Miscibility Studies Indicating a Low Temperature Smectic A Phase in Biaromatic Liquid Crystals with Re-entrant Behaviour *

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Recent reports [1] have shown that compounds of the homologous series of the 4(4-n-alkyloxybenzoyloxy)-4'-cyanobenzotriazoles (CN; n = 1 – 12), all have a low temperature smectic A phase (SΑ′′). The homologues with alkyl chain length n ≥ 9 exhibit in addition a high temperature smectic A phase (SΑ′), separated from the first one by a re-entrant nematic phase (Ν(Οθ)). Homologues of this series were used for miscibility studies with some compounds of the biaromatic liquid crystal series of the 4-cyano-4'-n-alkyloxy biphenyls (4 CBP) and of the 4-cyanobenzylidene-4'-n-alkyloxyanilines (CN· n). The phase diagrams studied show that the smectic A phases of biaromatic liquid crystalline nitrile compounds correspond to the high temperature smectic SΑ′ type and are not miscible with the low temperature SΑ′′ phase. Moreover, the shapes of the transition temperature curves to the SΑ′′ phase indicate a low temperature smectic A phase (SΑ′′) for the biaromatic compounds. This suggests that for biaromatic compounds with re-entrant behaviour, the dependence of liquid crystalline phase sequences on the alkyl chain length is very similar to that of triaromatic compounds.

1. Introduction

Liquid crystals with a terminal nitrile group often differ from the classic phase sequence behaviour in that their smectic A phase changes to a re-entrant nematic phase upon cooling [2, 3]. Up to now studies of aromatic substances have shown that the occurrence of this re-entrant phenomenon is to a large extent independent of the structure of the molecular core. In particular no principle difference has been found between biaromatic and triaromatic compounds [2, 3]. The addition of a third aromatic ring causes the clearing point to rise considerably whereas the melting point increases to a lesser degree, so that a wider range of the re-entrant nematic phase, often even enantirotropic, can generally be observed.

When triaromatic compounds are further cooled the re-entrant nematic phase sometimes transforms into a second smectic A phase [1, 2, 4]. X-ray examinations of 4(4-octyloxybenzoyloxy)-4'-cyano-stilbene (T8) [5] and of 4(4-n-onyloxybenzoyl-oxo)-4'-cyanobenzotriazoles (CN) [6] have confirmed that this low temperature smectic phase is also of the SΑ type, however the layer spacing is less than that of the high temperature phase. The isomorphism of both phases could also be confirmed by miscibility studies with suitable compounds [1, 2, 7]. On the other hand it was not possible to confirm an isomorphism of the two smectic A phases by mixing homologous compounds with each other, neither for the 4(4-n-alkyloxybenzoyloxy)-4'-cyano-stilbene series [2] nor for the 4(4-n-alkyloxybenzoyl-oxo)-4'-cyanobenzotriazoles (CN) series [8]. In all the phase diagrams studied, the two smectic A phases were separated by a re-entrant nematic phase, thus allowing the distinction between a high and a low temperature phase, SΑ′ and SΑ′′ respectively.

The above results suggested that biaromatic liquid crystals with re-entrant behaviour should also be examined for a second smectic A phase, and that an attempt should be made to classify the smectic A phases as SΑ′ or SΑ′′ using miscibility studies with triaromatic re-entrant compounds.

2. Experimental Results

In earlier experiments [8] on the homologous series of the triaromatic CN, the transition temperatures as a function of the alkyl chain length, as shown in Fig. 1, were obtained. Whereas the low temperature smectic phase SΑ′′ exists even for the shortest-chained compounds, the high temperature phase SΑ′ appears only when the alkyl chain length n is 9 or more. Even for n = 16 (not shown in Fig. 1),
a virtual phase transition of the high temperature smectic phase into a re-entrant nematic phase $N^{re}$ (not identified separately in the diagrams) was found, and a low temperature smectic phase $S_A''$ is also most probably formed.

Figure 2 shows the phase diagram of the system 4-cyanobenzylidene-4'-octyloxyaniline (CBOOA, CN·8)/C$_9$, where C$_9$ is the shortest-chained homologue with a high temperature smectic phase $S_A'$. The result is a continuous region linking the high temperature phase $S_A'$ of C$_9$ with the $S_A$ phase of the CBOOA. The re-entrant nematic region increases rapidly with increasing CBOOA concentration and with a relatively small addition of CBOOA, the transition into the low temperature phase $S_A''$ cannot be observed because of crystallization.

If on the other hand CBOOA is mixed with a short-chained homologue of the series C$_n$, which only exhibits the low temperature smectic phase $S_A''$, phase diagrams (studied by the contact method) of the type shown in Fig. 3 are always obtained. For more detailed studies, the C$_4$ homologue was chosen, mainly because preliminary examinations had shown that with this substance it was possible to observe, without crystallisation, the $N$–$S_A''$ phase boundaries over a wide concentration range. The smectic A phase of the CBOOA is bounded by the nematic phase and is nowhere linked with the low temperature phase $S_A''$ of C$_9$. Thus, Fig. 2 and 3 demonstrate that the $S_A$ phase of CBOOA is miscible with the $S_A'$ phase of C$_9$, but differs however from the $S_A''$ phase of the C$_n$ series.

The plot of the phase transition temperatures $N$–$S_A''$ for the system CN·8 (CBOOA)/C$_4$, which can be observed over a wide concentration range (Fig. 3), is only slightly curved and therefore an extrapolation to pure CBOOA appears permissible. This indicates that pure CBOOA exhibits a second smectic A phase of the $S_A''$ type with a virtual phase transition temperature, $N^{re}$–$S_A''$, of approximately $-65^\circ$C.

Earlier experiments [3] have demonstrated that the smectic A phases of biaromatic compounds are always miscible with each other. Consequently they
are of the same type, which according to the above results has to be classified as SA'. Thus, the CBOOA/C₄ phase diagram shown in Fig. 3 should also be representative of other binary mixtures of biaromatic nitrile compounds which have different middle groups. This is confirmed by the phase diagram 4-n-octyloxy-4'-cyanobiphenyl (8 CBP)/C₄ also shown in Fig. 3 where the plot of the N-SA' phase transition temperature versus concentration is almost linear and an extrapolation to pure 8 CBP gives a virtual N(re)-SA'' phase transition temperature of approximately —80 °C.

Several other triaromatic compounds (4(4-n-alkylbenzoyloxy)-4'-cyanotolanes, 4(4-n-alkyloxybenzoyloxy)-4'-cyanotolanes, 4(4-n-alkyloxybenzoyloxy)-4'-cyanostilbenes, 4(4-n-alkyloxybenzoyl)-benzylidene-4'-cyanoanilines) [2] with a chemical structure comparable with the series Cₙ have been found, which show a similar behaviour with respect to the appearance of two smectic A phases (see Fig. 1). Independent of the occurrence of the high temperature phase all these triaromatic compounds, even the shortest-chained, exhibit a smectic low temperature phase.

To enable a comparison with biaromatic compounds, the non smectic homologues 4-cyanobenzylidene-4'-n-heptyloxyaniline (CN • 7) and 4-n-heptyloxy-4'-cyanobiphenyl (7 CBP) are chosen for miscibility studies with C₄. As can be seen in Fig. 4 the N-SA'' phase transition temperature plot is almost linear in both cases, giving by extrapolation virtual transition temperatures of approximately —45°C and —65°C for pure CN • 7 and 7 CBP respectively. It is of interest to note that both N-SA'' virtual transition temperatures are higher than those of the corresponding longer-chained homologues CN • 8 and 8 CBP, this being in accordance with the behaviour of the above mentioned triaromatic compounds with similar chain length.

3. Discussion

The results from the miscibility studies reported in this paper, show that the Sₐ phase which occurs in biaromatic liquid crystal nitrile compounds with re-entrant behaviour, belongs to the high temperature Sₐ' type. It should be noted that this smectic phase is present both in biaromatic and triaromatic compounds having alkyl chain lengths equal to or greater than 8 and 9 respectively.

The high pressure behaviour is comparable with this [9]. The Sₐ phase of the biaromatic compounds 8 CBP and CBOOA as well as the high temperature Sₐ' phase of T₈ can be inhibited by increasing the pressure. In contrast, the phase transition of the low temperature smectic phase Sₐ'' to the re-entrant nematic phase N(re) behaves very differently: with increasing pressure the temperature of the phase transition Sₐ''-N(re) increases almost linearly.

This paper indicates, at least for the homologous series n CBP and CN • n with n = 7 and 8, that a low temperature Sₐ'' phase most probably exists for biaromatic compounds as well. This will possibly be confirmed by appropriate high pressure measurements, which are in preparation elsewhere [10].

Generalizing the results obtained, it is anticipated that the phase sequence behaviour of biaromatic homologous nitrile compounds is very similar to that of the triaromatic series Cₙ shown in Figure 1. This is in accordance with the theoretical prediction [11] that the re-entrant nematic phase always changes into a second smectic A phase when cooled, provided that this is not prevented by crystallisation or the formation of other smectic phases.

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