Evidence for the Existence of the McMillan Phase in a Binary System of a Metallomesogen and 2,4,7-Trinitrofluorenone**

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The design of soft matter, well organized at different length scales is a topic of interdisciplinary research which is important for both materials science and life science. Such materials include block copolymers, surfactant aggregates, colloidal systems, and liquid crystals. Layer structures such as lamellar phases of detergent–solvent systems and smectic liquid crystals appear to be quite simple and belong to the best known and most investigated states of soft matter. Interest has focused again on these systems in light of the recent discovery of rather complex new types of supramolecular organization with interesting new properties. For example, macroscopic polar order and spontaneous chiral symmetry breaking have been realized with achiral banana-shaped molecules organized in liquid layers.[1]

Nearly three decades ago a quite unusual layer structure was predicted theoretically.[2] In addition to the well-known subgroups of smectic phases, such as SmA and SmC (see Figure 1a and b, respectively), a biaxial smectic phase with orthogonally aligned molecules in the layers should exist. In contrast to the well-known SmA phase, in which the molecules can freely rotate around their long axes and which therefore is optically uniaxial, in this new phase the molecules should have a preferred direction within the layer planes (SmA_b, see Figure 1c) leading to an optical biaxiality of this orthogonal phase.[3] This new phase is associated with a reduction of the symmetry from $D_{\infty h}$ (SmA) to D_{2h} (SmA_b). Further possible variants of packing can occur in the case of banana-shaped molecules for which the packing of the molecules can lead to a polarization within the layers (Figure 1d).[1]

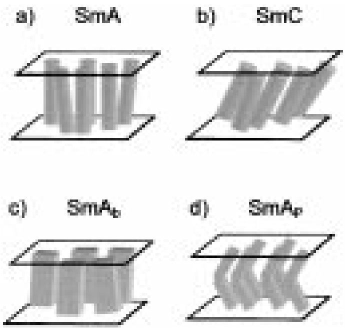

Figure 1. Schematic representation of a section of one layer of a) a smectic A (SmA) phase, b) a smectic C (SmC) phase (in the SmC phase the molecules in the adjacent layers have the same tilt direction (synclinic interlayer correlation), in the SmC_A subtype the tilt direction alternates from layer to layer (anticlinic interlayer correlation)), c) a biaxial smectic (SmA_b) phase, built up by orthogonally arranged boardlike molecules (McMillan phase, C_M), and d) a possible arrangement in a smectic A phase with polarization (SmA_p) within the layers.

de Gennes suggested calling the biaxial smectic A phase (SmA_b) the C_M phase, where M stands for McMillan.[2] Brand, Cladis, and Pleiner have predicted the properties of this special phase.[4] Accordingly, a Schlieren texture comprising exclusively two-brush disclinations (defects of the strength $S = \pm 1/2$; two dark brushes meet at the disclination points, see, for example, Figure 2b) should be observed by microscopy between crossed polarizers. Many attempts have been made to realize such a nontilted biaxial smectic mesophase in practice. This phase can be expected to occur for molecules with a pronounced boardlike (sanidic) shape, and there have been two reports in which such SmA_b phases were observed conoscopically after alignment of the materials in a magnetic[5] or an electric field;[6] however, in both cases, for the nonaligned samples, the textural pictures revealed uniaxial SmA phases.[5, 6]

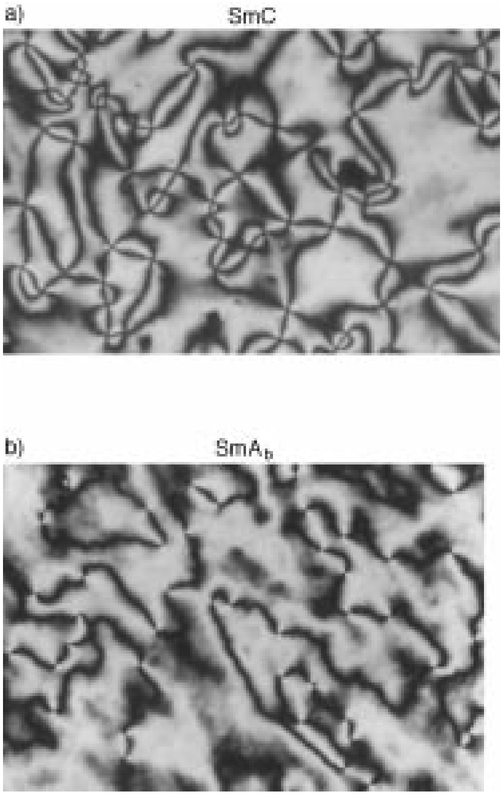

Figure 2. Schlieren textures of a) the SmC phase of **1** at 108 °C and b) the SmA_b phase of the **1**/TNF mixture at 120 °C in the homeotropically aligned regions (crossed polarizers).

Herein we report the first example of a McMillan phase that shows the predicted textural characteristics of this phase together with an orthogonal alignment of the molecules within the layers as proven by X-ray diffraction studies. In contrast to earlier reported SmA_b phases, in our case this organization is formed spontaneously in the absence of external fields.

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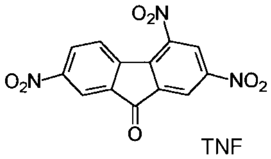
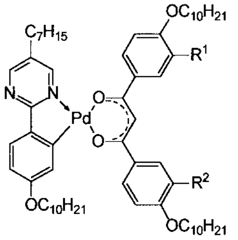
This new phase occurs in binary systems consisting of the metallomesogens **1**–**3**[7, 8] and the electron acceptor 2,4,7-trinitrofluorenone (TNF, m.p. 175 °C).[9] The transition temperatures of compounds **1**–**3** and of their binary systems with TNF are given in Table 1. The system **1**/TNF, as a representative example, was investigated in more detail.



TNF

The binary phase diagram of the **1**/TNF system is shown in Figure 3. In the contact region between **1** and TNF, the SmC phase and the SmA phase of the pure compound are drastically destabilized. At a TNF concentration of about 4–6 mol % a new phase is induced (M), which is continuously stabilized until the TNF concentration reaches 60 mol %, whereafter the stability strongly decreases again.[10] Between crossed polarizers, this induced phase M occurs with a typical fan-shaped texture (Figure 4 a, left-hand side), interrupted by extended regions in which the molecules are homeotropically aligned. These areas are optically isotropic and appear completely black between crossed polarizers. Hence, this phase M shows the typical textural features of a SmA phase, and because this phase M is separated from the SmA phase of the pure compound **1** by an isotropic liquid region it is incompatible with the latter and therefore a different structure is expected.

Table 1. Phase transition temperatures of the pure compounds **1**–**3**[8] and their mixtures with TNF[a] as determined by polarized light optical microscopy.[a]



Compound	R^1	R^2	Pure compounds T [°C]	T_{max} [°C] with TNF[b]
1	H	H	K 113 SmC 117 SmA 133 Iso	SmA_b 178 M 210 Iso
2	$OC_{10}H_{21}$	H	K 117 (SmA 101) Iso	SmA_b 162 M 179 Iso
3	$OC_{10}H_{21}$	$OC_{10}H_{21}$	K 115 Iso	SmA_b 128 M 165 Iso

[a] Abbreviations: K = crystalline solid, SmC = smectic C phase, SmA = smectic A phase, SmA_b = optically biaxial smectic A phase (McMillan Phase, C_M), M = induced mesophase with the typical texture of a SmA phase, Iso = isotropic liquid. [b] The maximum temperatures for the transitions SmC_M–M and M–Iso, as obtained by investigation of the contact regions between compounds **1**–**3** and TNF are given. They can, however, occur at different TNF concentrations (see Figure 3).

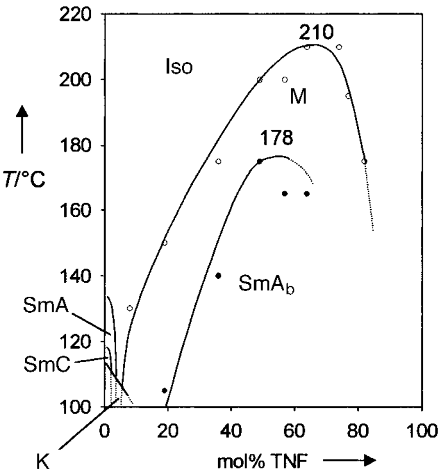


Figure 3. Simplified binary phase diagram of the **1**/TNF system. Broad biphasic regions (at ca. 20 K) were found for the transition from the induced M phase to the isotropic liquid state (Iso). Only the upper temperature limits of these biphasic regions are shown in the phase diagram; for the abbreviations, see footnote [a] in Table 1.

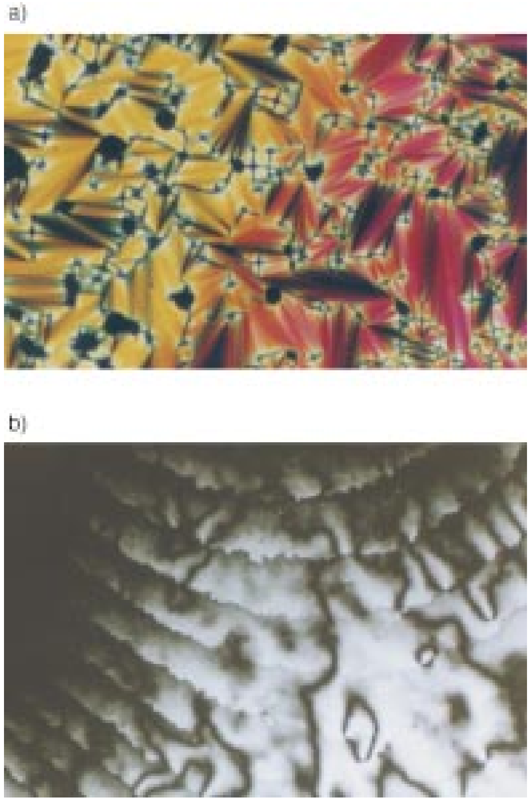


Figure 4. Transition from the induced high-temperature mesophase M to the SmA_b phase in the **1**/TNF mixture as seen between crossed polarizers at 140 °C: a) in regions with a fan-shaped texture (M: yellow fans at the left-hand side, SmA_b: red fans at the right-hand side), b) in the homeotropically aligned regions of the induced phase (M: dark area at the left-hand side, SmA_b: birefringent texture at the lower right-hand side) with the typical stripe pattern occurring directly at the transition.

In the following we focus our interest on a new phase found at lower temperature and at a TNF content of at least about 20 mol %. At the transition into this low-temperature phase only a change of the birefringence can be detected in the region with the fan-shaped texture (see Figure 4 a, right-hand side). In the homeotropically aligned regions the transition can be seen by the formation of a striped pattern (see Figure 4 b)[11] which immediately turns into a Schlieren texture (see Figure 2 b). The low-temperature phase cannot be homeotropically aligned, which indicates that this phase should be optically biaxial. Thus, the SmC phase of the pure compound and the induced low-temperature phase are optically biaxial phases and both have Schlieren textures. However, exclusively four-brush disclinations ($S = \pm 1$) can be found in the SmC phase of pure **1** (see Figure 2a), whereas exclusively two-brush disclinations ($S = \pm \frac{1}{2}$) were found in the induced phase of the mixed system (see Figure 2b). Hence, both phases should be quite different, but most importantly, the textural features of the induced low-temperature phase (Schlieren texture with two-brush disclinations and fan-shaped texture) exactly match with the textural features predicted theoretically for the $\mathrm{SmA_b}$ phase (McMillan phase).[4]

To investigate the induced mesophases in more detail, X-ray scattering experiments with the pure compound **1** and with a defined mixture of compound **1** and TNF (**1**:TNF = 2:1; phase sequence $\mathrm{SmA_b}$ 140 M 180 Iso) have been performed by using the Guinier film method and by investigation of well aligned monodomains with a two-dimensional detector.

The X-ray diffraction pattern of the pure compound **1** (Guinier film method) is typical for conventional SmA and SmC phases. One sharp reflection is found in the small-angle region with $d = 2.94$ nm at 130 °C (SmA phase) and with $d = 3.04$ nm at 112 °C (SmC phase).[12] Additionally, in both phases a diffuse scattering is observed in the wide-angle region. In contrast, the X-ray diffraction pattern of the induced mesophases occurring in the binary mixture is more complicated. The pattern of the nonoriented samples of the low-temperature phase display sharp reflections with instrumentally limited line shapes at $q_1 = 2\pi/2.8\ \mathrm{nm^{-1}}$, $q_2 = 2q_1$, and $q_3 = 3q_1$ ($T = 130$ °C). This indicates that this phase has a well-defined layer structure with a layer thickness of 2.8 nm at 130 °C and 2.7 nm at 170 °C. Beside these reflections four diffuse scattering maxima of weak intensity appear at $q_4 = 2\pi/1.08\ \mathrm{nm^{-1}}$, $q_5 = 2\pi/0.68\ \mathrm{nm^{-1}}$, $q_6 = 2\pi/0.47\ \mathrm{nm^{-1}}$, and $q_7 = 2\pi/0.34\ \mathrm{nm^{-1}}$. The pattern, obtained by investigation of monodomains[13] of this phase is shown in Figure 5a. It displays preferred directions of the scattering. The scattering with q_1, q_2, and q_3 is positioned at the meridian, and the scattering with q_4 and q_7 is directed perpendicular to these, indicating additional electron density modulations perpendicular to the layer normal. The scattering with q_7 corresponds to 0.34 nm, a value typical for the face-to-face distance in aromatic π-stacking systems. It has a rather small full width at half maximum, indicating a rather well-defined parallel alignment of the flat molecules. The position of the scattering at the equator of the pattern proves that the aromatic parts of the molecules are aligned parallel to the layer normal, although optical biaxiality is observed. The scattering with $q_4 = 2\pi/1.08\ \mathrm{nm^{-1}}$ can be related to the width of the aromatic cores of the molecules **1** (1.1 nm according to CPK models). It is very diffuse, indicating that this electron density modulation is only of short-range order. The diffuse scattering with q_6 does not show any preferred direction and can be attributed to the average distance between the highly disordered alkyl chains (0.47 nm). The diffuse scattering with q_5 is of very low intensity and could be detected by the Guinier film method only. The latter may be due to the mean distance between short-range ordered fluctuating clusters built up between **1** and TNF molecules (0.68 nm).

Hence, all experimental findings confirm that the low-temperature phase of the binary mixture **1**/TNF should have the structure shown in Figure 6b. It is a layer structure built up by flat molecules arranged parallel to each other and orthogonal to the layer planes. Within the layers the molecules have two different degrees of positional order. In one direction (z) there is a rather well-defined face-to-face organization of the molecules, whereas in the other direction (x) only short-range positional order is found. In other words, this phase has exactly that structure which has been suggested for the McMillan phase.[14, 15] Remarkably, despite the rather high degree of order, this phase is highly fluid similar to conventional SmA and SmC phases.

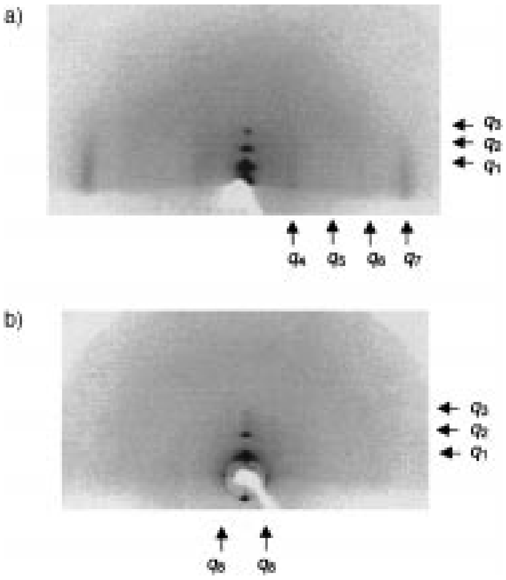


Figure 5. Two-dimensional (2D) X-ray diffraction pattern of a monodomain of the **1**/TNF mixture at 30 °C (a) and at 175 °C (b).

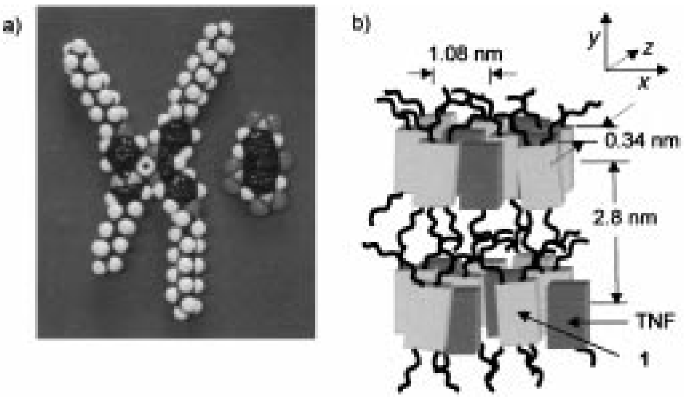


Figure 6. Arrangement of the molecules in the $\mathrm{SmA_b}$ phase of the mixed system **1**/TNF: a) CPK models of molecule **1** and TNF, b) proposed organization of the molecules in the $\mathrm{SmA_b}$ phase (corresponds to Figure 1c).

The X-ray diffraction pattern changes a little in the high-temperature phase (M). Again, the scattering with $q_1 - q_3$ is observed at the meridian (Figure 5b). Also the diffuse scattering with q_6 resulting from the liquidlike chains remains. The intensities of the scattering with q_4, q_5, and q_7 decrease with increasing temperature and could not be detected with the 2D detector. Only by the film method and with sufficiently long exposure time was the very weak and smeared out scattering with q_4 and q_7 observed. These findings resemble those discussed for the so-called $D_{ho}-D_{hd}$ transitions,[16] for which the parallel packing of disclike molecules in columns gets lost. In the case under discussion the decrease in the intensity corresponds to the increase of the rotational disorder within the layers around the axes parallel to the layer normal, that is the orientational order of the molecules within the layers is reduced which leads to the loss of optical biaxiality. However, striking is the (reproducible) appearance of a spotlike reflection nearly perpendicular to the layer normal at the transition to the high-temperature phase. The appearance of this reflection implies a periodicity perpendicular to the layer normal. Thus, because reflections with higher or mixed Millers indices [(20) or (11)] cannot be observed and because the *d* value of the additional peak corresponds with the length of the molecules (equal with the period along the meridian), we assume that the additional reflection is caused by molecular rotational disorder around an axis perpendicular to the flat molecular planes. This suggests a lamellocolumnar structure of this mesophase,[17] but further studies are necessary to exclude other possibilities.

In summary, the results of texture observations and the X-ray diffraction studies reported provide experimental proof for the theoretically predicted biaxial smectic A phase (McMillan phase). In contrast to earlier reported SmA_b phases this special molecular organization is obtained spontaneously, without previous alignment in an external field.[18] The fan-shaped texture indicates a layer structure. The existence of a Schlieren texture proves the biaxiality of the phase, whereas the X-ray pattern of oriented samples prove the orthogonal arrangement of flat molecules in layers. The strong face-to-face packing of the molecules within the layers, indicated by an electron-density wave perpendicular to the layer normal, provides additional confirmaiton of the biaxiality.

Notably, compound **1** itself has the molecular shape necessary for the formation of the SmA_b phase, but the rotation around the molecular long axis is fast, so that only an uniaxial SmA phase can be observed. However, in mixed systems with a sufficiently large TNF concentration the attractive face-to-face interactions between TNF and the flat aromatic cores of compounds **1** strongly reduce the molecular rotation around the long axis, leading to the biaxiality. We suggest that attractive face-to-face attraction could also lead to biaxial nematic phases if the formation of a layer arrangement could be suppressed. Finally it should be mentioned that the dimensions of the TNF molecules fit perfectly with the dimensions of the sublayers of the aromatic core regions of the metallomesogen **1** in the smectic phases (see Figure 6b). This could additionally contribute to the stabilization of this special phase structure over a quite large concentration and temperature region.

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[9] The induction and stabilization of columnar and nematic columnar mesophases of disclike liquid crystalline molecules with TNF is a well-known phenomenon: a) H. Ringsdorf, R. Wüstefeld, E. Zerta, M. Ebert, J. H. Wendorff, *Angew. Chem.* **1989**, *101*, 934; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 914; b) H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff, R. Wüstefeld, *Adv. Mater.* **1990**, *2*, 41; c) K. Praefcke, D. Singer, B. Kohne, M. Ebert, A. Liebmann, J. H. Wendorff, *Liq. Cryst.* **1991**, *10*, 147; d) K. Praefcke, D. Singer, B. Gündogan, K. Gutbier, M. Langner, *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 1358; e) K. Praefcke, J. D. Holbrey, N. Usol'tseva, *Mol. Cryst. Liq. Cryst.* **1996**, *288*, 189; f) K. Praefcke, D. Singer, *Handbook of Liquid Crystals*, *Vol. 2B* (Eds.: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**, p. 945.

[10] The phase diagrams of the systems **2**/TNF and **3**/TNF are similar with the difference that the SmC phase is missing.

[11] The origin of this stripe pattern is not clear.

[12] Usually, a decrease of the layer thickness in the SmC phase occurs due to the appearance of a tilt, but examples are known, in which the decrease is compensated by an increase of the length of the molecules caused by changes of the molecular conformation on decreasing the temperature, see for example: W. Weissflog, L. Kovalenko, I, Wirth, S. Diele, G. Pelzl, H. Schmalfuss, H. Kresse, *Liq. Cryst.* **2000**, *27*, 677.

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[14] Subtypes of the SmC phases such as the anticlinic SmC_A phase can be excluded because in the 2D X-ray pattern the outer diffuse scattering maxima are positioned at the equator. That exclusively two-brush disclinations were detected in the Schlieren texture excludes the SmA_p phase (Figure 1 d), for which the occurrence of two-brush disclinations is excluded by theory.[4]

[15] This phase can also be regarded as a special subtype of the discotic lamellar phases (D_L). However, to the best of our knowledge all reported D_L phases are built up by layers of tilted disclike molecules: K. Ohta, H. Muroki, A. Takagi, K.-I. Hatada, H. Ema, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst.* **1986**, *140*, 131; Y. Shimizu, M. Miya, A. Nagata, K. Ohta, A. Matsumura, I. Yamamoto, S. Kusubayashi, *Chem. Lett.* **1991**, 25.

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