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A new high temperature mesophase of a double-swallow-tailed compound with weak optical anisotropy

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Preliminary Communications

A new high temperature mesophase of a double-swallow-tailed compound with weak optical anisotropy

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A new six-ring double-swallow-tailed compound is presented which shows four liquid crystalline phases. In addition to a smectic C phase and two columnar phases (oblique and hexagonal), a high temperature mesophase was observed which exhibits a very weak birefringence and which shows unusual optical textures.

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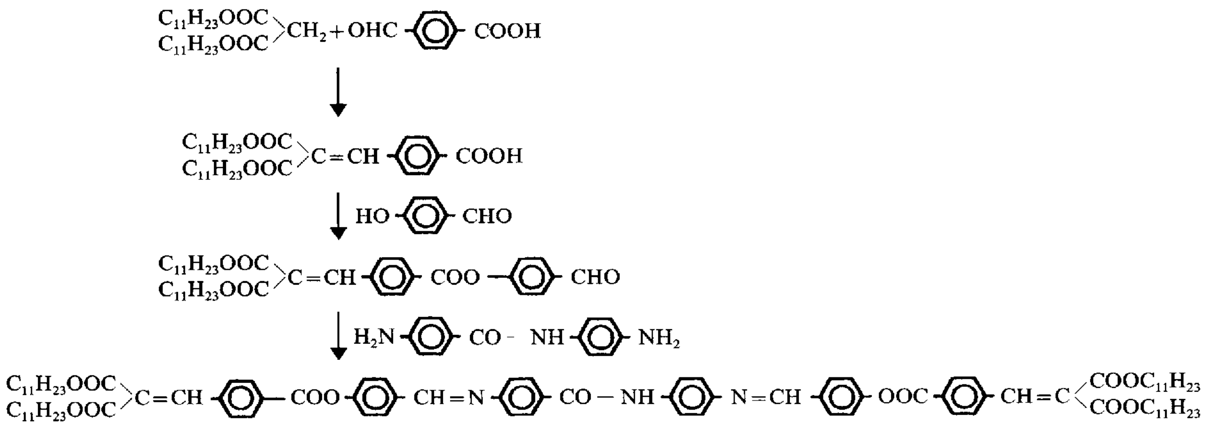
Double-swallow-tailed compounds can be considered as tetracatenar compounds where the terminal branches are not directly attached at the terminal rings, but at a terminal linking group [1]. Five- or six-ring double-swallow-tailed compounds can exhibit nematic, smectic C, cubic or different types of columnar phases depending on the structure of the rod-like core and the length of the terminal chains [1–4]. This behaviour is similar to that of biforked tetracatenar compounds, where the alkyl chains are substituted in *p*- and *m*-positions of the terminal phenyl rings [5, 6]. If lamellar and columnar phases occur in the same substance in the case of double-swallow-tailed compounds, the lamellar (smectic C) phase is always the low temperature phase with respect to the columnar phases. Furthermore, among columnar phases, the hexagonal columnar phase (Φ_h) is the high temperature phase.

In this paper we present a six-ring double-swallow-tailed compound which exhibits tetramorphism in the liquid crystalline state. We focus our attention on the high temperature mesophase which shows some unusual properties.

The six-ring double-swallow-tailed compound was synthesized according to the following synthetic route:



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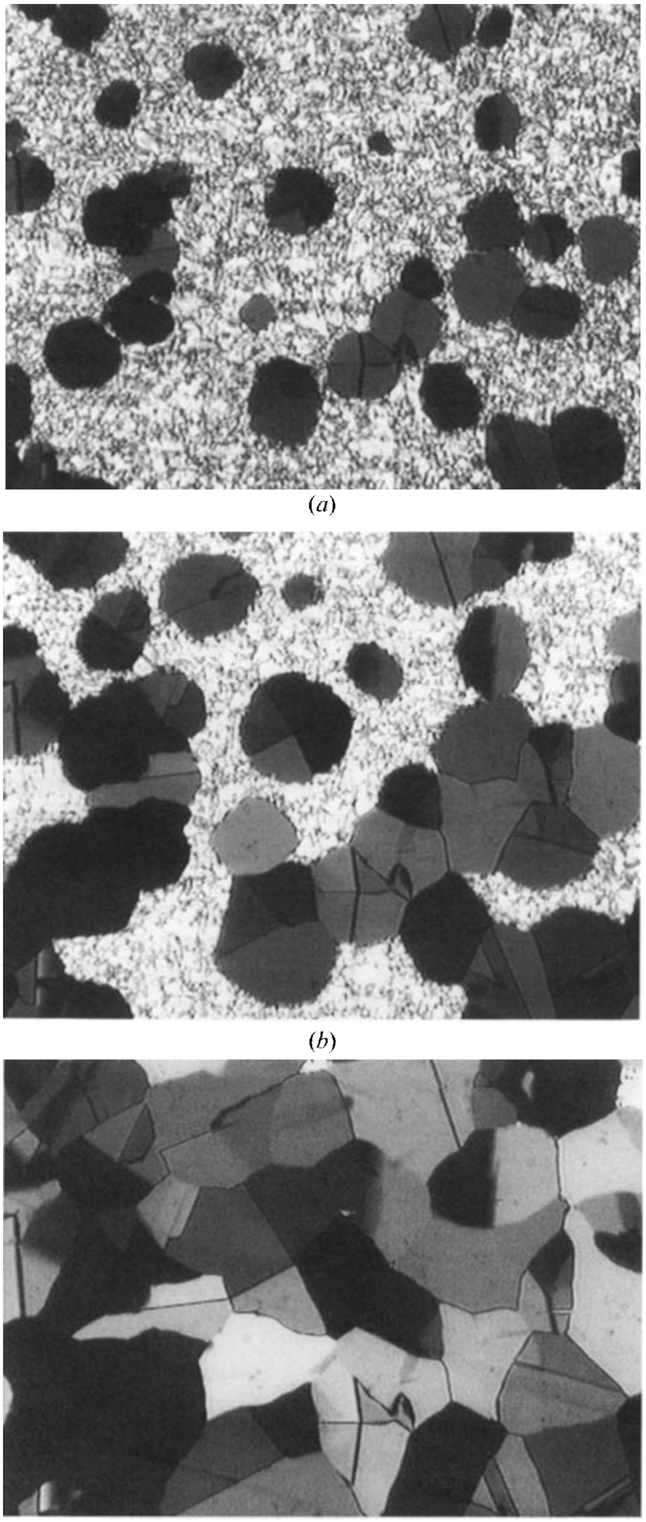
(*a*)

(*b*)

(*c*)

Figure 1. Growth of the M_x phase within the hexagonal columnar phase at 190°C: (a) after 1 min, (b) after 13 min, (c) after 55 min; (magnification: 100 ×).

The phase transition temperatures were determined by differential scanning calorimetry (DSC 7, Perkin–Elmer) and by optical microscopic investigations. The liquid crystalline phases were identified by observation of the microscopic textures. If possible the mesophases were also characterized by X-ray diffraction measurements using a Guinier focusing camera equipped with a heated sample holder.

According to the calorimetric and microscopic investigations, the following transition scheme is found:

$$\begin{tikzcd} \mathrm{Cr} \arrow[r, "133^{\circ}\mathrm{C}", "(43.27)"'] & S_C \arrow[r, leftrightarrow, "165^{\circ}\mathrm{C}", "(0.27)"'] & \Phi_{ob} \arrow[r, leftrightarrow, "181^{\circ}\mathrm{C}", "(2.06)"'] & \Phi_h \arrow[r, leftrightarrow, "188^{\circ}\mathrm{C}", "(0.25)"'] & M_X \arrow[r, leftrightarrow, "243^{\circ}\mathrm{C}", "(1.68)"'] \arrow[lll, bend left, "\sim 160^{\circ}\mathrm{C}"] & \mathrm{I} \end{tikzcd}$$

Below the transition temperatures (°C), the transition enthalpies (kJ mol^{-1}) are given in parentheses. It is seen that this compound forms four mesophases. The smectic C phase appears as a typical schlieren texture. The layer thickness was found to be 40 Å, whereas the molecular length of the most stretched conformation is 72 Å. The texture of the low temperature columnar phase is not specific, but X-ray investigations point to an oblique columnar phase (Φ_{ob}) with the lattice parameters $a = 42{\cdot}3$ Å, $b = 38{\cdot}9$ Å and $\gamma = 115{\cdot}0°$. On heating, at 181°C the Φ_{ob} phase is transformed into a hexagonal columnar phase (Φ_h) which is indicated by a focal-conic-like texture and which is confirmed by X-ray diffraction measurements from which a lattice parameter of 54·3 Å can be deduced. At a temperature of 188°C, within the Φ_h phase, domains of a new mesophase grow to form a mosaic texture (see figure 1). These domains increase

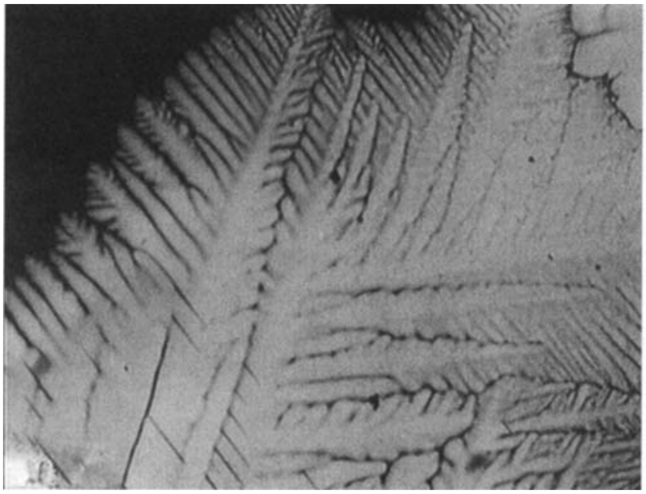
Figure 2. Growth of the M_x phase from the isotropic liquid (235°C, magnification: 100 ×).

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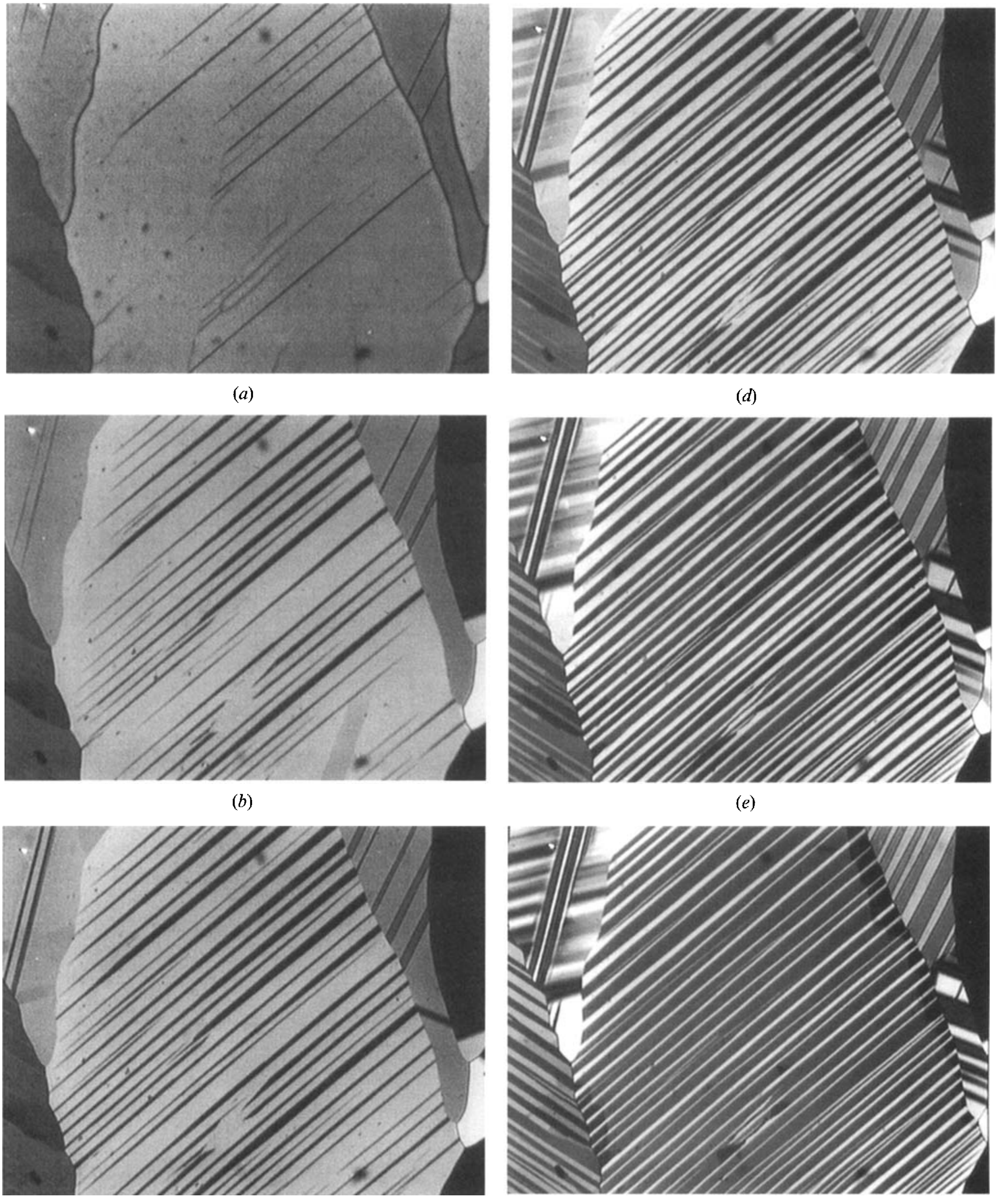

(*a*) (*d*)

(*b*) (*e*)

(*c*) (*f*)

Figure 3. Occurrence of the series of parallel black lines on cooling the M_x phase: (a) 236°C, (b) 232°C, (c) 226°C, (d) 215°C, (e) 198°C, (f) 170°C; (crossed polarizers, magnification: 100 ×).

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very slowly at the constant temperature ($T = 188°\mathrm{C}$); on rapid heating this transition is extended over a temperature interval (188–215°C). This delayed transition is also reflected in a very broad calorimetric peak from which a transition enthalpy of 0·25 kJ mol^{-1} could be determined. The new phase designated as $\mathrm{M_x}$ is transformed into the isotropic liquid at 243°C. Unfortunately, because this phase is formed at high temperatures, X-ray investigations have not yet been performed.

On cooling the isotropic liquid, this high temperature mesophase reappears a few degrees below the clearing temperature; this phase transition is also extended over a temperature interval of several degrees. If the cooling rate is very slow, relatively large homogenous domains can be obtained which are distinguished by shaded grey tones on observation between crossed polarizers (see figure 1). Sometimes—at a very slow cooling rate—dendrite-shaped domains occur which become homogenous on further cooling (figure 2).

If a particular domain is observed between crossed polarizers and the sample is turned by rotating the microscope stage, it will become optically extinct in four positions at intervals of 90°, and between these extinction positions, the domain is illuminated, being brightest at 45° from the extinction position. Optically such domains behave like uniform birefringent plates. In order to determine the polarization direction of the larger refractive index (n_γ) and the smaller index (n_α) within a particular domain, a λ-plate was inserted between sample and analyser. Using a Brace–Köhler compensator, a maximum path difference of 33 nm was measured for a sandwich cell of 10 µm thickness from which a very weak double refraction of about $3{\cdot}3 \times 10^{-3}$ can be estimated. It should be noted that the path difference of the different domains varies between 20 and 33 nm.

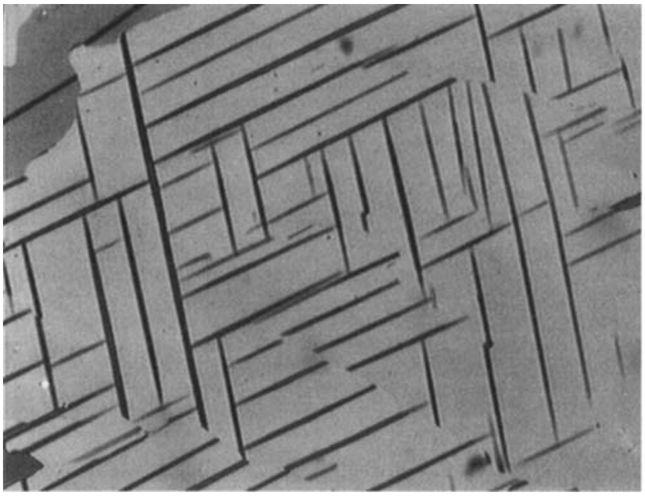

Figure 4. Texture of the $\mathrm{M_x}$ phase with sets of crossed parallel lines (210°C; magnification: 100 ×).

On cooling the homogeneous domains, a series of parallel black stripes (homeotropic or isotropic) occurs which are more or less parallel to n_γ. As seen in figures 3 (*a–f*), with decreasing temperature the number and the width of the parallel lines increase. Often the set of parallel lines is crossed by another set of parallel lines (see figures 4 and 5). Furthermore, another type of parallel line arises; these are birefringent, and they too can be crossed and are broadened with falling temperature. For this reason, with decreasing temperature the optical picture of the $\mathrm{M_x}$ phase becomes more and more complex as seen in figure 6.

It should be emphasized that on cooling the $\mathrm{M_x}$ phase, the Φ_h and Φ_ob phases do not occur, so that the $\mathrm{M_x}$ phase is directly transformed into the smectic C phase at about 160°C. Furthermore, we found that in the

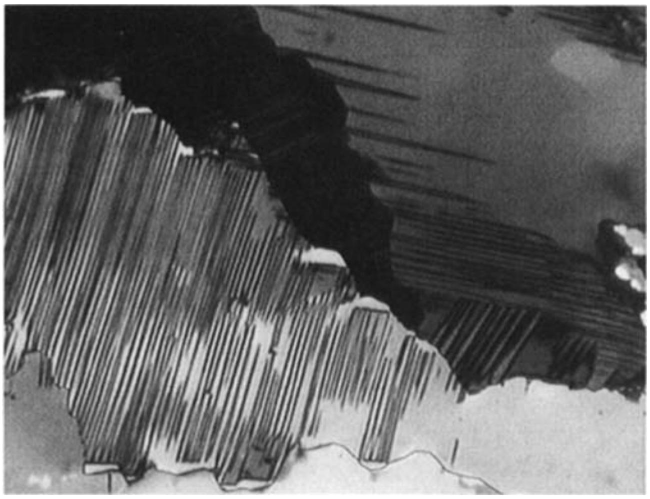

Figure 5. Texture of the $\mathrm{M_x}$ phase with sets of crossed parallel lines (200°C; magnification: 100 ×).

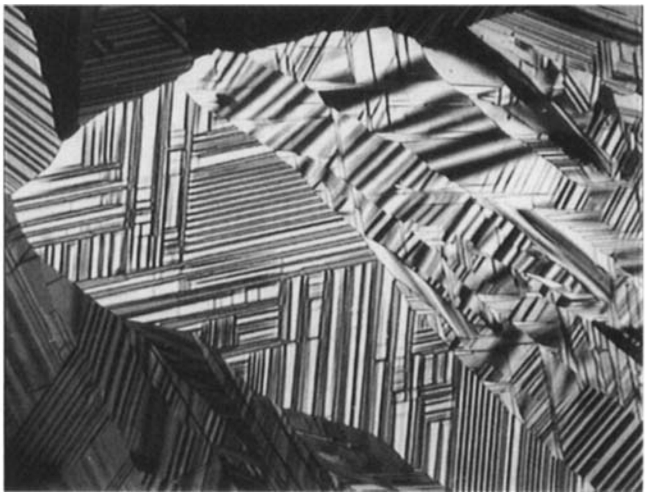

Figure 6. Multi-domain texture of the $\mathrm{M_x}$ phase at 190°C (magnification: 100 ×).

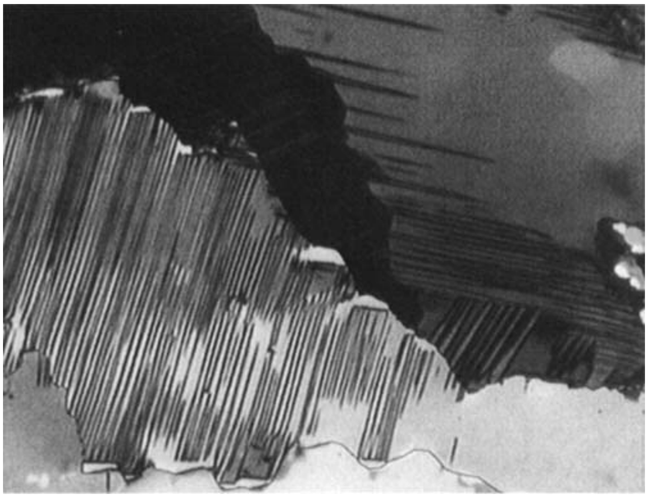

Figure 7. M_x texture with parallel lines generated by an external strain (220°C; magnification 100 ×).

original homogeneous areas of the M_x phase, the black lines can also be induced by mechanical strain. If the strain is relatively weak, the induced parallel lines disappear when the strain is removed. Under stronger strain, the striped pattern becomes permanent (figure 7). If the strain is very high, the homogeneous domains are destroyed. We found no correlation between the shearing direction and the lines produced. Some properties of this new phase remind one of the cubic phase; for example the phase transitions $\Phi_h \rightarrow M_x$, isotropic$\rightarrow M_x$, or $M_x \rightarrow S_C$ are delayed and extended over a distinct temperature interval.

It should be mentioned that for some chiral compounds, a weakly birefringent high temperature mesophase has been found. This phase was called the smectic Q phase and is characterized by a three-dimensional tetragonal lattice superimposed upon a short range liquid order of the centres of mass [7, 8]. However, this phase shows a mosaic texture without such patterns of parallel stripes as found for the M_x phase. It may also be mentioned that according to ref. [8], the occurrence of the Q phase is connected with the chirality of the molecules. It does not form in racemic mixtures.

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