NOTIZEN

Frozen Cholesteric Phase of a β-Estradiol Derivative
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Cholesteric Liquid Crystals, β-Estradiol Derivative

A new β-estradiol derivative was synthesized. The compound shows LC behaviour (cholesteric phase between 119 and 151 °C). On cooling the LC state, the liquid crystalline structure is preserved. The mesophase persists at room temperature. To our knowledge, such a thermotropic behaviour has only been observed in the case of polymeric liquid crystals.

During recent years, several research groups have focussed their attention on the synthesis of thermotropic liquid crystalline polymers [1–3], in an effort to prepare stable nematic or cholesteric phases for technological applications [4]. The combination of properties which are a feature of liquid crystals and those exhibited by polymers is characteristic of these systems. For example, the liquid crystalline state of an amorphous polymer can be frozen and is retained in the glassy state without causing any change in structure [5, 6]. This procedure may have certain practical applications, because it allows the preservation of information held by the texture in the glassy state [7]. So far, this behaviour has not been observed in the case of low molecular weight liquid crystals.

In this communication, we wish to report on a new compound (I), a derivative of β-estradiol, which exhibits novel thermotropic liquid crystalline properties.

The diester I was prepared by reacting 4-allyloxybenzoic acid chloride [8] with β-estradiol [9] in the molten state. The compound recrystallized from isopropanol/THF is a colourless and crystalline material.

Figure 1 shows the DSC curves of the diester I. Upon heating, melting transition appeared at 119 °C with an intense endothermic peak, followed by a small endothermic transition caused by the liquid crystalline-to-isotropic phase change. The clearing point is 151 °C.

Study under a microscope confirmed that the first endothermic transition (119 °C) in the heating cycle (a) corresponds to the melting point. On cooling (b), an endotherm corresponding to the isotropic-mesophase transition was observed, but not the one for recrystallization. In a second heating cycle (c), the only endotherm observed was that of the clearing transition. The second heating cycle was carried out after the sample had been left for 24 h at room temperature. These observations indicate that the mesophase can persist at room temperature, in a highly supercooled state.

Upon exceeding the melting point, the compound exhibits strong birefringence. The microscopic picture shows a typical finger print texture for a cholesteric mesophase, as it first appears on cooling the isotropic phase.

Stability of this frozen cholesteric phase is relatively high. For example, the compound was sandwiched between a microscope slide and a covering glass, and the frozen mesophase was exposed to the laboratory atmosphere. After 18 months, no change was seen. This observation was confirmed by selective reflection of circularly polarized visible light and X-rays [10].

Experimental

2.05 g (0.0075 mole) of Estratrien-(1,3,5(10))-diol-(3,17β) and 2.69 g (0.015 mole) 4-allyloxybenzoyl chloride were reacted at 80 °C in a nitrogen atmosphere. This temperature was maintained until formation of HCl ceased. At this stage, the temperature was raised in a stepwise manner to 120 °C to complete the reaction. HCl produced was removed from the flask by continually passing N₂ through it. When no additional HCl formation was observed, the product was cooled and recrystallized from isopropanol/THF 1:8 (V/V). Yield was 3.3 g (74%). Combustion, IR and ¹H NMR analyses were consistent with the reported structure (I). Moreover, the structure of

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this diester was confirmed by Field Desorption Mass Spectrometry. The spectrum showed only two intense peaks: \( m/e \) 592 (\( M^+ \), rel. intensity 45%) and \( MH^+ \) as the base peak.

Transition temperatures were recorded on a Leitz-hof stage microscopic melting point apparatus with crossed polarizers, and confirmed on a Perkin-Elmer DSC-2C.

![DSC curves of the diester I.](image)

**Fig. 1.** DSC curves of the diester I.

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