound. Phase diagrams were established by the single concentration method, and phase transitions were measured using a Linkam THMS600 hot stage unit mounted on a PZO polarizing microscope.

3. Results and discussion

In figure 1 (*a*), the phase diagram of the 7CBB–5*OCB system, together with the induced smectic A_d phase boundaries for similar bicomponent mixtures of 7CBB with three different unbranched analogues of 5*OCB, is presented. Comparing the 7CBB–5*OCB phase diagram with that for 7CBB–4OCB, one notes that the smective A_d phase induction is much stronger in the former case; by strength of induction, we mean the area of the phase's existence on the temperature-concentration phase diagram. For 7CBB–5*OCB, the maximum A_d–N transition temperature is 240°C and is higher than for any mixture with 4OCB. The temperature–concentration contour of the induced phase is different in the two cases. 4OCB induces the smectic A_d phase in such a way that, on the phase diagram the smectic A_d phase existence range has the shape of a narrow and elongated (along the temperature axis) 'elliptical island' surrounded by the nematic phase. The induction of the smectic A_d by 5*OCB is so strong that it exists at temperatures which are so low that they cannot be reached because of difficulties in supercooling the samples; this is why the contour of the induced smectic A_d phase is not closed. The extension of the smectic A_d phase range to both low and high temperatures indicates that the steric hindrance favours the layered structure, i.e. probably reduces diffusion of molecules between the layers. The ability of 5*OCB to create the smectic A_d phase is somewhat stronger than for 6OCB, but weaker than for 7OCB, cf. figure 1 (*a*).

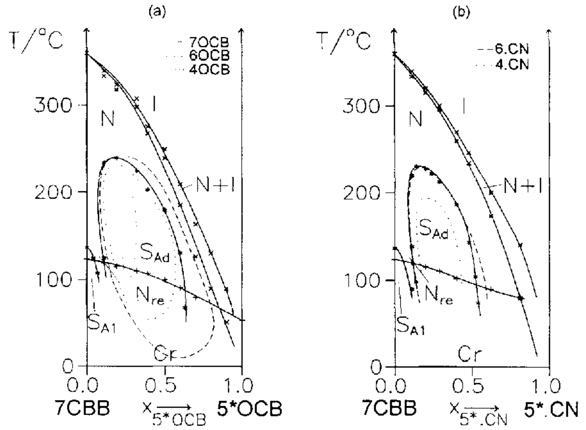


Figure 1. Phase diagrams of bicomponent mixtures: (*a*) 7CBB–5*OCB, with the S_{Ad}–N transition lines marked for mixtures 7CBB–*n*OCB, *n* = 7, 6, 4 and (*b*) 7CBB–5*.CN, with S_{Ad}–N transition lines marked for mixtures 7CBB *n*.Cn, *n* = 6, 4.

Yet another example of the big role played by steric hindrance in the formation of smectic layers is presented in figure 1 (*b*). Again, smectic A_d phase induction by 5*.CN is much stronger than by 4.CN (unbranched analogue of the fomer) in admixture with 7CBB. The ability of 5*.CN to inject the smectic A_d phase is comparable to that of longer members of the *n*.CN homologous series, such as *n* = 6.

The phase diagram of 7CBB–8*OCB system shows the influence of another branched aliphatic chain on the smectic A_d induction phenomenon, see figure 2. 8*OCB which has a 1-methylheptyloxy end group, is an isotropic liquid. For 8*OCB the maximum A_d–N phase transition temperature is again higher than for its unbranched analogue (7OCB); the phase diagram for 7CBB–7OCB is presented in figure 2 for comparison. The branching

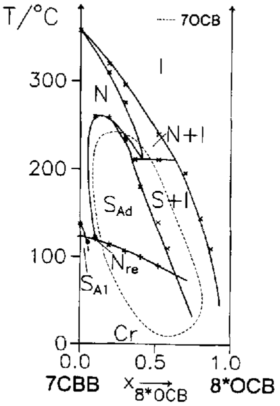


Figure 2. Phase diagram of bicomponent mixtures of 7CBB and 8*OCB and the contour of the smectic A_d phase for the 7CBB–7OCB system.

methyl group in 8*OCB is closer to the benzene ring than in the case of 5*OCB. Steric hindrance due to the 1-methylheptyloxy group is thus more severe, acting against parallel arrangement of the molecules and, at the same time, enforcing the dimer structure. The persistence of the injected smectic A_d phase in the system with 8*OCB is comparable to that with 10OCB (cf. figure 4 in [3]); even 10OCB as an individual compound exhibits the smectic A_d phase.

The examples already presented have involved branched alkyl chains in the two-ring compounds. Alkyl chain branching of a four-ring compound is also important for smectic A_d phase induction and acts similarly. The complete phase diagram of the 5*CBB–9.CN system is presented in figure 3 (*a*). The smectic A_d phase region is again larger than that for a mixture with the unbranched analog of 5*CBB, i.e. 4CBB, cf. figure 3 (*a*). The persistence of the smectic A_d phase is larger for 5*CBB than for 5CBB, but smaller than for 6CBB. We note that the smectic A_d existence range is not extended as much to low temperatures as is observed for the branched two-ring molecules, (cf. figures 1 (*a*) and (*b*)); therefore the re-entrant nematic phase is observed over a broader concentration range. This is probably due to the fact that in the case of long *n*CBB molecules, there is a size mismatch between the cavity and the guest molecule; thus steric effects are less favourable and the dimers are less stable at lower temperatures. When 5*CBB is mixed with 7OCB, the induced smectic A_d phase appears in the form of an 'elliptical island', see figure 3 (*b*). Such a shape suggests that the dimer concentration strongly depends on temperature. The island exists below the melting curve on the phase diagram, but the mixtures do not crystallize easily when cooled and it is possible to observe the re-entrant nematic (N_{re})–smectic A_d and smectic A_d–nematic (N) phase transitions. For all the systems presented with chiral compounds, the existence range of the induced phase is additionally surrounded by a narrow fringe or stripe of the TGB_A phase. In the 5*CBB–7OCB system, the stripe is the widest, and is therefore marked on the phase diagram, see figure 4. Notably, the unbranched analogue of 5*CBB, namely 4CBB, and also 5CBB, does not cause smectic A_d phase induction in the mixture with 7OCB. However, 6CBB as the first member of this homologous series is able to form the smectic A_d phase and the effect is very strong, cf. figure 3 (*b*).

The induction of the smectic A_d phase is also possible in mixtures of two chiral compounds, although the effect is much weaker. Phase diagrams of mixtures of 5*CBB with 5*CB, 5*OCB, and 5*.CN are presented in figure 5 (*a*), and with 8*OCB in figure 5 (*b*). In comparison to the binary mixtures with only one chiral component, the induced smectic A_d phase is observed at lower temperatures. The compound with the branched methyl group closer to the benzene ring causes the stronger induction.

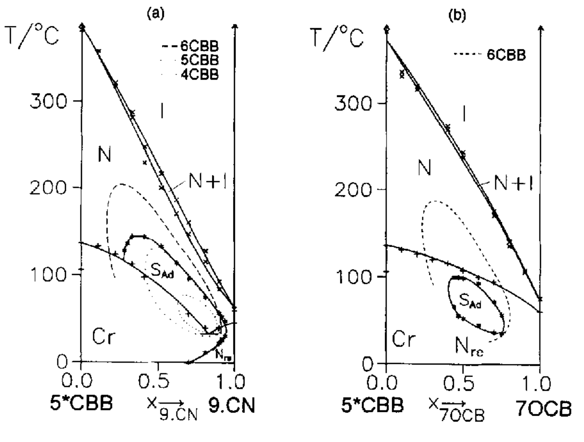


Figure 3. Phase diagrams of bicomponent mixtures: (*a*) *n*CBB–9.CN, $n=5^*$, 6, 5, 4, and (*b*) *n*CBB–7OCB, $n=5^*$, 6.

4. Conclusion

The persistence of the smectic A_d phase observed in mixtures of polar compounds is enhanced by steric effects from branched end chains. Steric hindrance arising from branching is not however the only factor

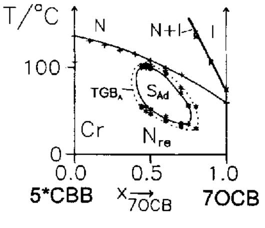


Figure 4. Phase diagram of the bicomponent mixtures of 5*CBB and 7OCB with the stripe or fringe of the TGB_A phase indicated.

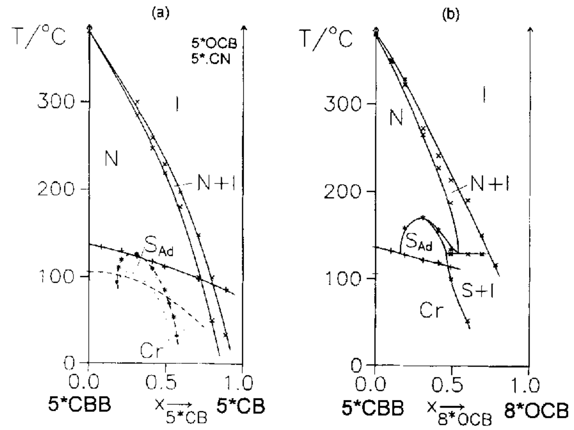


Figure 5. Phase diagrams of bicomponent mixtures: (*a*) 5*CBB–5*CB, with the S_{A_d}–N transition lines marked for mixtures 5*CBB–5*OCB and 5*CBB–5*CN, and both melting curves Cr_I–N and Cr_{II}–N; (*b*) 5*CBB–8*OCB.

responsible for the appearance of the smectic A_d phase; it is also observed in mixtures of polar compounds with longer alkyl chains and without branched chains. The branching of aliphatic chains is an additional factor which increases the tendency to stabilize the smectic A_d phase. We suspect that steric hindrance decreases free diffusion of molecules between layers, increases the stability of dimers of strongly polar molecules, and thus favours the layered structure. The reasons for smectic A_d phase induction may be similar to those for antiferroelectric phase formation.

Compounds with a branched aliphatic chain have a stronger tendency than their unbranched analogues to induce the smectic A_d, e.g. the 2-methylbutyl group has a greater ability for induction in comparison with the butyl group, but roughly the same ability as the unbranched alkyl chain, two or three carbon atoms longer, such as hexyl or heptyl.

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