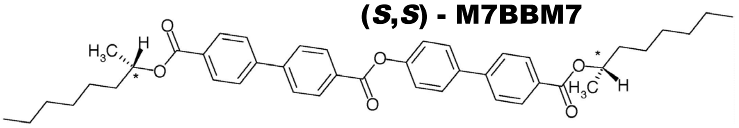
CHIRAL SMECTIC C SUBPHASES INDUCED BY MIXING A BISTEREOGENIC ANTIFERROELECTRIC LIQUID CRYSTAL WITH A NON-CHIRAL LIQUID CRYSTAL

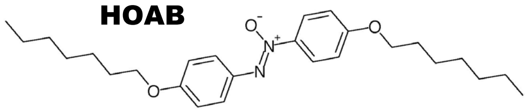
JAN LAGERWALL[a], FRANK GIESSELMANN[a], SEBASTIAN RAUCH[b], GERD HEPPKE[b], PER RUDQUIST[c], SVEN LAGERWALL[c]
[a]University of Stuttgart, Institute for Physical Chemistry, 70569 Stuttgart, Germany; [b]Technical University Berlin, Department of Chemistry, 10623 Berlin, Germany; [c]Chalmers University of Technology, Department of Microtechnology & Nanoscience, 41296 Göteborg, Sweden

By mixing a bistereogenic antiferroelectric liquid crystal (AFLC) compound, exhibiting only the SmQ* and SmC$_a$* mesophases, with the achiral N-SmC liquid crystal HOAB we could induce all three AFLC SmC-type subphases, SmC$_\alpha$*, SmC$_\beta$* and SmC$_\gamma$*. This seems to be in contradiction with two recent postulations regarding the subphase stability, one of which suggests that the subphases appear as a result of strong chiral interactions, the other that these phases require high smectic order, something one would generally not expect in mixtures. We have studied the helical pitch, optical tilt angle, spontaneous polarization and the x-ray diffraction due to the smectic layering, as a function of mixing ratio in order to better understand the relation between phase sequence and mixture composition. The smectic layer spacing shows a strongly non-linear behavior, suggesting that the basic structure of the pure AFLC substance is retained up to a HOAB content of about 75%.

Keywords Antiferroelectric liquid crystals; Chiral smectic C subphases; Chirality; Liquid crystal mixtures; Smectic layer spacing; Smectic order



Cr. - 56 - SmC$_a$* - 65 - SmQ* - 85 - Iso. / °C



Cr. - 74 - SmC - 95 - N - 127 - Iso. / °C

FIGURE 1. Chemical constitutions and phase sequences of the two components used in the mixture study: the AFLC (*S*,*S*) - M7BBM7 with one stereogenic center in each end chain, and the achiral HOAB. The (*S*,*S*) - M7BBM7 molecule is here drawn maximally extended, a conformation which may not be the most favorable since it requires two neighboring ester dipoles to point in the same direction.

INTRODUCTION

The origin of the two chiral smectic C subphases SmC$_\beta$* and SmC$_\gamma$*, observed between the antiferroelectric SmC$_a$* phase and the ferroelectric SmC* phase (or the third subphase, SmC$_\alpha$*), has been an issue of debate since they were first discovered in the antiferroelectric liquid crystal (AFLC) compound MHPOBC [1, 2]. (For a motivation of our choice of phase notation, *cf.* reference [3].) Recently, two different lines of reasoning have been presented for explaining the appearance, and disappearance, of the subphases in AFLC materials of varying purity. Gorecka *et al.* proposed that the subphases are a result of strong chiral interactions, and that the common observation of the subphases disappearing from the phase sequence of an AFLC when its optical purity is reduced can be understood in terms of weakened chiral interactions [4]. Lagerwall and coworkers proposed a different interpretation and an approach where the important parameter is that of smectic order, suggesting that the subphases will be allowed only if the smectic layer boundaries are well defined [3]. Hence, they proposed that any substance added to an AFLC, whether it differs in constitution or only in the absolute configuration, that has an adverse effect on the smectic order will destabilise the subphases.

In this context, a study carried out by Bennemann *et al.* in 1995, where a mixture of the bistereogenic AFLC (*S*,*S*) - M7BBM7 and the achiral liquid crystal HOAB (*cf.* Figure 1) was investigated [5], becomes highly interesting. Based on texture observations and DSC, they came to the conclusion that these two liquid crystals in certain ratios produce a mixture exhibiting all three chiral smectic C subphases, whereas these phases are absent in both components on their own. We have now made a more thorough investigation of this mixture system, utilizing x-ray scattering, electrooptic methods and dielectric spectroscopy, in order to better understand the origin of the subphases in the mixtures. At first sight, the generation of the subphases would seem to be in contradiction with both proposed models, since the subphases in this system appear at reduced optical and chemical purity, *i.e.* where the chiral interactions as well as the smectic order can be expected to be weaker than in the AFLC compound – not exhibiting any subphases – on its own.

EXPERIMENTAL

Eleven different mixtures of HOAB and (*S*,*S*) - M7BBM7, with molar proportions varying between 25/75 to 75/25, were prepared and studied in addition to the two compounds on their own. The phase sequences of the different samples are summarized in Figure 2. The samples were heated into the isotropic phase and filled into planar-aligning (polyimide coating) cells of 2.5 μm thickness (Chalmers MC2 assembly line) for electrooptical measurements. The optical tilt angle was measured using a

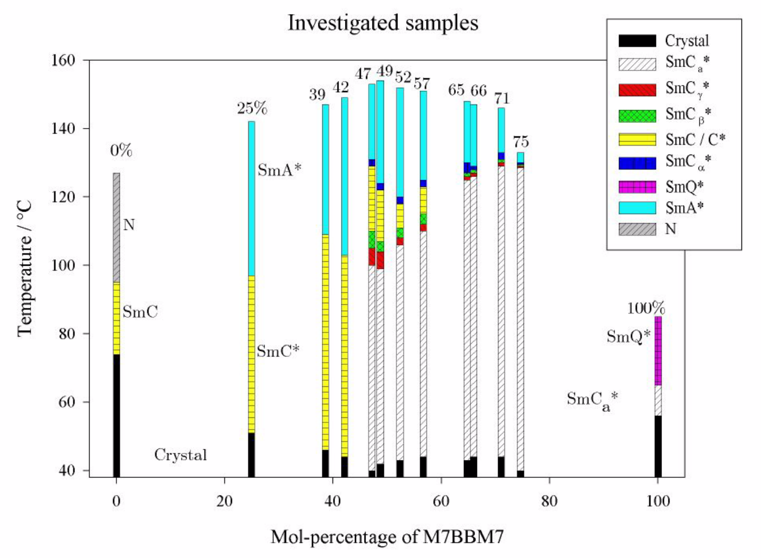


FIGURE 2. Phase sequences of HOAB (first column), (*S*,*S*)-M7BBM7 (last column) and the eleven studied mixtures between these two compounds.

technique first proposed by Bahr and Heppke where the optical transmission (T) of both states during saturated square wave switching was measured for several consecutive sample orientations φ. By fitting two $\sin^2$ functions to the two resulting $T(\varphi)$ data sets the tilt angle can be extracted [6]. The spontaneous polarization was measured by integrating the polarization reversal current while switching the sample with a triangular wave [7]. For dielectric spectroscopy studies 23.5 μm planar-aligning cells of the same construction were used.

X-ray (Cu-K_α radiation) experiments were carried out using Mark capillary tubes of 0.7 mm diameter. Samples with seven of the mixtures and the two pure compounds were prepared and investigated by means of a Kratky Compact camera and an M. Braun 1D detector. A function containing multiple Lorentz peaks and a baseline was fitted to the scattering profile in order to get not only the layer thickness (d) but also the relative strengths of the first- and second-order peaks. By comparing these we can get a rough estimate of the smectic order.

RESULTS AND DISCUSSION

The phase sequences of the different mixtures

From the diagram in Figure 2 we see that all mixtures studied exhibit the SmA* phase, a phase which neither pure component possesses. The clearing point is pushed upwards and the melting point downwards in the mixtures, giving these a considerably larger mesophase range than both pure components. Furthermore, it is quite striking that when the SmC$_a$* phase enters the phase sequence as we add more and more (S,S) - M7BBM7 to HOAB, it does not appear at temperatures below those of the SmC* phase of the preceding mixtures, but it actually appears at approximately the same temperatures as the SmC* phase. In other words, when the SmC$_a$* phase appears in the 47/53 mixture, it replaces the SmC* phase of the 42/58 mixture, a phase which is now pushed upwards in temperature towards a region where the 42/58 mixture exhibited the SmA* phase. We also notice that the three subphases appear together with the SmC$_a$* phase; they are absent at an M7BBM7 concentration less than or equal to 42%, but they are all present in all of the prepared mixtures with larger amount of the AFLC molecule, whereas the ferroelectric SmC* phase disappears from the phase sequence between 57% and 65% M7BBM7. The distinction between FLCs and AFLCs is generally that the former only exhibits SmC* as tilted phase, whereas the latter exhibits at least the SmC_a* phase but can also exhibit other chiral smectic C-type phases. With this distinction, we can thus say that the system changes from FLC to AFLC behavior at about 45/55 mixing ratio.

A striking characteristic of the HOAB + (*S*,*S*) - M7BBM7 system was that in the vicinity of 50/50 mixing ratio the tilted phases seemed to show a quite extraordinary tendency towards coexistence with one another. In Figure 3 the texture of the 57/43 mixture at ~115°C is shown. The picture looks as if it was taken while a temperature gradient was present across the sample, but this is not the case. (When decreasing the magnification we saw that the coexistence pattern repeated itself back and forth in different directions, following an irregular pattern that could not have been created by a temperature gradient in the hotstage.) The lower right part was the first to enter a new phase on heating, whereas the upper left was the last to stay in the old phase. This is most certainly not an example of phase coexistence in its strict definition, but rather a sign of spatial concentration variations resulting from a small degree of demixing, the origin of which is related to the nature of first-order transitions in mixtures, where phases of different composition coexist in biphasic regions. As we here have four first-order transitions (counting all three subphases in addition to SmC_a* and SmC*) very closely spaced in temperature the situation that arises can be quite complex. Since the AFLC subphases are

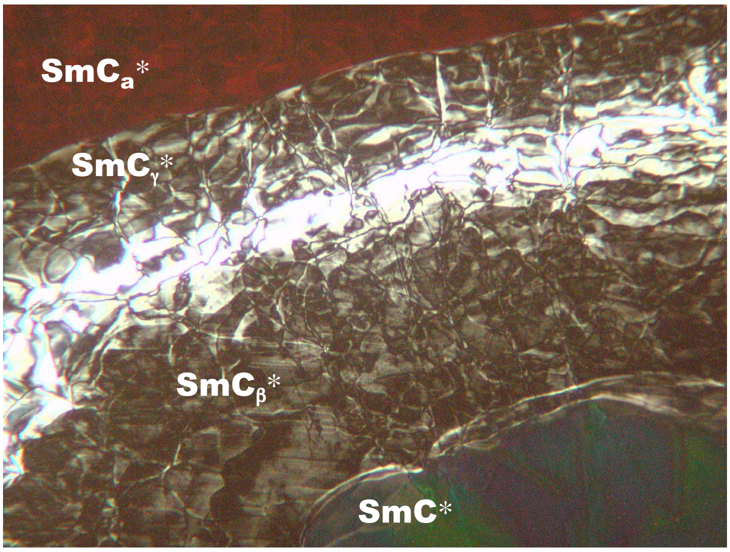


FIGURE 3. The texture in an untreated microscope slide preparation with the 57/43 mixture at 115°C. Note how, although there is no temperature gradient across the sample, the SmC_a*, SmC_γ*, SmC_β* and SmC* phases simultaneously exist next to one another.

normally observed only in pure compounds, whilst mixing often tends to suppress the subphase formation, such a situation is seldom encountered, explaining why one rarely observes all chiral smectic C phases existing next to one another in this manner. Supporting this conclusion was the observation that the variations usually grew larger after that the sample had been standing in the crystalline phase for some time (weeks - months), a state in which the miscibility of the two compounds is likely to be worse than in the liquid crystalline phases (in particular considering the difference in length of the two constituent molecular structures).

Looking at how the phase sequence changes between 40% and 60% (*S,S*) - M7BBM7 in Figure 2, the spatial variations in transition temperatures observed in ~50/50 mixtures become quite understandable. In this mixture range small changes in mixing ratio have considerable impact on the phase sequence of the system. Most conspicuously, a variation of the M7BBM7 concentration of ±2 - 3% in a 45/55 mixture would shift the system between one where the only tilted phase, down to room temperature, is SmC* and one where this phase does not form below ~100°C and where the SmC$_a$*, SmC$_\gamma$* and SmC$_\beta$* phases instead form at the temperatures where the other system was SmC*. In mixtures close to the border line between FLC and AFLC behavior even a very small degree of concentration variation will thus dramatically affect the phase sequence.

A consequence of the demixing tendency was that any measurement averaging over a large sample volume, such as a dielectric spectroscopy

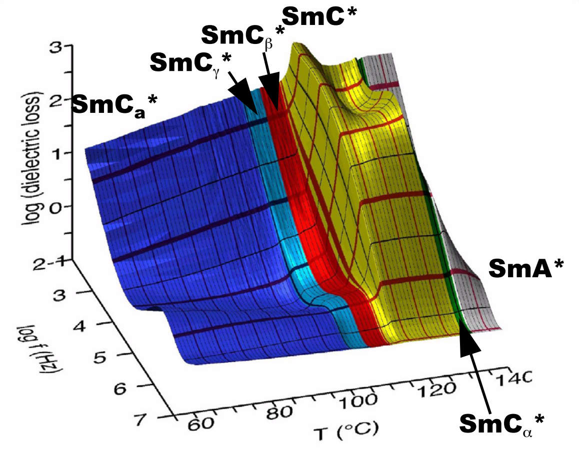


FIGURE 4. The dielectric absorption spectrum of the 47/53 mixture. The SmC$_\gamma$* and SmC$_\beta$* phases have very similar absorption spectra, both characterized by a very weak polar response. Most likely, the similarity is due to coexistence between the phases.

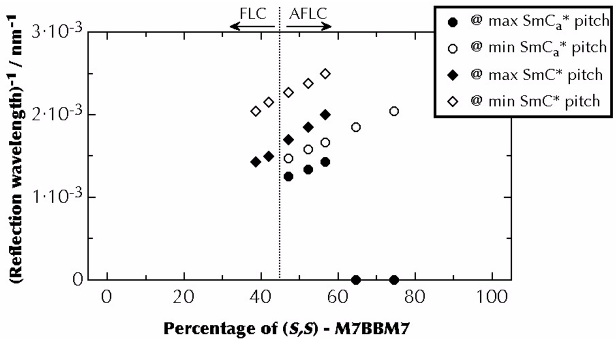


FIGURE 5. The inverse of the selective reflection wavelength as a function of mixing ratio (estimated values). For each mixture, the maximum and minimum wavelengths in the SmC* and SmC$_a$* phases are indicated. The two data points on the *x*-axis are due to the fact that the SmC$_a$* phase in the corresponding mixtures exhibited a helix inversion, rendering the pitch infinite at this temperature.

scan, will often reflect a mixture of phases in the temperature range between SmC$_a$* and SmC*. This is probably the reason why the SmC$_\gamma$* phase seemed to exhibit an unusually weak dielectric absorption, and why the SmC$_\beta$* phase always did exhibit a stronger absorption than in the other antiferroelectric phase, SmC$_a$*, *cf.* the example from the 47/53 mixture shown in Figure 4.

Pitch, optical tilt angle and spontaneous polarization

Since the absolute value of the helical pitch is not of prime interest to this work, but the trend of the pitch as a function of mixing ratio is all the more so, we only estimated the pitch by looking at the selective reflection colors in SmC* and SmC$_a$* in the mixtures where these phases appeared. In practice we used interference color filters to monochromatize the light passing through the sample, set between crossed polarizers, and changed filter until maximum transmission was obtained[1]. The result is summarized in Figure 5, plotted as inverse selective reflection wavelength. As expected, the inverse wavelength depends roughly linearly on the mixing ratio. However, the temperature dependence of the helical pitch was different between the mixtures, sometimes making it difficult to find adequate points of comparison. For instance, the mixtures with more than

---

[1] At the selective reflection wavelength the light is divided into two circularly polarized components, one of which is selectively reflected and one which is transmitted. The latter will not be blocked by the linear analyzer and a maximum transmission will therefore be seen at the selective reflection wavelength.

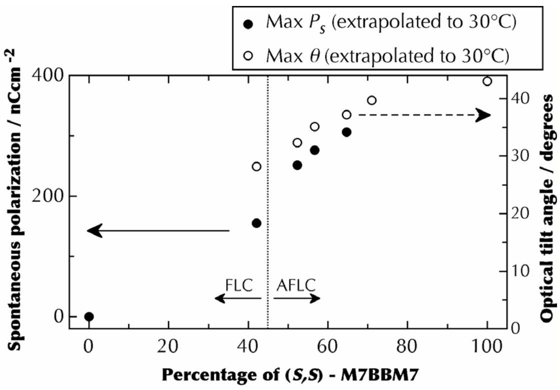


FIGURE 6. Spontaneous polarization and optical tilt angle as a function of mixing ratio.

60% M7BBM7 were found to exhibit a helix inversion in the SmC$_a$* phase, making the maximum SmC$_a$* pitch infinite in these cases, as seen by the two data points lying on the *x*-axis in Figure 5.

The spontaneous polarization and optical tilt angle was measured for a few selected mixtures, and a power law function was fitted to the data in order to extrapolate each variable to the 30°C value. The result is presented in Figure 6. Also this diagram contains no surprises; the spontaneous polarization monotonously increases as more chiral component is added. The tilt angle as well showed a monotonous increase with increasing M7BBM7 content throughout the mixture range that was measured. The tilt angle in the achiral HOAB liquid crystal could not be reliably measured by electrooptic methods (the response to electric fields is dielectric and the effective optical tilt angle is very much affected by the particular structure formed in the cell).

X-ray scattering results

Whereas inverse pitch, tilt and spontaneous polarization all showed a monotonous and more or less close to linear (within the range studied) dependence on mixing ratio, the smectic layer spacing showed a completely different behavior. As can be seen in Figure 7, the layer spacings *d* of all mixtures are larger than the *d* value of either single component. (However, the *d* values of pure (*S*,*S*) - M7BBM7 are very uncertain because the transition to the SmC$_a$* phase is in this compound inhibited for kinetic reasons, making a direct transition between Crystal and SmQ* common, on cooling as well as on heating. Hence, we don’t know for certain what phase structure the measured *d* values for this compound actually correspond to.) Particularly interesting are the 42/58 and 47/53 mixtures, as

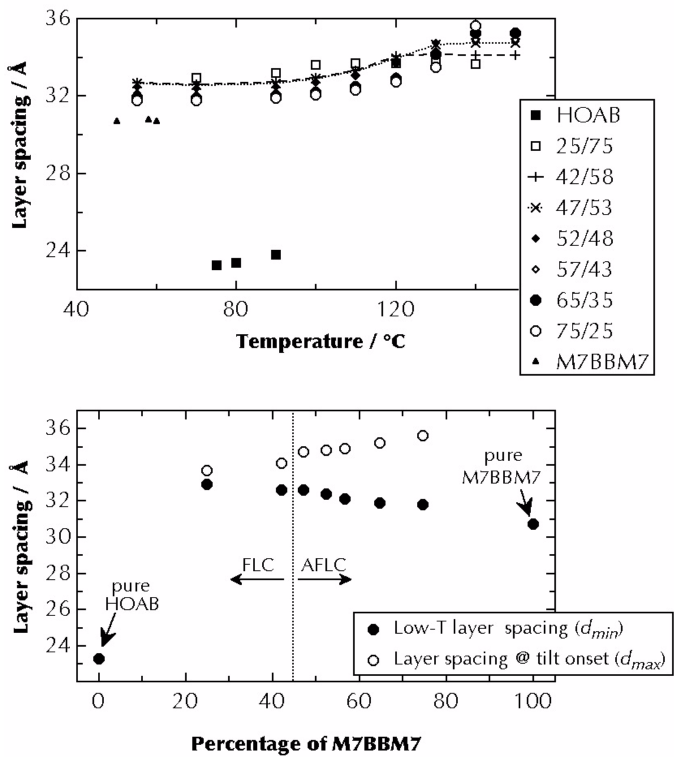


FIGURE 7. The smectic layer spacing as a function of temperature (top) and as a function of mixing ratio (bottom). In the top diagram the data of the two mixtures surrounding the border between FLC and AFLC behavior have been connected with dashes (FLC) and dots (AFLC), respectively.

these lie on opposite sides of the border between FLC and AFLC behavior. It is striking that *d* in the tilted phases of these two mixtures are almost identical, whereas the 47/53 AFLC mixture exhibits a slightly larger SmA* layer spacing. (To make this easier to see, the data for these two mixtures have been connected in the upper diagram of Figure 7, the 42/58 mixture with dashes, the 47/53 with dots.)

Since pure HOAB has *d* considerably smaller than in all mixtures, between which the variation in *d* is only 1 - 2 Å, there must be a rather sudden change in layer spacing somewhere between 0% and 25% M7BBM7. The common behavior when mixing two smectogens with different layer spacing is that the layer spacing of the mixture shows a more or less linear dependence on the mixing ratio [8]. The very non-linear behavior observed in our system resembles that reported by Diele and co-workers in a series of investigations on mixtures of swallow-tailed molecule liquid crystals with compounds having smaller rod-shaped molecules [9]. They explained the phenomenon using a concept they called “filled smectics” where the smaller molecules fill the free volume that is formed between the larger swallow-tailed molecules due to their bulky ends.

Do we have a similar phenomenon responsible for the layer spacing behavior in our mixture system ? The M7BBM7 molecule is not swallow-tailed, but it may be that the most likely conformation is slightly bent-shaped, as illustrated in Figure 8. Such a conformation would not only correspond to neighboring ester dipoles pointing in opposite directions, but also to the two chiral methyl groups being directed antiparallely, *i.e.* this conformation would lead to a cancellation of both electric dipoles and ‘steric dipoles’. With the M7BBM7 molecule in this conformation, it is quite easy to fit the HOAB molecule together with the M7BBM7 molecule in such a way that the central HOAB dipole aligns with the central dipole of M7BBM7 and, at the same time, the packing efficiency is quite high. Since the effective length of the molecule pair formed in this way is roughly the same as that of a single M7BBM7 molecule, one should not expect a large change in layer spacing if such a pair aggregation can take place. But if the number of short molecules by large exceeds the number of long molecules the overall packing can no longer be efficient in a smectic structure with large layer thickness, and this is why the layer thickness rapidly decreases once the amount of HOAB exceeds ~75% of the mixture.

One should not understand this reasoning as if the molecules adopt one particular conformation, pair up two and two and stay that way. The thermal motion must be considered, which means that the molecules constantly undergo variations in conformation, as well as translations and rotations on a very fast time scale [10]. On the other hand, it would be incorrect to treat the molecules as being completely independent of one another. Leadbetter introduced a ‘coherence volume’, with a size on the order of ten molecules, setting a microscopic limit below which one can

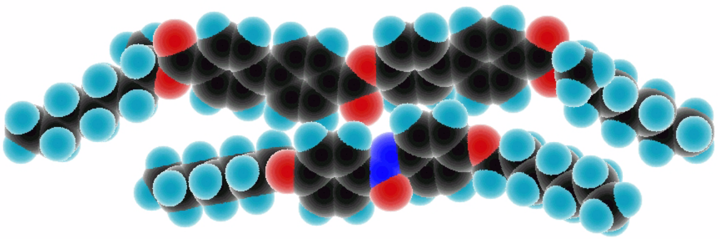


FIGURE 8. A possible way that the M7BBM7 (top) and HOAB (bottom) molecules may pair-aggregate, explaining why the smectic layer spacing is almost independent of mixing ratio over a large concentration range.

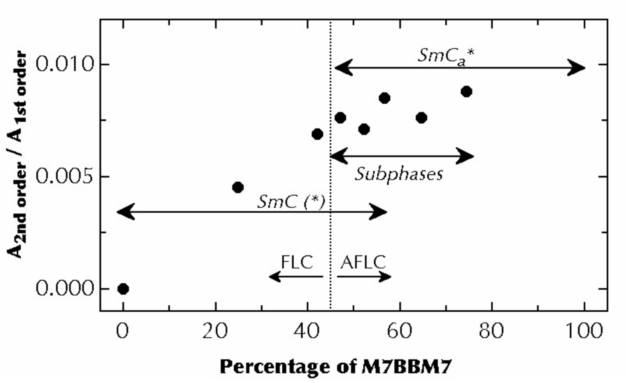


FIGURE 9. The ratio between the amplitudes of the first- and second-order x-ray diffraction peaks, used as an estimate of the degree of translational (smectic) order.

expect some collective behavior in any liquid crystal phase [11, 12]. The idea of molecular pair aggregation should be understood as some degree of correlated dynamics of neighboring HOAB and M7BBM7 molecules, promoted by certain combinations of conformations and relative positions leading to a particularly efficient packing, such as illustrated in Figure 8.

With respect to the model suggesting that the subphase appearance requires high smectic (translational) order, it is of course interesting to study this parameter in our system. However, the definition of a smectic order parameter, and its extraction from experimental data, is far from simple. As a rough estimate, we have chosen to compare the amplitudes of the first- and second-order x-ray diffraction peaks due to the periodic stacking of smectic layers. The higher the smectic order, the stronger the second-order peak can be expected to be, as compared to the first-order peak. The result is shown in Figure 9. Obviously, there is no maximum in this smectic order estimate in the mixtures where the subphases are maximally stable. Nevertheless, all mixtures differed distinctly from the pure HOAB compound, which had no second-order peak visible at all. The data is too scattered and too scarce to be conclusive (in particular, data for the pure AFLC compound is missing, due to the difficulties in securing that the sample was in the SmC_a* phase) but it at least seems that the decrease rate of smectic order with increasing amount of HOAB is higher once the mixtures do not exhibit any AFLC-type phases any more (more than ~55% HOAB).

CONCLUSIONS

When mixing the SmQ*-SmC$_a$* liquid crystal (*S,S*) - M7BBM7 with the achiral N-SmC liquid crystal HOAB all three chiral smectic C subphases, SmC$_\alpha$*, SmC$_\beta$* and SmC$_\gamma$*, as well as the SmA* phase show up in the phase diagram. The transition between FLC and AFLC behavior takes place close to the 50/50 mixing ratio, where the SmC* and SmC$_a$* phases replace one another on the two sides of the border. For mixtures close to this border considerable spatial variations in transition temperatures were observed, related to a small degree of demixing.

The helical pitch and the spontaneous polarization, being the only two obvious experimental measures of chiral strength in the system, both follow monotonous behaviors as a function of mixing ratio, with the pitch getting longer and the polarization getting smaller as more and more HOAB is added. Hence there is no sign that the appearance of the subphases is related to any effective strengthening of chiral interactions. On the other hand, the smectic layer spacing shows a very different behavior as the concentrations of the two components are varied. As one starts adding M7BBM7 to pure HOAB the smectic layer spacing rapidly increases. It reaches its maximum value at a mixing ratio around 25/75 and then decreases, but with a much smaller derivative, as more M7BBM7 is added to the system. On crossing the borderline between FLC and AFLC behavior the layer spacing changes remarkably little in the tilted phases, but in the SmA* phase the AFLC mixture has distinctly larger layer spacing. The estimations of the smectic order are inconclusive but show that the pure HOAB sample has considerably lower smectic order than what is the case when M7BBM7 is added. In any case, the strongly non-linear behavior of the smectic layer spacing as a function of mixing ratio is a strong indication that the type of smectic ordering is important for which variations of the chiral smectic C-type phases are formed, with ordinary ferroelectric SmC* on one side, and the SmC$_a$* phase together with the three subphases on the other.

Acknowledgements
Financial support from the EU research program SAMPA (Synclinic and Anticlinic Mesophases for Photonics Applications) and from the Alexander von Humboldt foundation is gratefully acknowledged.

References

[1] M. Fukui, H. Orihara, Y. Yamada, N. Yamamoto and Y. Ishibashi, *Jap. J. Appl. Phys. Lett.*, **28**, *5*, pp. L849-850 (1989)

[2] A.D.L. Chandani, Y. Ouchi, H. Takezoe and A. Fukuda, *Jap. J. Appl. Phys. Lett.*, **28**, *7*, pp. L1261-4 (1989)

[3] J.P.F. Lagerwall, P. Rudquist, S.T. Lagerwall and F. Giesselmann, *Liq. Cryst.*, **30**, *4*, pp. 399 - 314 (2003)

[4] E. Gorecka, D. Pociecha, M. Cepic, B. Zeks and R. Dabrowski, *Phys. Rev. E*, **65**, pp. 061703-1 - 061703-4 (2002)

[5] D. Bennemann, G. Heppke, D. Lötzsch, and S. Paus, Poster P27 presented at the 24th Freiburger Arbeitstagung, Freiburg, Germany , 1995

[6] F. Giesselmann, A. Langhoff and P. Zugenmaier, *Liq. Cryst.*, **23**, *6*, pp. 927-931 (1997)

[7] K. Miyasato, S. Abe, H. Takezoe and A. Fukuda, *Jap. J. Appl. Phys. Lett.*, **22**, p. L661 (1983)

[8] S. Diele, *Ber. Bunsenges. Phys. Chem.*, **97**, pp. 1326 - 1336 (1993)

[9] S. Diele, G. Pelzl, W. Weissflog and D. Demus, *Liq. Cryst.*, **3**, p. 1047 (1988)

[10] J. Goodby, Ph. D. thesis, University of Hull, Hull, UK (1978)

[11] A.J. Leadbetter and E.K. Norris, *Mol. Phys.*, **38**, *3*, pp. 669-686 (1979)

[12] A.J. Leadbetter and P.G. Wrighton, *J. Phys. Colloque*, **40**, *C-3*, pp. 234-242 (1979)