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

A. Göbl-Wunsch, G. Heppke, and R. Hopf
Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin

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Recent reports [1] have shown that compounds of the homologous series of the 4(4-*n*-alkyloxybenzoyloxy)-4′-cyanoazobenzenes (C_n; $n=1-12$), all have a low temperature smectic A phase (S_A''). The homologues with alkyl chain length $n \geqq 9$ exhibit in addition a high temperature smectic A phase (S_A'), separated from the first one by a re-entrant nematic phase ($N^{(re)}$). Homologues of this series were used for miscibility studies with some compounds of the biaromatic liquid crystal series of the 4-cyano-4′-*n*-alkyloxybiphenyls ($\bar{n}$ CBP) and of the 4-cyanobenzylidene-4′-*n*-alkyloxyanilines (CN · $\bar{n}$). The phase diagrams studied show that the smectic A phases of biaromatic liquid crystalline nitrile compounds correspond to the high temperature smectic S_A' type and are not miscible with the low temperature S_A'' phase. Moreover, the shapes of the transition temperature curves to the S_A'' phase indicate a low temperature smectic A phase (S_A'') 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 enantiotropic, 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-*n*-octyloxybenzoyloxy)-4′-cyanostilbene (T8) [5] and of 4(4-*n*-nonyloxybenzoyloxy)-4′-cyanoazobenzene (C_9) [6] have confirmed that this low temperature smectic phase is also of the S_A 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′-cyanostilbene series [2] nor for the 4(4-*n*-alkyloxybenzoyloxy)-4′-cyanoazobenzene (C_n) 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, S_A' and S_A'' 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 S_A' or S_A'' using miscibility studies with triaromatic re-entrant compounds.

2. Experimental Results

In earlier experiments [8] on the homologous series of the triaromatic C_n, the transition temperatures as a function of the alkyl chain length, as shown in Fig. 1, were obtained. Whereas the low temperature smectic phase S_A'' exists even for the shortest-chained compounds, the high temperature phase S_A' appears only when the alkyl chain length n is 9 or more. Even for $n = 16$ (not shown in Fig. 1),

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Reprint requests to Prof. Dr. G. Heppke, Sekr. C 2, TU Berlin, Straße des 17. Juni 135, D-1000 Berlin 12.

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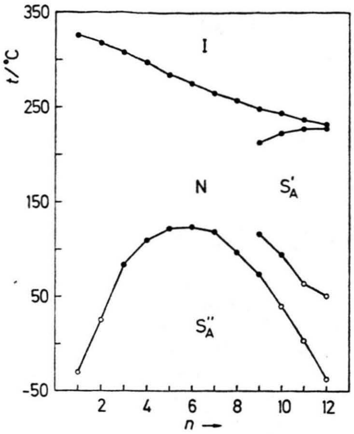

Fig. 1. Liquid crystal transition temperatures of the 4(4-*n*-alkyloxybenzoyloxy)-4′-cyanoazobenzenes (C_n) obtained with a polarizing microscope (●) and by extrapolation from binary mixtures (○) against the alkyl chain length *n*. I: isotropic; N: nematic; S_A' and S_A'': high and low temperature smectic A phase respectively.

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′-*n*-octyloxyaniline (CBOOA, CN · $\bar{8}$)/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 · $\bar{8}$ (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 °C.

Earlier experiments [3] have demonstrated that the smectic A phases of biaromatic compounds are always miscible with each other. Consequently they

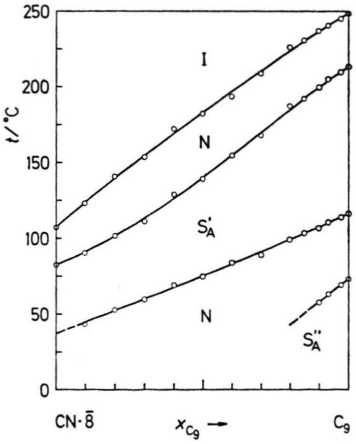

Fig. 2. Phase diagram of the system 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CN · $\bar{8}$, CBOOA)/4(4-*n*-nonyloxybenzoyloxy)-4′-cyanoazobenzene (C_9) (without melting points).

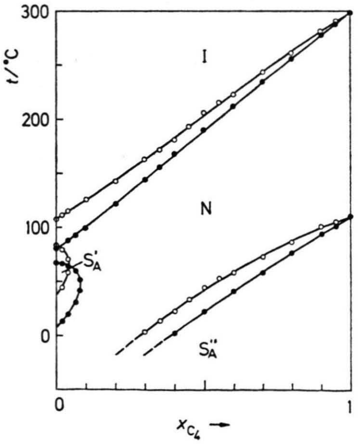

Fig. 3. Phase diagrams of binary mixtures of 4(4-*n*-butyloxybenzoyloxy)-4′-cyanoazobenzene (C_4) with (○) CN · $\bar{8}$ and (●) 4-*n*-octyloxy-4′-cyanobiphenyl ($\bar{8}$ CBP).

are of the same type, which according to the above results has to be classified as S_A'. Thus, the CBOOA/C_4 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 ($\bar{8}$ CBP)/C_4 also shown in Fig. 3 where the plot of the N–S_A'' phase transition temperature versus concentration is almost linear and an extrapolation to pure $\bar{8}$ CBP gives a virtual $N^{(re)}$–S_A'' 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*-alkyloxybenzoyloxy)-benzylidene-4'-cyanoanilines) [2] with a chemical structure comparable with the series C_n 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 · $\bar{7}$) and 4-*n*-heptyloxy-4'-cyanobiphenyl ($\bar{7}$ CBP) are chosen for miscibility studies with C_4. As can be seen in Fig. 4 the N–S_A'' 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 · $\bar{7}$ and $\bar{7}$ CBP respectively. It is of interest to note that both N–S_A'' virtual transition temperatures are higher than those of the corresponding longer-chained homologues CN · $\bar{8}$ and $\bar{8}$ CBP, this being in accordance with the behaviour of the above mentioned triaromatic compounds with similar chain length.

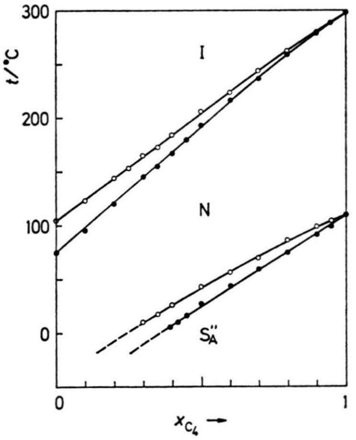

Fig. 4. Phase diagrams of binary mixtures of C_4 with (○) 4-cyanobenzylidene-4'-*n*-heptyloxyaniline (CN · $\bar{7}$) and (●) 4-*n*-heptyloxy-4'-cyanobiphenyl ($\bar{7}$ CBP).

3. Discussion

The results from the miscibility studies reported in this paper, show that the S_A phase which occurs in biaromatic liquid crystal nitrile compounds with re-entrant behaviour, belongs to the high temperature S_A' 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 S_A phase of the biaromatic compounds $\bar{8}$ CBP and CBOOA as well as the high temperature S_A' phase of T8 can be inhibited by increasing the pressure. In contrast, the phase transition of the low temperature smectic phase S_A'' to the re-entrant nematic phase $N^{(re)}$ behaves very differently: with increasing pressure the temperature of the phase transition S_A''–$N^{(re)}$ increases almost linearly.

This paper indicates, at least for the homologous series $\bar{n}$ CBP and CN · $\bar{n}$ with $n = 7$ and 8, that a low temperature S_A'' 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 C_n 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.

Acknowledgements

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