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W. Weissflog^a; I. Letko^a; G. Pelzl^b; S. Diele^b

^a Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systeme, Halle, Germany ^b Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Halle, Germany

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Re-entrant isotropic behaviour of a pure double-swallow-tailed compound†

by W. WEISSFLOG*

Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systeme, Mühlporfte 1,
D-06108 Halle, Germany

I. LETKO, G. PELZL and S. DIELE

Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie,
Mühlporfte 1, D-06108 Halle, Germany

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Two new six-ring double-swallow-tailed mesogens were prepared. The phase behaviours of these compounds were studied by optical methods and by calorimetry. One of them shows the very unusual phase sequence crystalline-smectic C-cubic-isotropic-nematic-isotropic.

1. Introduction

Double-swallow-tailed compounds are tetracatenar mesogens. The terminal branches are not directly fixed at the terminal rings, and are in groups such as $-\text{CONR}_2$, $-\text{CH}=\text{C}(\text{COOR})_2$, $\text{COO}-\text{N}=\text{CR}_2$. This chemical structure is different from the structures of biforked and polycatenar substances described by Malthete, Nguyen *et al.* [1-4] which bear two or three alkyloxy groups at each of the terminal phenyl rings. Although all the mesogens mentioned have a comparable molecular shape there are interesting differences in the liquid crystalline properties.

Swallow-tailed compounds involving the chemical structure of dialkyl benzylidenemalonates in the terminal position have been derivatives of interest for a long time [5]. It was found that appropriate four- and five-ring double-swallow-tailed compounds form nematic and smectic C phases [5,6]. But six-ring double-swallow-tailed substances can exhibit, in addition, columnar mesophases, which unlike those of biforked or phasmidic mesogens were identified as rectangular columnar phases [6].

In this paper, we present for the first time two homologous six-ring double-swallow-tailed compounds with a slightly changed chemical structure. As a result of inversion of the direction of two carboxy groups, the derivatives now form additionally a cubic mesophase, whereby for one compound, the cubic phase occurs together with a re-entrant isotropic phase in a spectacular phase sequence.

* Author for correspondence.

† Dedicated to Prof. Alfred Saupe on the occasion of his 70th birthday.

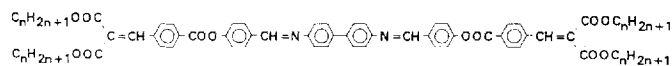
The existence of a re-entrant isotropic phase was observed for the first time by Yu and Saupe [7] in the lyotropic mixture of potassium dodecanoate, decan-1-ol and water. In the field of thermotropic liquid crystals, Destrade *et al.* [8], reported a re-entrant isotropic phase in a binary mixture of discotic compounds: 2,3,7,8,12,13-hexa(4-*n*-dodecyloxybenzoyloxy)truxene and 2,3,7,8,12,13-hexa(*n*-tetradecanoyloxy)truxene. The only pure component in which a stable re-entrant isotropic phase has been observed was described by Warmerdam *et al.*, in 1988 [9,10] and belongs to the same substance class: 2,3,7,8,12,13-hexa(4-*n*-octadecanoyloxy)truxene. Praefcke *et al.* [11] also observed the existence of an unstable re-entrant isotropic phase in mixtures of disc-like 1,2,3,5,6,7-hexakis(substituted phenylenthy-nyl)naphthalines. Two years ago Percec *et al.* [12], described an isotropic re-entrant behaviour for poly-{4-[3,4,5-tris(*n*-dodecanyloxy)benzoyloxy]-4'-[(2-vinyl-oxy)ethoxy]biphenyls} characterized by a low degree of polymerization (about 5) with a narrow molecular-weight distribution.

In summary, for all examples given in the literature, the isotropic re-entrant phase and the upper isotropic phase surround a columnar phase. The shape of all the molecules deviates strongly from being rod-like. Up to now the truxene derivative mentioned above has been the only pure compound exhibiting this rare phenomenon.

Now we can report a second example of a single substance exhibiting a re-entrant isotropic phase.

The substances **1** and **2** (see below) under investigation were obtained by condensation of 4,4'-diaminobiphenyl with the appropriate 4-formylphenyl 4-[2,2-bis(alkyloxy-

carbonyl)ethenyl]benzoates by heating under reflux in ethanol under nitrogen in the presence of toluene-4-sulphonic acid. After cooling, the precipitates were separated and recrystallized from dimethylformamide. The detailed chemical pathway to preparing the compounds will be given in connection with the investigation of the complete homologous series [13].



1 $n = 8$

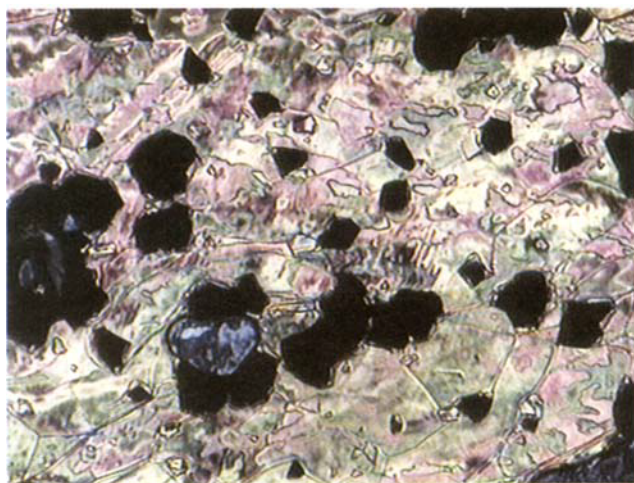
2 $n = 9$

The transition temperatures were determined by microscopical investigations and by calorimetric measurements and are given together with the transition enthalpies (kJ mol^{-1}) in the following scheme:

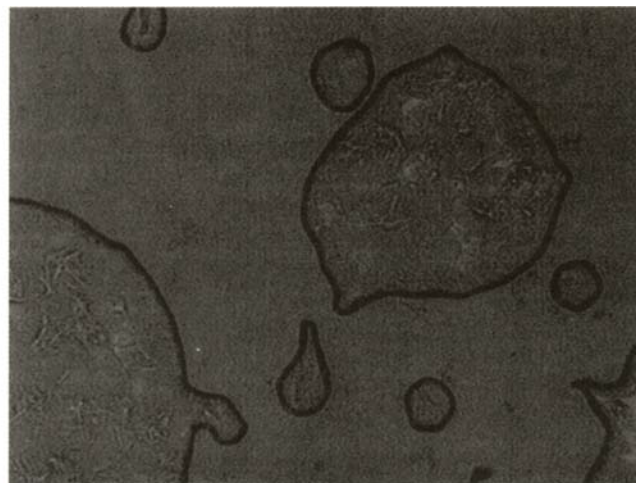
1 Cr 126 S_C 195 cub 243 I_{re} 250 N 312 I
(58.83) (0.89) (2.15) (0.47) (0.39)

2 Cr 125 D_{ob} 158 S_C 195 cub 238 I
(55.10) (0.03) (0.75) (1.90)

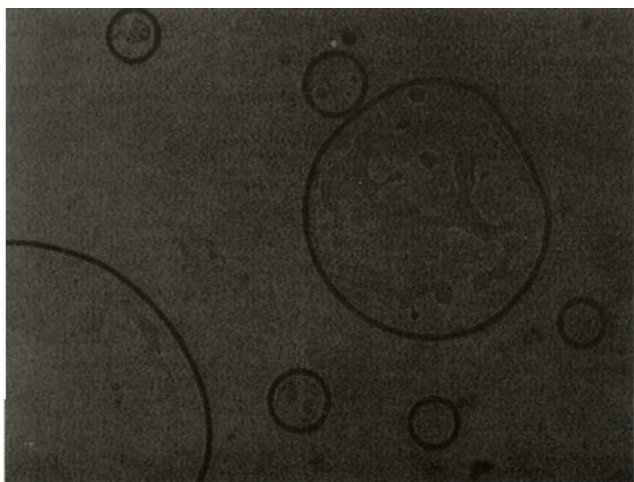
It is seen from the transition scheme that the nonyl homologue **2** shows a columnar D_{ob}, a smectic C phase, and a cubic phase. The S_C phase adopts a typical schlieren



(a)



(b)



(c)



(d)

Figure 1. Microscopic textures of different phases of compound **1** with increasing temperature. (a) Phase transition smectic C–cubic at 201°C. (b) Cubic phase at 210°C. (c) Isotropic phase at 245°C. (d) Phase transition isotropic–nematic on heating at 251°C.

texture or a broken fan-shaped texture. The transition of the smectic C phase into the optically isotropic cubic mesophase is somewhat delayed and occurs over a temperature interval depending on the heating rate. Therefore in the transition scheme, the temperature marking the beginning of this process is given. Also, a clear supercooling of this phase transition can be observed which also depends on the cooling rate. The transition of the cubic into the isotropic phase is difficult to detect because both phases are optically isotropic and therefore dark between crossed polarizers. But at this transition, the viscosity suddenly decreases and this is indicated at the borderlines of air bubbles. Otherwise, the transition can be definitely detected by calorimetry ($\Delta H = 1.90 \text{ kJ mol}^{-1}$). The classification of the columnar phase seems to be difficult. Although the texture reminds one of layer structures like S_C , the X-ray pattern points to the existence

of a columnar structure. The 2D oblique columnar unit cell can be described with the parameters, $a = 64.8 \text{ \AA}$ and $b = 36.5 \text{ \AA}$ and with the angle $\gamma = 33.4^\circ$. The mesophase will be a subject of further investigation.

The homologous octyl derivative **1** shows a very unusual phase behaviour. After melting, the schlieren texture of smectic C phase can be observed. At 195°C , cubic areas begin to grow into the smectic phase. This is a kinetically controlled process; figure 1(a) shows the phase transition at 201°C , and in figure 1(b) the whole field of views is optically isotropic at 210°C . The fringed shape of the borderlines between the substances and air bubbles points to a high viscosity of the cubic phase which decreases strongly at the phase transition cubic–isotropic (see figure 1(c)). However, on further heating of the isotropic liquid, at 250°C a nematic phase arises (see figure 1(d)) which is transformed again into an isotropic liquid at 312°C . All transitions can be observed by optical microscopy and confirmed by calorimetric measurements. In figure 2, the DSC trace of the first heating run is given, together with the transition enthalpies. It is remarkable that all transitions are combined with measurable changes of the enthalpies, for it should be emphasized that

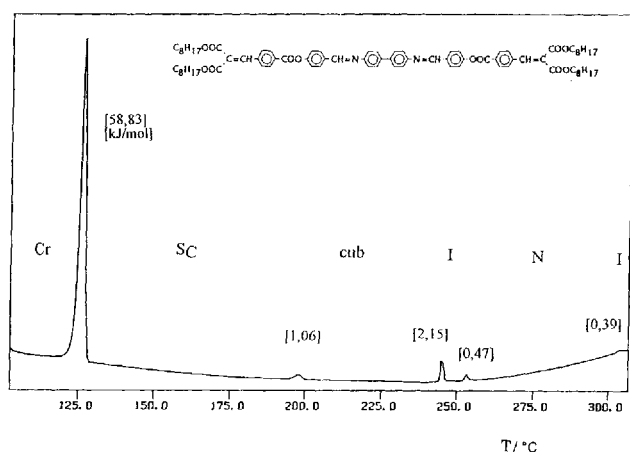


Figure 2. Calorimetric trace for compound **1** on first heating (heating rate $10^\circ\text{C min}^{-1}$).

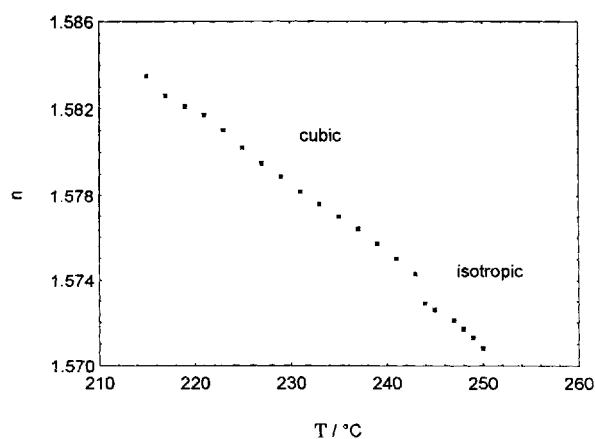


Figure 3. Refractive indices of the cubic and isotropic re-entrant phase of substance **1** as a function of temperature.

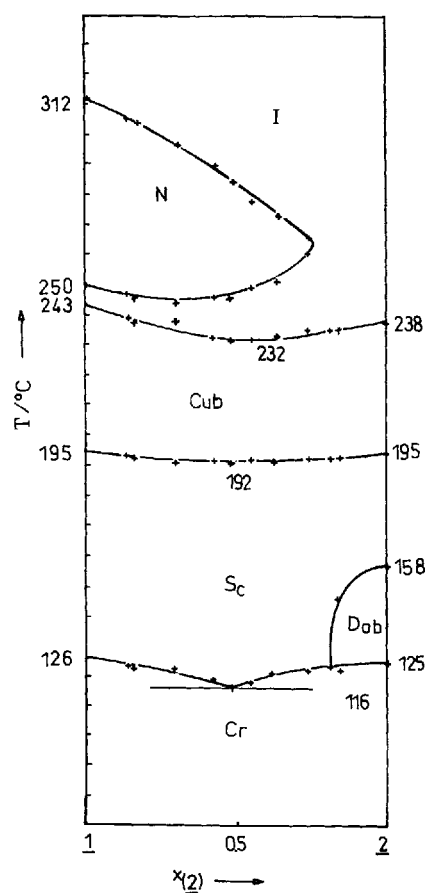


Figure 4. Binary phase diagram of the homologues **1** and **2**.

Warmerdam *et al.* [10], could not find any transition enthalpy either on heating or on cooling through the N_D - I_{re} - D_{hd} transitions of the truxene derivative. However Percec *et al.* [12] have measured calorimetric data for the re-entrant isotropic transition of the mixture of oligomers.

The transition of the cubic phase into the re-entrant isotropic liquid phase is also indicated by refractometric measurements, displayed in figure 3. At this transition point a small but clearly detectable drop in the refractive index is found which is obviously due to the discontinuous decrease in the density.

Figure 4 presents the phase diagram of the binary system of the neighbouring homologues **1** and **2**. As expected, the cubic phases and S_C phases of both components are miscible. But it is seen that the isotropic phase of compound **2** is also completely miscible with the re-entrant isotropic phase of substance **1**. It is remarkable that the re-entrant isotropic phase, as well as the nematic phase exist in a relatively wide concentration range up to 75 mol% of **2**. The enthalpies for the re-entrant isotropic-nematic and nematic-isotropic transitions decrease continuously with increasing amount of compound **2** and cannot be detected when the concentration of **2** is higher than about 60 mol%.

Unfortunately, X-ray investigations of the re-entrant isotropic phase cannot be performed on the pure substance because of the high transition temperatures. However, appropriate measurements on mixtures containing substance **1** with a re-entrant isotropic phase at lower temperatures are in progress.

The experimental results found clearly prove the existence of a re-entrant isotropic phase in the new double-swallow-tailed mesogen **1**. It is not the first case of liquid crystalline materials exhibiting a re-entrant isotropic phase, but up to now this phenomenon had never been observed on cooling a nematic phase. There are a lot

of open question, for example, the molecular origin of the re-entrance of the isotropic phase, the structural differences between both isotropic phases or the temperature dependence of the orientational order of the nematic phase of compound **1**.

Finally, the marked difference in liquid crystalline behaviour of two neighbouring members of a homologous series with regard to polymorphism and to the level of the isotropization temperatures is very unusual, and it is hoped that further studies of the complete series will offer an explanation for the results presented.

References

- [1] MALTHETE, J., LEVELUT, A. M., and NGUYEN HUU TINH, 1985, *J. Phys. Lett., Paris*, **46**, L875.
- [2] NGUYEN HUU TINH, DESTRADE, C., LEVELUT, A. M., and MALTHETE, J., 1986, *J. Phys. Lett., Paris*, **47**, 553.
- [3] DESTRADE, C., NGUYEN HUU TINH, and LEVELUT, A. M., 1988, *Molec. Crystals liq. Crystals*, **159**, 163.
- [4] MALTHETE, J., NGUYEN HUU TINH, and DESTRADE, C., 1993, *Liq. Crystals*, **13**, 171.
- [5] WEISSFLOG, W., WIEGELEBEN, A., DIELE, S., and DEMUS, D., 1984, *Cryst. Res. Technol.*, **19**, 983.
- [6] DIELE, S., ZIEBARTH, K., PELZL, G., DEMUS, D., and WEISSFLOG, W., 1990, *Liq. Crystals*, **8**, 211.
- [7] YU, L. J., and SAUPE, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
- [8] DESTRADE, C., FOUCHER, P., MALTHETE, J., and NGUYEN HUU TINH, 1982 *Physics Lett. A*, **88**, 187.
- [9] WARMERDAM, T., FRENKEL, D., and ZIJLSTRA, R. J. J., 1988, *Liq. Crystals*, **3**, 149.
- [10] WARMERDAM, T. W., NOLTE, R. J. M., DRENTH, W., VAN MILTENBURG, J. C., FRENKEL, D., and ZIJLSTRA, R. J. J., 1988, *Liq. Crystals*, **3**, 1087.
- [11] PRAEFCKE, K., KOHNE, B., GUTBIER, K., JOHNNEN, N., and SINGER, D., 1989, *Liq. Crystals*, **5**, 233.
- [12] PERCEC, V., LEE, M., HECK, J., BLACKWELL, H. E., UNGAR, G., and ALVAREZ-CASTILLO, A., 1992, *J. mater. Chem.*, **2**, 931.
- [13] WEISSFLOG, W., PELZL, G., LETKO, I., and DIELE, S., *Molec. Crystals liq. Crystals*, in preparation.