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A three-dimensional mesophase with rhombohedral structure formed by double-swallow-tailed compounds

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In five double-swallow-tailed compounds a weakly birefringent high temperature phase occurs which exhibits a characteristic optical texture. On the basis of X-ray diffraction measurements on well oriented monodomains, the structure of this phase could be described by a rhombohedral lattice of space group $R3c$ or $R32/c$; the lattice parameters are not far from a cubic lattice. In spite of the three dimensional superstructure with long range character, the lateral packing of the molecules is liquid-like—similar to the well known cubic mesophases.

1. Introduction

Polycatenar mesogens consist of a rod-like core and two half disc-shaped moieties [1, 2]. Depending on the length and the structure of the rod-like core and the number, position and length of the terminal chains, polycatenar compounds form nematic, lamellar, columnar and three-dimensional mesophases [2–4]. Some tetracatenar (biforked) compounds for which lamellar and columnar phases occur for the same substance are of particular interest [2, 3]. Double-swallow-tailed compounds can be regarded as special variants of tetracatenar compounds. The only difference from biforked mesogens is that the branches are not directly attached at the terminal rings, but at terminal linkage groups [5]. The liquid crystalline behaviour is quite similar to that of biforked compounds. Also double-swallow-tailed compounds are able to form lamellar and columnar phases for the same substance depending on the length and structure of the rod-like core and on the length of the terminal chains [6–9]. Recently we reported a six ring double-swallow-tailed compound which exhibits quite an interesting phase sequence. Besides a lamellar (SmC) and two columnar (Col_{ob}, Col_h) phases, a weakly birefringent high temperature phase with an unusual texture occurs which was previously designated by the symbol M_x [10]. Now, we have found further materials which possess this high temperature mesophase and we were able to obtain monodomains for X-ray studies to elucidate the structure of this phase. These studies suggest the existence of a three-dimensional structure with a rhombohedral lattice. Therefore we now designate this phase with the code letter Rh.

2. Materials

Table 1 presents structural formulae, the phase transition temperatures (°C) and the phase transition enthalpies (kJ mol^{-1}) of the substances studied.

Compound C4 was the subject of an earlier paper [10], while compound C6 was first described in ref. [11]. The other compounds (C1–C4) are new materials. The synthesis of the compounds under investigation was carried out according to a reaction scheme given in ref. [11]. Condensation of 4-formylphenyl 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoates with 4,4′-diaminobenzanilide, 4,4′-diaminobiphenyl or 4,4″-diamino-*p*-terphenyl in ethanol in the presence of toluene-*p*-sulphonic acid under nitrogen yielded the final products. The purification was carried out by recrystallization more than once from ethyl acetate or dimethylformamide.

It is seen that all the seven ring terphenyl derivatives listed in table 1 exhibit the same phase sequence Col_{ob}, Col_h, Rh, but the new Rh phase exists in a rather high temperature region and further investigations were impossible. Compound C5 forms an additional smectic phase (SmC) which is the low temperature phase with respect to the columnar phases. The homologous compound C4 possesses a SmC and a cubic phase besides the Rh phase. As will be shown in § 4, compound C6 does not form a Rh phase on rapid heating. However, depending on the heating and cooling rate, the Rh phase can arise from the cubic phase or on cooling the isotropic liquid

3. Experimental

The phase transition temperatures were determined by optical microscopy (Leitz Orthoplan with a Linkam hot stage THMS 600), as well as by calorimetric measurements

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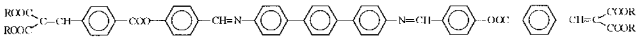
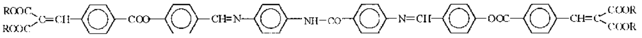
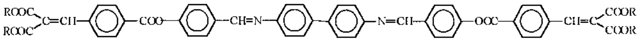
Table 1. Structure formulae, code letters, transition temperatures and transition enthalpies (in parentheses) for the compounds studied.

Compound	R	Transition temperatures (°C) and transition enthalpies (kJ mol^{-1})										
												
C1	C_8H_{17}	Cr	128 (35.5)	Col_{ob}	197 (1.71)	Col_h	329 ([a])	Rh	359 ([a])	I		
C2	C_9H_{19}	Cr	128 (37.9)	Col_{ob}	202 (2.24)	Col_h	303 (0.24)	Rh	352 (3.93)	I		
C3	$C_{10}H_{21}$	Cr	130 (45.4)	Col_{ob}	208 (2.24)	Col_h	271 (0.43)	Rh	354 (2.62)	I		
												
C4	$C_{10}H_{21}$	Cr	135 (46.5)	SmC	185 (1.96)	cub	210 (0.24)	Rh	247 (0.16)	I		
C5	$C_{11}H_{23}$	Cr	133 (43.3)	SmC	165 (0.27)	Col_{ob}	181 (2.06)	Col_h	188 (0.25)	Rh	243 (1.68)	I
												
C6	$C_{10}H_{21}$	Cr	120 (68.1)	Col_{ob}	192 (2.13)	Cub	220 (1.9)	I				

[a] These transition enthalpies could not be determined because of rapid decomposition.

(DSC7, Perkin Elmer). The structural characterization was obtained by X-ray diffraction measurements. Patterns of non-oriented samples were obtained with a focusing Guinier geometry (film set-up and goniometer). The study of oriented samples was made using a 2D detector (HI-STAR, Siemens). The sample-detector distance could be varied between 90 and 250 mm. The temperature was controlled within ± 0.5 K.

4. Results

4.1. *Microscopic observations*

As seen from table 1, the Rh phase is always the high temperature phase with respect to the columnar (or cubic) phases. On heating the columnar phase (compounds C1–C3, C5) or the cubic phase (C4), the Rh phase appears as a weakly birefringent mosaic texture. Usually, the formation of the Rh phase is delayed, as is also indicated by the broad calorimetric signal. Otherwise, on cooling the isotropic liquid, the Rh phase reappears a few degrees below the clearing temperature over an interval of several degrees. If the cooling rate is slow (0.5–1 K min^{-1}), large homogeneous domains are obtained which are distinguished by shaded grey tones on observation of samples between crossed polarizers. If the sample is turned by rotating the stage of the microscope, each domain becomes extinct in four positions at intervals of 90°. The domains are brightest at 45° from the extinction positions. This behaviour indicates that within the domains the optical axes are parallel or somewhat tilted with respect to the substrate planes. For compound C5 the double refraction of the Rh phase was estimated to be 3.3×10^{-3} [10]. On further cooling, a set of parallel black stripes occurs within the homogeneous domains which are more or less parallel to the direction of maximum refractive index n_γ. With decreasing temperature, the number of stripes increases; frequently the parallel lines are crossed by another set of parallel lines giving rise to the characteristic 'parquet-like' texture (see figure 1).

According to table 1, compound C6 does not form a Rh phase. This phase is only found on rapid cooling of the isotropic liquid or on very slow heating of the cubic phase. As seen from the transition scheme of figure 2, at a heating rate α of 30°C min^{-1} the phase sequence given in table 1 is observed. However, on cooling the isotropic liquid, the formation of the cubic phase is suppressed. Instead of the cubic phase, an anisotropic hexagonal columnar phase appears which is transformed into the Col_{ob} phase between 180 and 176°C. Using intermediate heating and cooling rates (5–20°C min^{-1}), the phase behaviour becomes rather complicated. On heating the Col_{ob} phase, the cubic phase is formed over a temperature interval. Within the cubic phase grey domains of

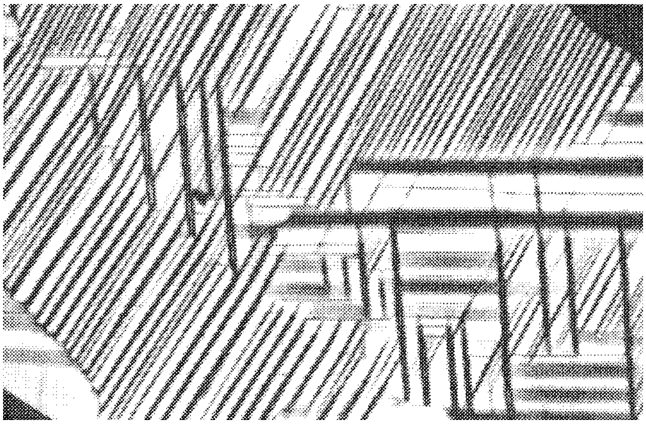


Figure 1. 'Parquet-like' texture of the Rh phase of compound C5 at 190°C.

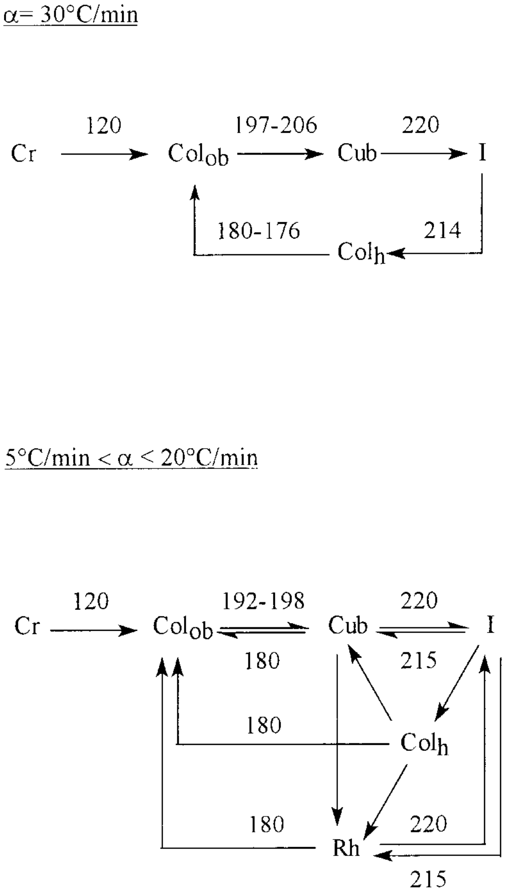


Figure 2. Transition scheme for compound C6 for different heating and cooling rates. The numbers on the arrows designate the transition temperatures in °C.

the Rh phase grow and at the clearing point both phases simultaneously disappear. By annealing the cubic phase at constant temperature for a longer time, the Rh phase is formed over the whole sample. The hexagonal columnar phase (Col_h) only arises on cooling the isotropic liquid phase, but simultaneously the Rh and cubic phases also appear, so that the three mesophases coexist (see figure 3); all are transformed into the Col_{ob} phase at about 180°C.

4.2. *X-ray investigations*

Due to the high temperature region of the Rh phase we have focused our X-ray studies on the six-ring compound C5. Figure 4 shows a schematic sketch of the observed small angle reflections and their relative intensities obtained on non-oriented samples of the different phases (SmC, Col_{ob}, Col_h, Rh). The diagrams exhibit in the wide angle regions only a diffuse scattering maximum indicating the short range order concerning the lateral packing of the molecules.

The alteration in the pattern in the small angle region reflects the phase sequence observed with increasing temperature. The structural parameters derived from the patterns in the different phases are summarized in table 2.

In order to obtain an oriented sample of the Rh phase, a drop of the isotropic liquid placed on a glass plate was cooled down very slowly.

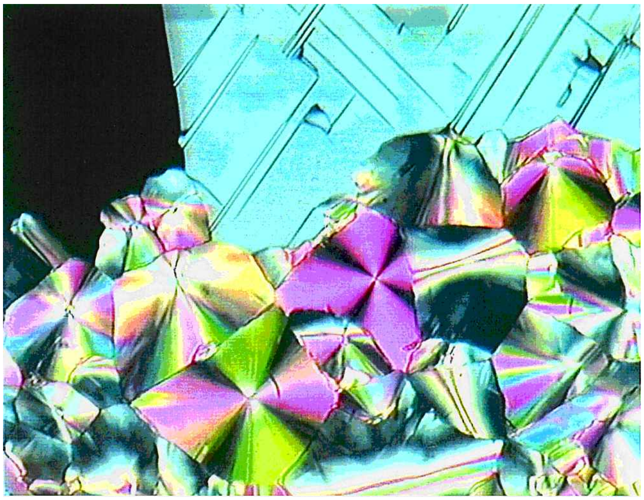


Figure 3. Coexistence of the strongly birefringent Col_h phase, the weakly birefringent Rh phase and the isotropic cubic phase of compound C6 (190°C).

Table 2. Structural parameters of the SmC, Col_{ob}, Col_h and Rh phases of compound C5.

Phase	Parameter
SmC	$d = 4\,\text{nm}; \varphi = 56°$
Col_{ob}	$a = 4.23\,\text{nm}; b = 3.89\,\text{nm}; \gamma = 115°$
Col_h	$a = 4.52\,\text{nm}$
Rh	$a = b = c = 7.0\,\text{nm}, \alpha = \beta = \gamma = 85°$

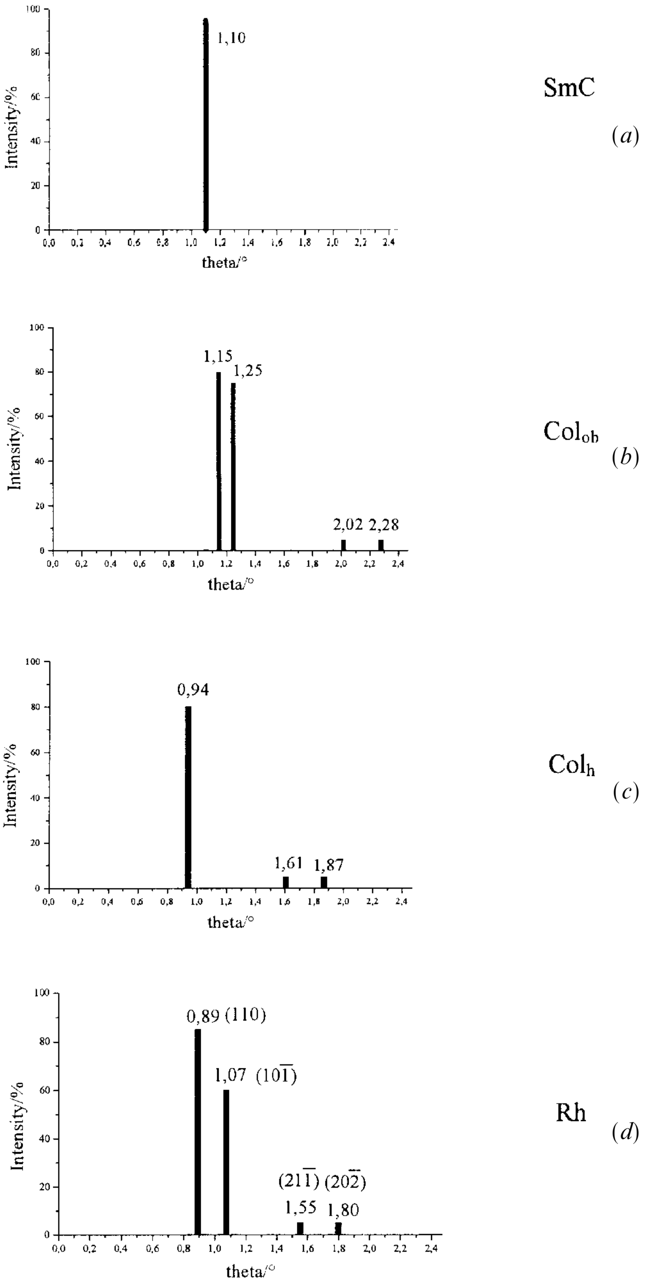


Figure 4. Position and relative intensities of the X-ray small angle reflections in the SmC (*a*), Col$_{ob}$ (*b*), Col$_h$ (*c*) and Rh (*d*) phases of compound C5.

The X-ray beam was incident parallel to the glass plate. Because of this special sample preparation, mainly the scattered intensitiy of the upper half of the reciprocal space could be recorded. Figure 5 displays the X-ray diffraction pattern of such an oriented sample; (*a*) small and wide angle region, (*b*) small angle region, only. In figure 5 (*c*) a schematic sketch including indexing of the reflections is given. From the position of the reflections there is a clear hexagonal symmetry. Three-fold axes can be found in hexagonal or cubic systems, only. The latter can be excluded because of the observed weak double refraction. The powder-like pattern rules out a simple hexagonal arrangement of columns. Therefore, a combination of the different results leads to the reliable assignment of the phase under discussion to the rhombohedral group. Among the seven space groups with rhombohedral axes, only the space groups *R*3*c* and *R*32/*c* have extinction rules of the reflections which are fulfilled in the pattern shown in figure 5. The lattice parameter is of the order of magnitude of the molecular length, and the lattice angle was found to be 85° (see table 2). The structure is obviously not that far from a cubic structure which explains the rather weak birefringence.

5. Discussion

A rhombohedral phase was first found in lyotropic systems [12]. There, the phase was observed in the neighbourhood of a cubic phase with the possible space group $Im\bar{3}m$. In thermotropic liquid crystals, non-cubic three dimensional superstructures were first reported for biforked compounds [4]. On cooling down a Col$_{ob}$ phase, 12 small angle reflections could be observed for a powder-like sample; these reflections were described by a rhombohedral lattice of space group *R*3*c* [4]. On the basis of the reported lattice parameters of the hexagonal axes, the parameters $a = b = c = 10.8$ nm and $\alpha = 48°$ for the corresponding axes can be calculated. Obviously there are some differences between the Rh phase under discussion and the rhombohedral phase described in ref. [4]:

(1) The Rh phase is always the high temperature phase with respect to the Col$_h$ phase or cubic phase (see table 1).
(2) The lattice parameters correspond more to a cubic structure ($\alpha = 85°$); in compound C4 the Rh phase is the high temperature phase with respect to the cubic phase.
(3) The Rh phase has been found to be only weakly birefringent.

A characteristic feature of the Rh phase is a relatively high viscositiy compared with the Col$_h$, Col$_{ob}$ or SmC phase. In this respect the Rh phase also behaves similarly to a cubic phase. There are double-swallow-tailed compounds where obviously the energetic barrier between the cubic phase and Rh phase is rather low. As found for compound C6, on cooling the isotropic liquid not only the cubic phase reappears, but also the Rh phase and the columnar hexagonal phase. This means that in this case three mesophases can coexist, dependent on the cooling rate which should be 5–20°C min^{-1}. This is plausible because the nucleation of the three-dimensional

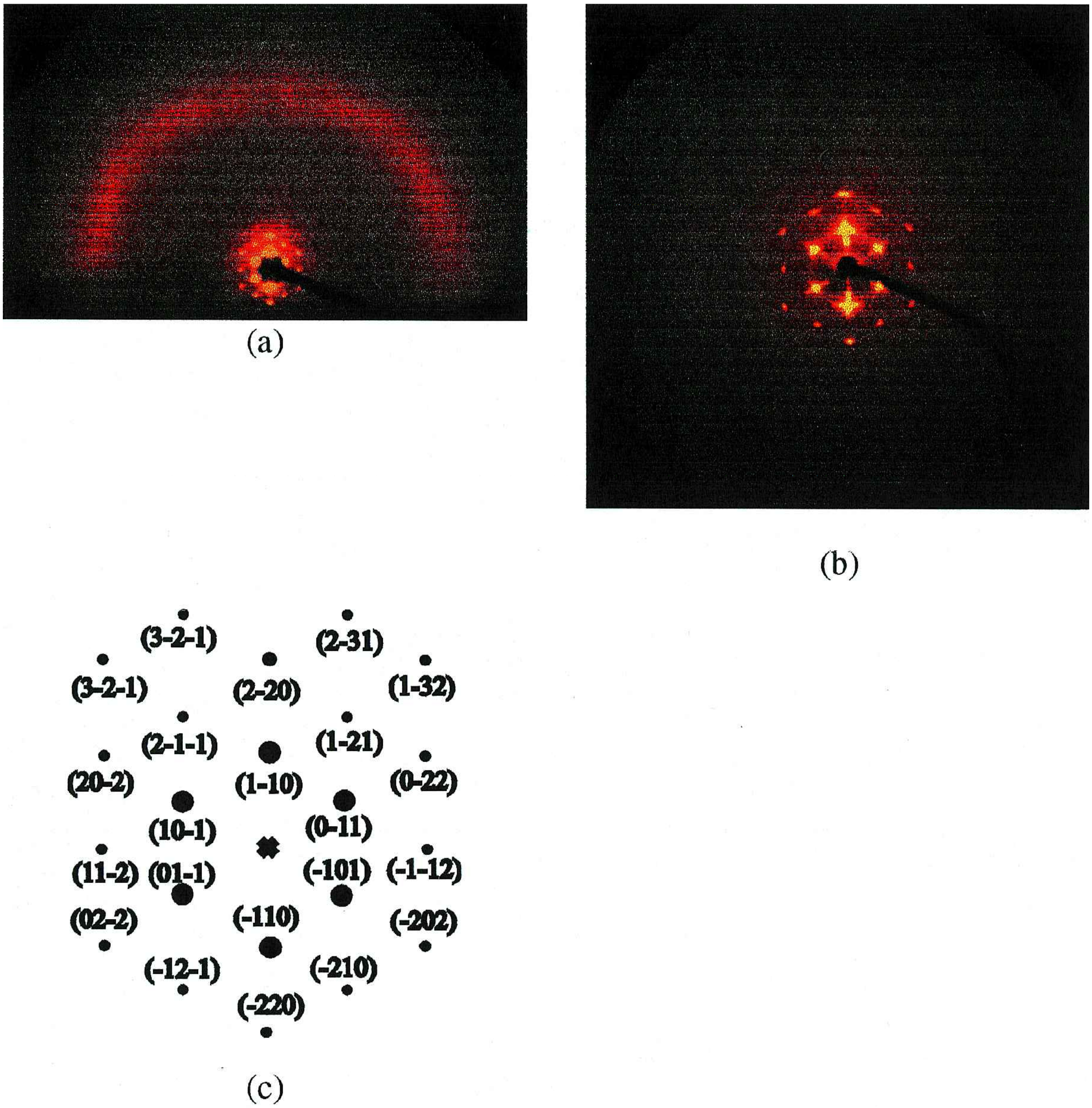


Figure 5. X-ray pattern of a Rh monodomain at 190°C; incident beam parallel to the [1 1 1] direction. (*a*) Overview pattern, (*b*) small angle region, (*c*) schematic representation of the small angle region.

cubic and Rh phases is delayed so that kinetic factors (heating and cooling rates, boundary conditions) can play an important role.

The question arises as to what the structure of this rhombohedral phase is. The experimental results suggest that the Rh phase corresponds more to that described in lyotropic systems [12]. There, the neighbouring cubic phase of space group $Im\bar{3}m$ is described as a bicontinuous one and is discussed on the basis of the Schwarz minimal surface. This minimal surface divides the space into two subspaces which include two networks of rods parallel to the [1 0 0] direction and linked three by three at the centre and the corners of the cube. Assuming that the Rh phase corresponds to a distorted cubic structure, an analogous structural model of the Rh phase could be discussed.

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