Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A re-entrant smectic C phase in a sequence smectic C-oblique columnar-smectic C-nematic

W. Weissflog[ab]; M. Rogunova[ab]; I. Letko[ac]; S. Diele[ac]; G. Pelzl[ac]
[a] Max-Planck-Gesellschaft, Halle, Germany [b] AV Topchiev Institute of Petrochemical Synthesis, Moscow, Russia [c] Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Halle, Germany

To cite this Article Weissflog, W. , Rogunova, M. , Letko, I. , Diele, S. and Pelzl, G.(1995) 'A re-entrant smectic C phase in a sequence smectic C-oblique columnar-smectic C-nematic', Liquid Crystals, 19: 4, 541 — 544
To link to this Article: DOI: 10.1080/02678299508032016
URL: http://dx.doi.org/10.1080/02678299508032016

LIQUID CRYSTALS, 1995, VOL. 19, NO. 4, 541–544

A re-entrant smectic C phase in a sequence smectic C–oblique columnar–smectic C–nematic

by W. WEISSFLOG‡, M. ROGUNOVA‡, I. LETKO§, S. DIELE§, and G. PELZL§*

†Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systeme, Mühlpforte 1, 06108 Halle, Germany

‡AV Topchiev Institute of Petrochemical Synthesis, Leninski Prospect 29, 117991 Moscow, Russia

§Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, 06108 Halle, Germany

(*Received 15 May 1995; accepted 21 June 1995*)

A new six-ring double-swallow-tailed compound is presented which exhibits a re-entrant smectic C phase in the sequence smectic C–oblique columnar–smectic C–nematic. This unusual sequence detected by observation of the optical textures and by X-ray investigations is also confirmed by the phase diagrams with homologous compounds.

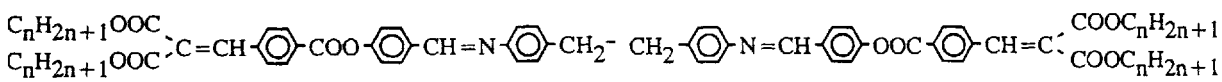
It was shown by the Bordeaux group that five- or six-ring tetracatenar compounds whose terminal alkyl chains are positioned in the *p*- and *m*-positions can exhibit both lamellar and columnar phases [1, 2]. The lamellar phase is always a smectic C phase because, for tetracatenar compounds, a tilted alignment allows a far greater packing efficiency compared with a molecular arrangement perpendicular to the smectic layer planes. The smectic C phase is the low temperature phase with respect to the columnar phases which were found to be hexagonal columnar or oblique columnar phases [1, 2]

Double-swallow-tailed compounds are special variants of tetracatenar compounds where the four terminal aliphatic chains are not directly attached at the terminal rings, but at a terminal linking group [3, 4}.

Five- or six-ring double-swallow-tailed compounds with an intermediate length of the terminal chains are also able to form both lamellar and columnar phases [4, 5]. But in this case the smectic C phase occurs at higher temperatures than the columnar phase.

In this paper we present a double-swallow-tailed compound which exhibits a smectic C phase together with a columnar phase, but also a re-entrance of the smectic C phase on cooling the columnar phase.

We used for our investigations homologous double-swallow-tailed compounds of the following general formula:



The phase behaviour and the transition temperatures of these compounds are given in table 1. The synthesis is described in [6]. The undecyloxy and tridecyloxy homologues (**DS11** and **DS13**) were used as mixing components with the dodecyloxy homologue (**DS12**).

The phase transition temperatures were determined by polarizing optical microscopy and differential scanning calorimetry (DSC7, Perkin–Elmer). The phases were identified by observation of microscopical textures and by X-ray diffraction measurements. These preliminary X-ray studies have been performed on non-oriented samples using a Guinier camera and a Guinier goniometer. The phase diagrams of two binary systems were established by the contact method and by determination of the transition temperatures for samples of known concentration.

The remarkable result of our investigations is the unusual phase sequence for the homologue **DS12**. For this compound, the nematic phase appears as a characteristic marbled or schlieren texture. On cooling the nematic phase, a smectic C phase arises at 187°C which exhibits a schlieren texture (see figure 1), or sometimes a broken fan-shaped texture. Between 154°C and 149°C, the schlieren texture of the smectic C phase is transformed into a texture which resembles a fan-shaped texture (see figure 2). On further cooling, the smectic C phase reappears over an interval between 117–112°C, as indicated by a typical schlieren texture (see figure 3).

The phase transitions from re-entrant smectic C → columnar and from columnar → smectic C are indicated by a broad and a small calorimetric peak, respectively. The transition enthalpies are estimated to be about 200 and 400 J mol^{-1}, respectively.

The re-entrance of the smectic C phase is clearly

*Author for correpondence

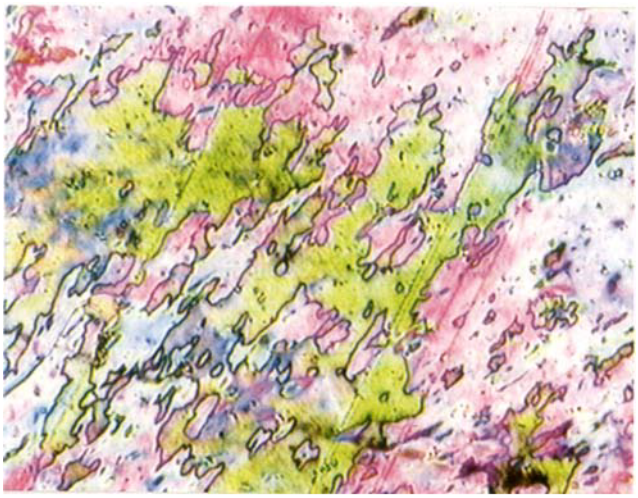


Figure 1. Schlieren texture of the smectic C phase of compound **DS12** (160°C, magnification: 100 ×).

Figure 2. Fan-like texture of the D_{ob} phase of compound **DS12** (125°C, magnification: 100 ×).

Figure 3. Schlieren texture of the re-entrant smectic C phase of compound **DS12** (113°C, magnification: 100 ×).

Table 1. Phase behaviour and transition temperatures for the compounds **DS11**, **DS12** and **DS13**.

Compound	*n*	Transitions/°C									
DS11	11	Cr106	S_C	189	N	219	I				
DS12	12	Cr95	S_C	117	D_{ob}	154	S_C	187	N	209	I
DS13	13	Cr102	D_{ob}	175	S_C	184	I				

Cr: crystalline; I: isotropic liquid; N: nematic; S_C: smectic C Phase; D_{ob}: olique columnar phase.

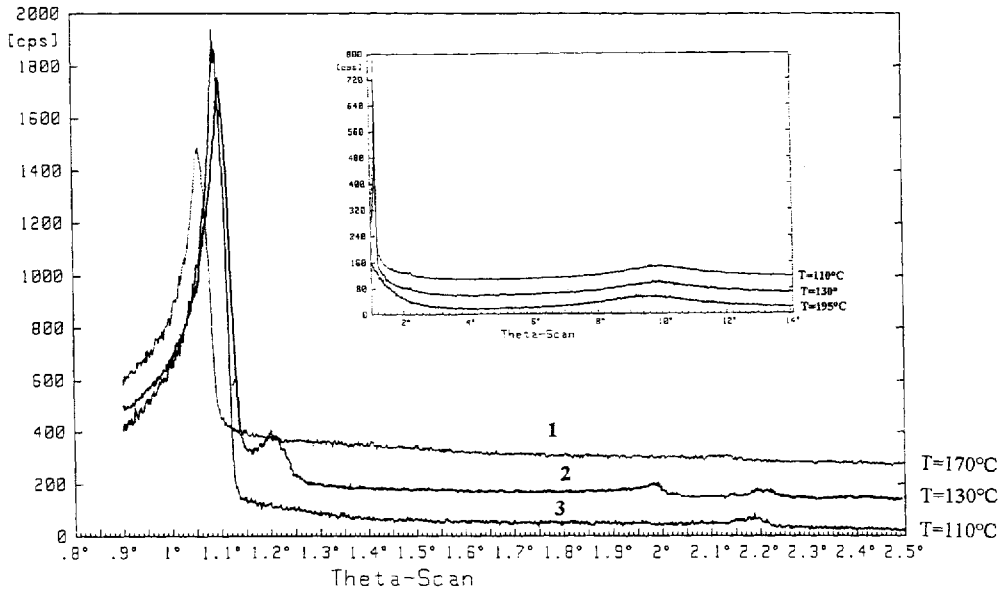


Figure 4. X-ray diffraction pattern for the smectic C (1-170°C), the D_{ob} phase (2-130°C) and the re-entrant smectic C phase (3-110°C) of compound **DS12**. Inset: see text.

detected by X-ray diffraction measurements. The inset in figure 4 displays the scattering profiles in the nematic, D_{ob} and re-entrant smectic C phases. The profile for the high-temperature smectic C phase is omitted for reasons of clearness. According to this part of figure 4, in all phases a diffuse scattering maximum at about 10° is found which corresponds to the average lateral distance between the molecules. In the main body of figure 4, the development of the layer structure with $d = 41{\cdot}6$ Å (curve 1) via a columnar structure (curve 2) and into a re-entrant layer structure with $d = 41{\cdot}5$ Å (curve 3) can be seen by the small angle reflections of scattering diagrams 1 and 3. The additional reflections indicated in curve 2 can be explained by a 2D oblique cell with the parameters $a = 45{\cdot}3$ Å, $b = 41{\cdot}9$ Å and $\gamma = 117{\cdot}6°$. Table 2 gives the observed reflections in the phases under consideration.

The re-entrance of the smectic C phase is confirmed by the phase diagrams relating to mixtures of **DS12** with the homologous compounds **DS11** or **DS13**.

It is seen from the diagram of the binary system **DS11/DS12** (see figure 5) that the smectic C phase of **DS11** is completely miscible with both smectic phases of **DS12**. On the other hand, the re-entrance of the smectic C phase disappears if the concentration of **DS12** is smaller than 76 mol%.

In the binary system **DS13/DS12** (see figure 6), the smectic C phase of **DS13** is only miscible with the high temperature phase of **DS12**, whereas the phase region of the re-entrant smectic C phase is restricted to a small concentration–temperature range.

To our knowledge the unusual phase sequence smectic C-oblique columnar–smectic C–nematic is the first example of a re-entrance of phases in which lamellar and columnar phases participate. This phase sequence could be clearly detected by texture observations, as well as by the X-ray investigations. The small calorimetric effects point to small energetic and structural changes at the transition between the smectic C phases and the columnar phase.

We suppose that the D_{ob} phase belongs to the so-called lamello-columnar phases where the local arrangement of the molecules is similar to that of smectics [2, 7].

Table 2. Bragg angles of the reflections observed in the re-entrant smectic C ($S_{C\,re}$), oblique columnar (D_{ob}) and smectic C (S_C) phases. The corresponding Miller's indices are given in brackets.

T/°C	Phase	Bragg angles/°			
110	$S_{C\,re}$	1·09 (001)			1·18 (002)
130	D_{ob}	1·10 (10)	1·20 (01)	1·98 (11)	2·20 (20)
170	S_C	1·06 (001)			

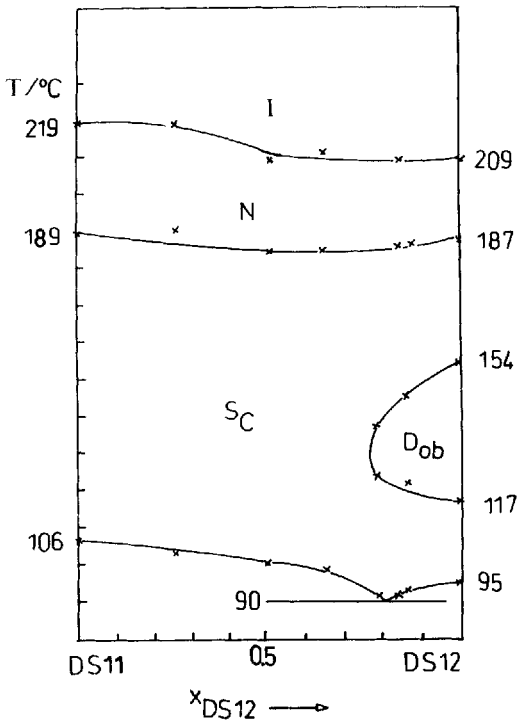


Figure 5. Phase diagram of the binary system **DS11/DS12**.

Further structural investigations will be performed to study transitions between lamellar and columnar phases in more detail.

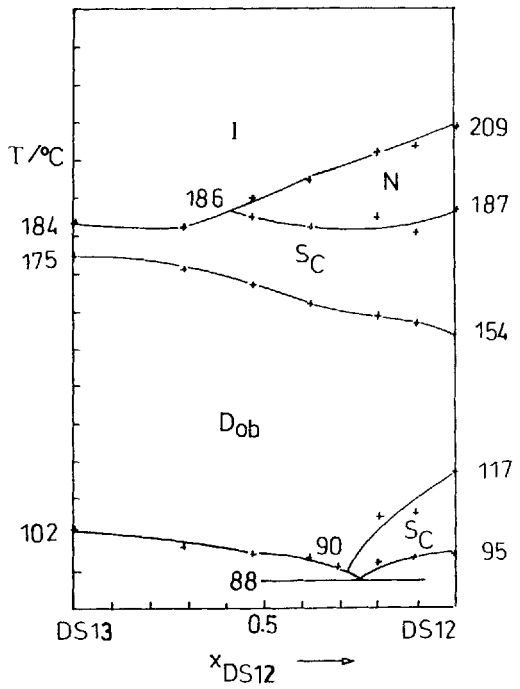


Figure 6. Phase diagram of the binary system **DS13/DS12**.

The financial support of the 'Deutsche Forschungmeinschaft' with the Sonderforschungsbereich 'Anisotrope Fluide' is gratefully acknowledged.

References

[1] Nguyen, H. T., Destrade, C., and Malthête, J., 1990, *Liq. Crystals*, **8**, 797.
[2] Malthête, J., Nguyen, H. T., and Destrade, C., 1993, *Liq. Crystals*, **13**, 171.
[3] Weissflog, W., Wiegeleben, A., Diele, S., and Demus, D., 1984, *Cryst. Res. Technol.*, **19**, 983.
[4] Diele, S., Ziebarth, K., Pelzl, G., Demus, D., and Weissflog, W., 1990, *Liq. Crystals*, **8**, 211.
[5] Weissflog, W., Pelzl, G., Letko, I., and Diele, S., 1995, *Molec. Cryst. liq. Crystals*, **260**, 157.
[6] Weissflog, W., Rogunova, M., Letko, I., Diele, S., and Pelzl, G., in preparation.
[7] Levelut, A. M., Malthête, J., Destrade, C., and Nguyen, H. T., 1987, *Liq. Crystals*, **2**, 877.