

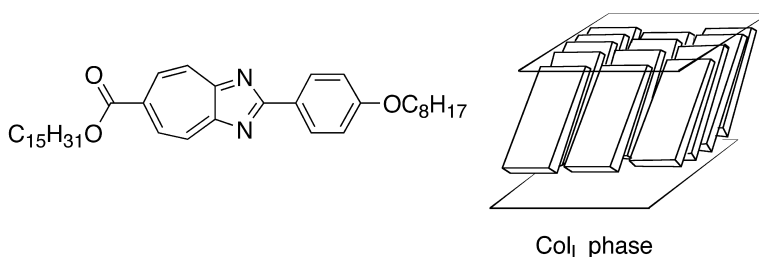
Communication

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A Novel Biaxial Smectic Liquid Crystalline Phase Formed by Rodlike Molecules with a 1,3-Diazaazulene Skeleton

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Recently, a great deal of attention has been paid to the self-organized states of liquid crystals (LCs), which have wide application in, for example, optoelectronic devices and electron-transporting materials.¹ Especially, several novel and quite interesting types of LC layer structures (smectic LCs) with special properties, such as optical biaxiality² and macroscopic polar order,³ caused by a restricted rotation of the molecules within the layers have been reported in recent years. From the standpoint of developing new types of LC materials, we are currently using the troponoid core and have often observed that these materials are mesomorphic, whereas the corresponding benzenoids are not.⁴ Typically, they form smectic phases, as the troponoids have a large dipole moment and an ionic character, which reinforce microsegregation⁵ when nonpolar alkyl or alkoxy substituents are grafted to the polar seven-membered ring.

In this communication, we have focused on the 1,3-diazaazulene skeleton, which is a candidate for LCs, with an especially large dipole moment ($\mu = 4.03$ D), located within the heteroaromatic core structure.^{6,7} In this report we will show that some homologues of **1** have a smectic mesophase with a quite unusual X-ray diffraction pattern. It is proposed that this new fluid smectic phase has a structure related to lamellar columnar (Col_L) phases formed by some disklike^{8–10} and boardlike molecules^{11–13} and a special type of metallomesogen.¹⁴

1,3-Diazaazulene derivatives **1a–c** were prepared by condensation of 5-alkoxycarbonyl-2-methoxytropones¹⁵ and 4-alkoxyphenylamidines as described in the Supporting Information. Investigation of these materials was performed using polarized light optical microscopy and differential scanning calorimetry (DSC) and X-ray diffraction analysis of aligned samples as well. The transition temperatures and enthalpies are summarized in Table 1. At temperatures between 129 and 132 °C, the optical textures of **1a** are characterized by regions of schlieren and focal-conic fan textures, similar to those observed for conventional smectic C (SmC) phases (Figure 1a). On cooling from the SmC phase, these textures change to a mosaic- and a fingerprint-like texture, respectively (Figure 1b). Compound **1b** has similar textures to **1a**, while **1c** shows exclusively SmC textures.

The X-ray diffraction pattern of an aligned sample of compound **1a** was investigated at 129 °C in the SmC phase, and a sharp reflection was observed in the small-angle region, which is related

Table 1. Phase Transition Temperatures ($T/^\circ\text{C}$) and Enthalpy Values ($\Delta H/\text{kJ mol}^{-1}$)^a

comp.	<i>n</i>	phase transitions						
		Cr ₁	Cr ₂	Col _L	SmC	Iso		
1a	8	•110• (10.4)	•124• (4.1)	•129• (5.5)	•132• (3.8)			
1b	10	•110• (8.0)	•116• (8.0)	•121• (4.1)	•127• (3.2)			
1c	12	•125• (6.7)	•126• (13.6)	•129• (1.5)				

^a Determined by DSC (second heating scan, 1 °C min⁻¹). ^b Obtained from the first cooling scan because the Cr–Col_L transition is partially overlapped by a Cr–Cr transition in the heating scan.

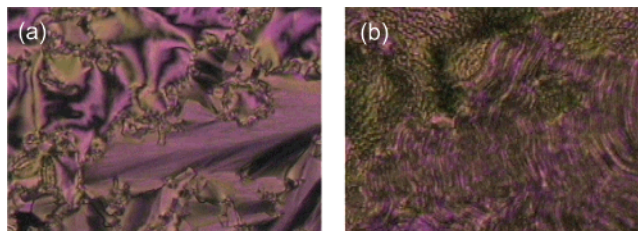


Figure 1. Textures of **1a** observed between crossed polarizers (a) SmC phase at 131.5 °C and (b) Col_L phase at 127 °C (the same section as shown in (a)).

to the layer spacing of $d = 33.7$ Å. The diffuse scattering (maximum at $D = 4.5$ Å) indicates that the alkyl chains have a liquidlike disordered structure. The maxima are located out of the equator, indicating a tilted structure with a tilt angle of 38°.

The X-ray diffraction pattern of the low-temperature mesophase at 128 °C (Figure 2a) is rather complex and quite distinct from that of the SmC phase. Three peaks assigned to the (001), (002), and (003) reflections of a layer structure were observed at 30.5, 15.2, and 10.0 Å on the meridian and indicate a regular repetition of layers with the periodicity $d = 30.5$ Å. In addition, three reflections with maxima corresponding to $D_1 = 5.4$, $D_2 = 4.4$, and $D_3 = 3.7$ Å were detected in the wide-angle region. The diffuse scattering at $D_2 = 4.4$ Å corresponds to the mean distance between the fluid alkyl chains and has four crescentlike maxima, located out of the equator, indicating an average tilt angle of about 18°. Another broad halo at $D_3 = 3.7$ Å also has four crescentlike maxima, in this case corresponding to a tilt angle of 45°. Additionally, two rather sharp halos at $D_1 = 5.4$ Å are centered on the equator.

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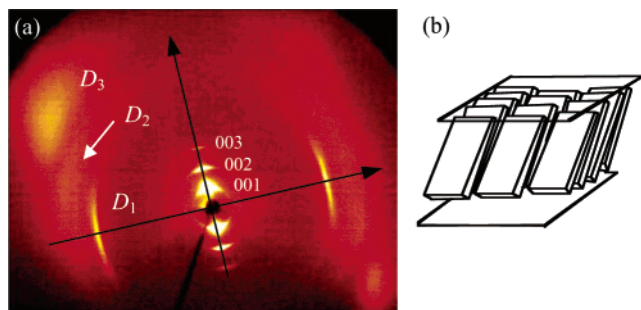


Figure 2. (a) X-ray diffraction pattern of an aligned sample of **1a** at 128 °C; the alignment was obtained by slow cooling (0.01 K min^{-1}) of a droplet of the sample (diameter ca. 1 mm) on a glass plate. Within the drop a monodomain is generated by surface interaction which is inclined with respect to the substrate plane; the incident X-ray beam (wavelength of the Cu $K\alpha$ line, 0.154 nm) was parallel to the substrate and the scattered intensity has been recorded using a 2D detector (HI-Star, Siemens, sample detector distance: 90 mm); due to the experimental setup the scattering in the lower part is shadowed; (b) packing model for the Col_L phase.

The presence of diffuse maxima in the wide-angle region confirms the truly LC nature of this mesophase. The occurrence of three distinct scattering angles in this region suggests that the rotation of the molecules around their long axis is greatly restricted. The scattering corresponding to $D_3 = 3.7 \text{ \AA}$ has a value which is quite typical for face-to-face distances between flat aromatic molecules. It is very diffuse, indicating that the electron density modulation has only short-range order. The position of the scattering out of the equator indicates a 45° tilted arrangement of these cores. The diffuse scattering at $D_2 = 4.4 \text{ \AA}$ is attributed to the mean distance between the fluid alkyl chains, which have a smaller average tilt angle. The scattering at $D_1 = 5.4 \text{ \AA}$ can be related to the width of the aromatic cores of the molecule **1a** (5.4 \AA as calculated by MM2). It has a rather small full width at half-maximum, indicating a rather well-defined lateral distance between them. These maxima are located on the equator, which indicates that the lateral direction of the aromatic cores is, in average, parallel to the layer planes. Hence, a model such as that shown in Figure 2b can be proposed, where the molecules are strongly tilted with respect to the long axis of the aggregates and the calamitic molecules have a restricted rotation around their long axis. This may be due to the flat, nontwisted structure of the aromatic 2-phenyl-1,3-diazaazulene core (MM2 calculations) and to the dipolar nature of this moiety, both of which contribute to attractive face-to-face interactions between adjacent molecules to form columnar aggregates. These columnar aggregates organize side by side with the formation of layers of the aromatic cores, separated by layers of fluid alkyl chains.

The reflections with maxima at $D_1 = 5.4 \text{ \AA}$ indicate a well-defined repeat distance parallel to the layer planes, caused by the parallel organization of the columns. Remarkably, however, no cross reflections, typical for a 2D organization of columns (as in columnar mesophases), can be found in the diffraction pattern. This means that the columns in adjacent layers have a long-range orientational, but only a short-range positional correlation. In other words, the individual layers can slide with respect to each other, as suggested for the sliding columnar phases.¹⁶ This organization of the molecules is closely related to the Col_L mesophases, formed by some disklike or boardlike molecules.^{8–13} However, the Col_L mesophase reported herein is formed by conventional rodlike molecules.¹⁷ Additionally, the mesophase appears at temperatures below a conventional SmC phase, i.e. by restriction of the molecular rotation around the long axis. Therefore, this phase can also be regarded as a novel type of tilted smectic low-temperature phase. However, in contrast to all

known tilted lamellar phases of calamitic molecules with restricted rotation around the molecular long axis (K and H mesophases¹), which in fact represent disordered crystalline mesophases with a 3D lattice and an *edge-to-face* organization of the aromatic cores, the molecules **1a** adapt a *face-to-face* organization in the mesophase reported herein. Furthermore, within the layers, the long-range positional order occurs only in one of the lateral directions, and a positional correlation between adjacent layers is missing. Hence, they represent truly LC phases.

By elongation of the terminal alkyl chains the stability of the Col_L phase is at first reduced (compound **1b**), and finally it is completely replaced by the SmC phase (compound **1c**). It seems that longer alkyl chains, due to their liquidlike nature, do not only increase the layer distance, d , but can also separate the molecules within the layers, leading to the loss of the face-to-face organization of the rigid aromatic units.

These results show that fine-tuning of the molecular structure of quite simple rodlike molecules can lead to amazingly complex new mesophase morphologies. Additionally, these LC phases with face-to-face arrangement of aromatic π -systems should provide charge transport properties. Hence, these materials may be promising candidates in the field of organic semiconductors, photoconductors, and other applications.^{12,13}

Supporting Information Available: Synthesis and analytical data of compounds **1a–c** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals* VCH: Weinheim 1998.
- (a) Pratiha, R.; Madhusudana, N. V.; Sadashiva, B. K. *Science* **2000**, *288*, 2184–2187. (b) Hegmann, T.; Kain, J.; Diele, S.; Pelzl G.; Tschierske, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 887–890.
- (a) Niori, T.; Sekine, F.; Watanabe, J.; Furukawa T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231–1233. (b) Dantlgraber, G.; Baumeister, U.; Diele, S.; Kresse, H.; Lühmann, B.; Lang, H.; Tschierske, C. *J. Am. Chem. Soc.* **2002**, *124*, 14852–14853.
- (a) Mori, A.; Uchida, M.; Takeshita, H. *Chem. Lett.* **1989**, 591–592. (b) Mori, A.; Takeshita, H.; Kida, K.; Uchida, M. *J. Am. Chem. Soc.* **1990**, *112*, 8635–8636. (c) Mori, A.; Kato, N.; Takeshita, H.; Uchida, M.; Taya, H.; Nimura, R. *J. Mater. Chem.* **1991**, *1*, 799–803. (d) Mori, A.; Takematsu, S.; Takeshita, H. *Chem. Lett.* **1997**, 1009–1010.
- Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529–543.
- First examples of conventional nematic and smectic phases were reported by: (a) Enzenberg, H.; Schödl, D.; Zschke, H. *Z. Chem.* **1982**, *22*, 59–60. (b) Krieg, B.; Kuhn, T. *Mol. Cryst. Liq. Cryst.* **1982**, *145*, 59–72.
- Kurita, Y.; Kubo, M. *J. Am. Chem. Soc.* **1957**, *79*, 5460–5463.
- Davison, P.; Levelut, A. M.; Strzelecka, H.; Gionis, V. *J. Phys. Lett.* **1983**, *44*, 823–828.
- (a) Shimizu, Y.; Miya, M.; Nagata, N.; Ohta, K.; Matsumura, A.; Yamamoto, I. *Chem. Lett.* **1991**, 25–28. (b) Shimizu, Y.; Miya, M.; Nagata, A.; Ohta, K.; Yamamoto, I.; Kusabayashi, S. *Liq. Cryst.* **1993**, *14*, 795–805.
- Sakashita, H.; Nishitani, A.; Sumiya, Y.; Terauchi, H. Ohta, K.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* **1988**, *163*, 211–219.
- Pressner, D.; Göltner, C.; Spiess, H. W.; Müllen, K. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1362–1364.
- Struijk, C. W.; Sieval, A. B.; Dakhorst, J. E. J.; van Dijk, M.; Kimkes, P.; Koehorst, R. B. M.; Donker, H.; Schaafsma, T. J.; Picken, S. J.; van de Craats, A. M.; Warman, J. M.; Zuilhof, H.; Sudhölter, E. J. R. *J. Am. Chem. Soc.* **2000**, *122*, 11057–11066.
- Méry, S.; Haristoy, D.; Nicoud, J.-F.; Guillon, D.; Diele, S.; Monobe, H.; Shimizu, Y. *J. Mater. Chem.* **2002**, *12*, 37–41.
- El-ghayoury, A.; Douce, L.; Skoulios, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1255–1258.
- Mori, A.; Hashimoto, M. Unpublished results.
- Lubensky, T. C.; O'Hern, C. S. In *Slow Dynamics in Complex Systems: Eighth Tohwa University International Symposium*; Tokuyama, M., Oppenheim, I., Eds.; The American Institute of Physics: Woodbury, NY, 1999; pp 105–116.
- Mesogens with a [1]benzothieno[3,2-*b*] [1]benzothiophene core (ref 13) can also be regarded as nearly rodlike, but their mesophases are optically uniaxial, having quite distinct diffraction pattern, and in these mesophases the molecules are organized in statistically distributed blocks of molecular pairs.

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