Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Destruction of an Intercalated Structure in a Smectic A Phase

S. Haddawi [a], D. Demus [a], S. Diele [a], H. Kresse [a], G. Pelzl [a], W. Weissflog [a b] & A. Wiegeleben [a]

[a] Martin-Luther-Universität Halle, Institut für Physikalische Chemie, Mühlpforte 1, D-O-4020, Halle/S, Germany

[b] Max-Planck-Gesellschafi, Arbeitsgruppe "Flüssigkristalline Systeme" an der Martin-Luther-Universität Halle, Mühlpforte 1, D-O-4020, Halle/S, Germany

Version of record first published: 04 Oct 2006.

To cite this article: S. Haddawi , D. Demus , S. Diele , H. Kresse , G. Pelzl , W. Weissflog & A. Wiegeleben (1994): Destruction of an Intercalated Structure in a Smectic A Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 109-116

To link to this article: http://dx.doi.org/10.1080/10587259408046919

Mol. Cryst. Liq. Cryst., 1994, Vol. 238, pp. 109–116
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Destruction of an Intercalated Structure in a Smectic A Phase

S. HADDAWI, D. DEMUS, S. DIELE, H. KRESSE, G. PELZL, W. WEISSFLOG† and A. WIEGELEBEN

Martin-Luther-Universität Halle, Institut für Physikalische Chemie, Mühlpforte 1, D-O-4020 Halle/S. Germany; and †Max-Planck-Gesellschaft, Arbeitsgruppe "Flüssigkristalline Systeme" an der Martin-Luther-Universität Halle, Mühlpforte 1, D-O-4020 Halle/S. Germany

(Received October 8, 1992; in final form January 25, 1993)

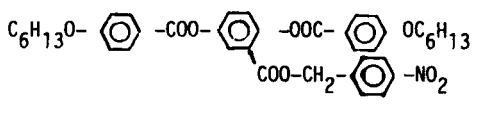
The destruction of the intercalated smectic A structure of a laterally bulky branched 1,4-phenylen dibenzoate A by addition of a rodlike cinnamate B was studied by the phase diagram as well as by calorimetric, x-ray and dielectric measurements. The thermal stability of the S_A phase of compound A and its phase transition enthalpy decrease with increasing concentration of B. Furthermore, the destruction of the short range order of A is characterized by increasing layer distances, decreasing dipolar correlation and an increasing dielectric relaxation frequency only of component A.

Keywords: intercalated S_A phase, mixture, short range interaction; calorimetric, dielectric, x-ray studies

1. INTRODUCTION

The variation of intermolecular interaction of mesogenic compounds has led to a great variety of mesomorphic liquid crystalline phases. This can be done either by a change of the chemical structure or—in binary systems—by addition of a second component. In the latter case the interaction under consideration can be systematically changed by the influence of the second component. In consequence of this a stabilization[1–4] or destabilization[5] of a phase can take place.

An example of a substance with a strong dipolar interaction has been proved to be the 4-nitrobenzyl 2,5-bis(4-*n*-hexyloxybenzoyloxy)benzoate derivative

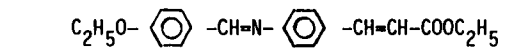


A

cr 383 S_A 425 N 427 is (T/K)

Based on x-ray studies an intercalated structure of the smectic A phase has been postulated.[6] By dielectric measurements an extreme tendency of an antiparallel order could be detected.[7] The antiparallel correlation in the short range scale is

difficult to destroy by addition of a second mesogenic component with rodlike molecular form.[8] In the following paper a new experiment is reported in which the smectogenic compound 4(4-ethoxybenzylideneamino)ethylcinnamate



B

cr 355 S_B 392 S_A 429 N 433 is

is added. Compound B has nearly the same temperatures of the phase transitions S_A/N and N/is as sample A and therefore, it is very useful for thermodynamical considerations.

2. THERMODYNAMICAL INVESTIGATIONS

The phase diagram was obtained by microscopic investigations under polarized light and by calorimetric measurements (DSC7, Perkin Elmer Corp.) Figure 1 shows that the nematic phases of both components are completely miscible. The clearing temperatures pass through a minimum and the phase transition enthalpies show a weak negative deviation from the ideal behaviour (Figure 2). Otherwise, the S_A phases of both components are separated by a pronounced nematic gap. The phase transition S_A/N is much stronger influenced by the second component.

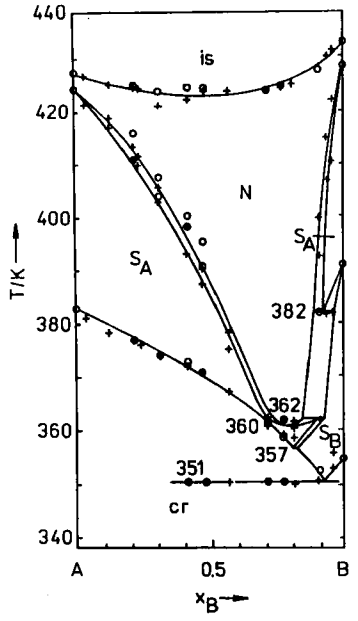


FIGURE 1 Phase diagram of the 4-nitrobenzyl 2,5-bis(4-*n*-hexyloxy-benzoyloxy) benzoate A and the cinnamate B, is-isotropic liquid, N-nematic phase, S_A, S_B-smectic A and smectic B phases, cr-solid phase: estimated by microscopic (+) and calorimetric (○) measurements. The heterophasic regions at the N/is transitions are small and cannot be detected by microscopic observations.

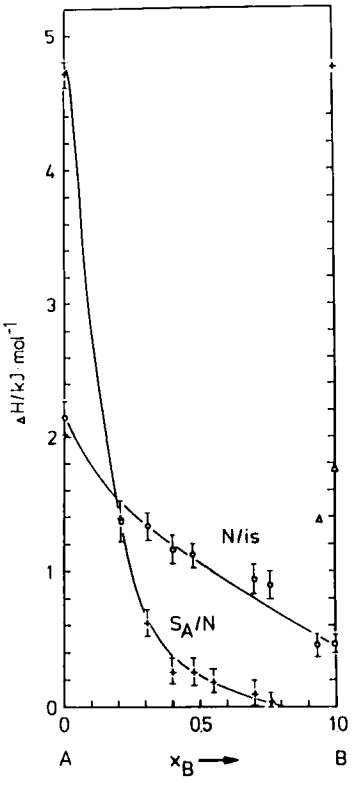


FIGURE 2 Phase transition enthalpies of the binary system. Δ:S_B/S_A-transition.

As seen from the calorimetric measurements (Figure 2) the S_A phase of component A is strongly destabilized by addition of substance B, e.g. for a mixture of 30 mol% B the phase transition enthalpy $\Delta H(S_A/N)$ decreases by one order of magnitude. On the other hand, the addition of 5 mole% A to sample B destroys the S_A phase to such an extent that the phase transition enthalpy was found to be below the instrumental noise level.

3. X-RAY MEASUREMENTS

X-ray measurements have been performed using a small-angle equipment and non-oriented samples as well as a flat film method in connection with magnetically oriented samples. The patterns exhibit the characteristic features of the S_A phase. The measured *d*-values (thickness of the smectic layers) have been found to be independent of the temperature. The *d*-value of component A is essentially smaller than the length of the molecule in its full extended form. It has been led to the assumption of an intercalated structure.[6] The peculiarity of the system under consideration is the increase of the *d*-value by addition of the second component B with a short molecular length as shown in Figure 3. Obviously the second component

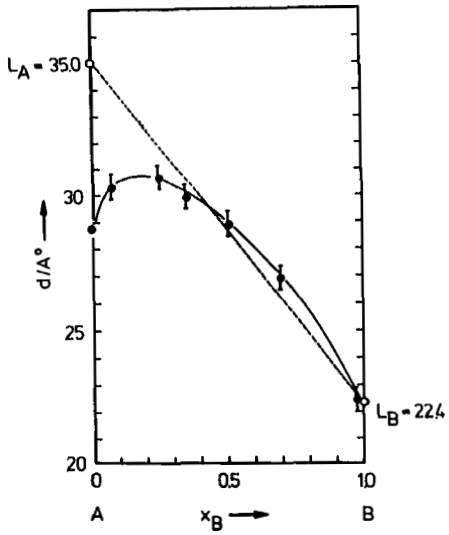


FIGURE 3 Thickness of the smectic layers d as function of the molar fraction x_B. The molecular lengths L_A and L_B are indicated by open circles (○). The linear relation between L_A and L_B is indicated by a dotted line.

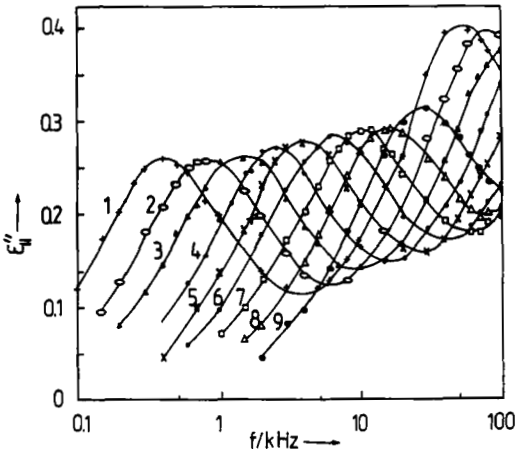


FIGURE 4 Dielectric absorption at x_B = 0.25, T_1 = 333.9 K, T_2 = 339.1 K, T_3 = 344.7 K, T_4 = 350.4 K, T_5 = 355.6 K, T_6 = 361.2 K, T_7 = 366.4 K, T_8 = 371.1 K, T_9 = 378.0 K. The conductivity part of $\varepsilon''_{\parallel}$ was separated. The conductivity contribution to the measured ε'' at T = 333.9 K and for f = 100 Hz is about 0.3.

destroys the intercalated structure and the d-values start to increase approaching a behaviour given by a linear relation of the molecular length L.

4. DIELECTRIC PROPERTIES

Dielectric measurements were performed on magnetically oriented samples in the frequency range from 10 Hz to 100 kHz. Data for the dielectric absorption curves

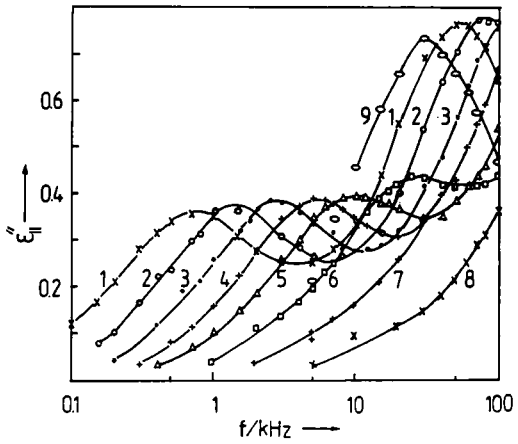


FIGURE 5 Dielectric absorption curves at $x_B = 0.51$, $T_1 = 330.8$ K, $T_2 = 336.3$ K, $T_3 = 342.8$ K, $T_4 = 349.7$ K, $T_5 = 355.8$ K, $T_6 = 367.5$ K, $T_7 = 382.0$ K, $T_8 = 397.1$ K, $T_9 = 324.7$ K (crystallization during measurements at $f = 10$ kHz).

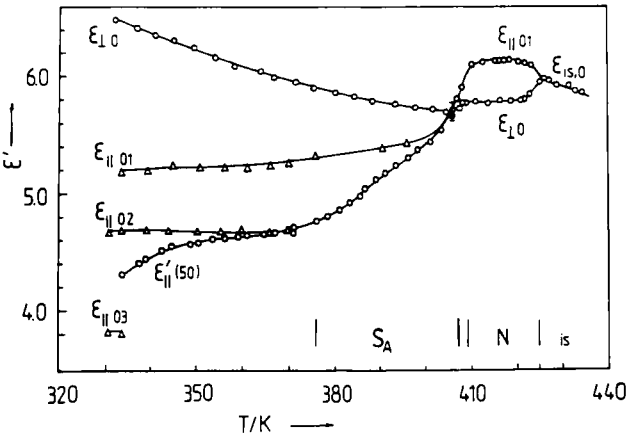


FIGURE 6 Dielectric constants as function of the temperature. The static values are $\varepsilon_{\|01}$ and $\varepsilon_{\perp 0}$. The dielectric increments $\varepsilon_{\|01} - \varepsilon_{\|02} = \Delta_A$ and $\varepsilon_{\|02} - \varepsilon_{\|03} = \Delta_B$ are related to the reorientation of A and B, respectively. Measured values are given for $f = 50$ kHz ($\varepsilon'_{\|}$ (50)).

at $x_B = 0.25$ and $x_B = 0.51$ are presented in Figures 4 and 5. There are two absorption ranges in the direction parallel to the director. The intensity of the high frequency one ($x_B = 0.25$, $\varepsilon''(\max) = 0.4$, $x_B = 0.51$, $\varepsilon''(\max) = 0.78$) increases with increasing molar fraction of B. That means it is connected with the reorientation of component B. The low frequency absorption, which we relate to the reorientation of A, has at $x_B = 0.25$ a smaller intensity ($\varepsilon''_{\|} = 0.26$) than at $x_B = 0.51$ ($\varepsilon''_{\|} = 0.38$) at $T = 340$ K. Usually the maximum of the absorption intensity decreases with decreasing concentration of the corresponding component. That means $\varepsilon''_{\|}(\max)$ and the dielectric increment Δ_A (here not presented) estimated from Cole-Cole plots[10] do not obey a simple dilution law. The different static and

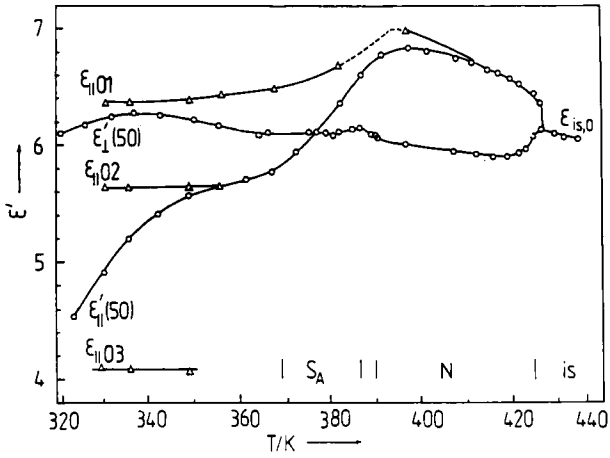


FIGURE 7 The dielectric constants at $x_B = 0.51$ as function of the temperature. The static ($\varepsilon_{\|01}$) and quasistatic values ($\varepsilon_{\|02}$, $\varepsilon_{\|03}$) were estimated from Cole-Cole plots.

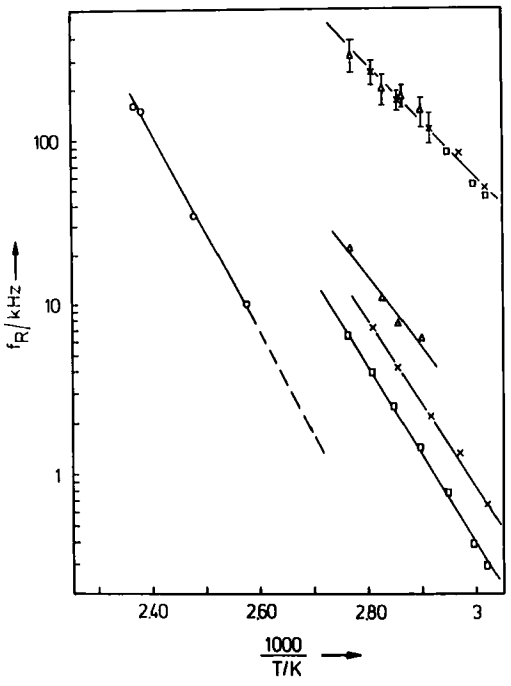


FIGURE 8 Arrhenius plot of the relaxation frequencies f_R at $x_B = 0.00$, $x_B = 0.25$ (□), $x_B = 0.51$ (×) and $x_B = 0.70$ (△) for the reorientation of A (low frequencies) and B around the short molecular axis.

quasistatic dielectric constants of $x_B = 0.25$ are given in Figure 6. Here $\varepsilon_{\|01}$ contains contributions of the reorientation processes of A and B around the short molecular axis and of a component of the fast reorientation around the long molecular axis.[11] The quasistatic $\varepsilon_{\|02}$ arises from the last two processes whereas $\varepsilon_{\|03}$ is caused only by the reorientation around the long molecular axis. In the nematic phase the static

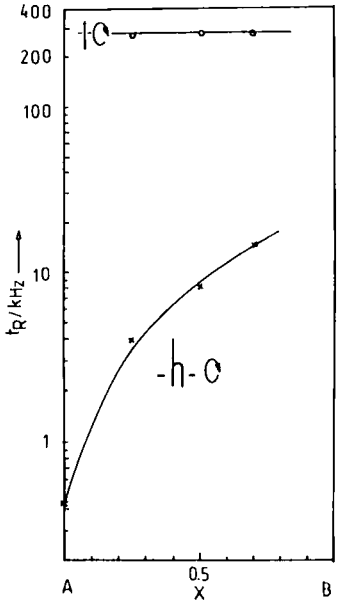


FIGURE 9 The relaxation frequencies of A (×) and B (○) for the reorientation around the short molecular axis at T = 357 K as function of the concentration (h and | are symbols of the components A and B).

dielectric constant $\varepsilon_{\|01}$ is greater than the static value $\varepsilon_{\perp 0}$. Whereas $\varepsilon_{\perp 0}$ is nearly not affected by the phase transition N/S_A $\varepsilon_{\|01}$ decreases strongly due to the antiparallel order of the longitudinal dipoles of A. This effect is more pronounced in the pure component A but at x_B = 0.25 it results also in a change of the sign of the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|01} - \varepsilon_{\perp 0}$. The decrease of $\varepsilon_{\|01}$ for x_B = 0.51 at the N/S_A transition is not so pronounced as demonstrated in Figure 7. Furthermore, $\varepsilon_{\|01}$ increases in the nematic phase with decreasing temperature. This indicates a destruction of the antiparallel correlation of the dipoles in the nematic state. But with decreasing temperature the driving forces for the antiparallel orientation of the dipoles becomes stronger and they form a smectic A structure which favours the compensation of the longitudinal dipoles. At x_B = 0.7 a normal behaviour of the dielectric constants with respect to the Maier-Meier model[11] in the nematic phase was found but also a decrease of $\varepsilon_{\|01}$ near to the N/S_A phase transition range.

The frequency at which the dielectric absorption has a maximum is the relaxation frequency f_R. Data for the pure compound A (x_B = 0.00) and the three mixtures are given in the Arrhenius plot in Figure 8. Taking into account the experimental errors we can recognize the greatest increase of the relaxation frequency of A between the pure A and x_B = 0.25.

The nearly independency of f_R for compound B on the concentration of component A at least up to $x_B \leqq 0.70$ is a further peculiarity of this binary system. The dynamical behaviour at T = 357 K again indicates the destruction of the intercalated structure of A by addition of compound B (see Figure 9). Here only f_R of component A systematically increases with dilution.

5. CONCLUSIONS

The main results of our investigations are:

1. In the pure nitro compound A the molecules are extremely antiparallel ordered in an intercalated structure of the S_A phase. Therefore, the dielectric anisotropy is negative. The intercalated arrangement of the molecules results also in a decrease of the relaxation frequency for the reorientation around the short molecular axis.

2. The addition of the component B destroys the intercalated structure indicated by an increase of the layer distance. It should be emphasized, that in a similar system reported earlier[6] the *d*-values of the laterally branched substances kept constant after addition of a second component with a short molecular length. There, however the ratio of the molecular length of component A to this of component B was somewhat higher than in the system under consideration. Here, the molecules of component B destroy the host structure, which approaches to an additive behaviour of the *d*-values on concentration range $x_B > 0.4$. Therefore, in this region the molecular length of component A ($L_A = 3.5$ nm) acts as one structure element that means $d = x_A \cdot L_A + x_B \cdot L_B$.

The destruction of the intercalated structure of component A can be also seen in the increasing relaxation frequencies of component A relative to those of compound B (Figure 9) and the low values of $\varepsilon_{\parallel 01}$. The extremely strong tendency of compound A to an antiparallel orientation in the short range decreases continuously by addition of compound B.

The smectic A phase of the rodlike component B is destroyed by addition of component A to a high extent shown in the phase diagram and in the calorimetric measurements. Obviously the molecular geometry of both S_A phases is too different to form an uninterrupted S_A phase range. This is only possible in the nematic phase where the molecular mobility is higher.

References

1. W. H. de Jeu, L. Longa and D. Demus, *J. Chem. Phys.*, **84**, 6410 (1986).
2. H. Heuer, H. Kneppe and F. Schneider, *Ber. Bunsengesellsch. Phys. Chem.*, **93**, 923 (1989).
3. D. Demus, A. Hauser, G. Pelzl, U. Böttger and S. Schönberg, *Cryst. Res. Technol.*, **20**, 381 (1985).
4. G. Pelzl, A. Humke, S. Diele, D. Demus and W. Weissflog, *Liq. Cryst.*, **7**, 115 (1990).
5. R. Dabrowski, B. Wozynska and B. Sosuovska, *Liq. Cryst.*, **1**, 415 (1986).
6. S. Diele, A. Mädicke, K. Knauft, J. Neutzler, W. Weissflog and D. Demus, *Liq. Cryst.*, **10**, 47 (1991).
7. H. Kresse and W. Weissflog, *Phys. Stat. Sol. (a)*, **106**, 89 (1988).
8. H. Kresse, S. Haas, S. Heinemann and F. Kremer, *J. Prakt. Chem.*, **333**, 101 (1991).
9. H. Kresse and Ch. Selbmann, *Z. Phys. Chem. (Leipzig)*, **259**, 897 (1978).
10. N. E. Hill, W. E. Vaughan, A. H. Price and M. Davis, Dielectric Properties and Molecular Behaviour (1969) (Princeton, New Jersey).
11. W. Maier and G. Meier, *Z. Naturforsch*, **16a**, 262 (1961); A. J. Martin, G. Meier and A. Saupe, *Symp. Faraday Soc. No. 5*, 119 (1971).