

Observation of a re-entrant isotropic phase in a pure disc-like liquid crystal

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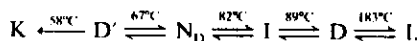
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We report the observation of an optically isotropic phase in the new disc-like mesogen 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene. On cooling, this optically isotropic phase goes over into a nematic phase, while on heating a columnar phase grows in. To our knowledge this is the first example of a pure discotic mesogen exhibiting an isotropic phase below the temperature existence of a columnar phase. Our findings are supported by refractive index measurements of this compound as a function of temperature.

Since the first synthesis of a liquid crystal composed of disc-like molecules [1], a number of other disc-like mesogens have been found, some of which exhibit a complex polymorphism [2]. In particular hexasubstituted esters of truxene exhibit an increasingly complex polymorphism with increasing alkyl chain length [3]. Depending on the temperature these compounds exhibit one or several columnar phases and a nematic phase. Furthermore the normal sequence (columnar nematic) is inverted in these compounds, and the long chain derivatives exhibit one or more re-entrant phases [3, 4]. It has been shown that re-entrant columnar phases and/or a re-entrant nematic phase can occur in a pure compound [2-5]. The occurrence of a re-entrant isotropic phase has, to our knowledge, not yet been reported for a pure compound, although it has been found in a mixture of two truxene derivatives [6]. Here we report the observation of a re-entrant isotropic phase in a new discotic mesogen: 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (cf. figure 1).

The synthesis of this new truxene derivative was carried out using a modification of the approach used by Nguyen Huu Tinh *et al.* [3]. Details of our synthesis will be described elsewhere [7]. The purity of the samples were checked by thin-layer chromatography and elemental analysis.

Observation of a sample of this material contained between two glass slides with a polarizing microscope equipped with a Mettler FP 52 heating and cooling stage showed the following phase transitions:



On cooling from the isotropic liquid phase a columnar phase (D) grows in at 183°C (cf. figure 2(c)). Below 89°C the texture slowly becomes totally black between crossed polarizers (cf. figure 2(d)), forming a re-entrant isotropic phase. Figure 2(e) shows the typical schlieren texture of the nematic phase which is obtained below 82°C. At 67°C

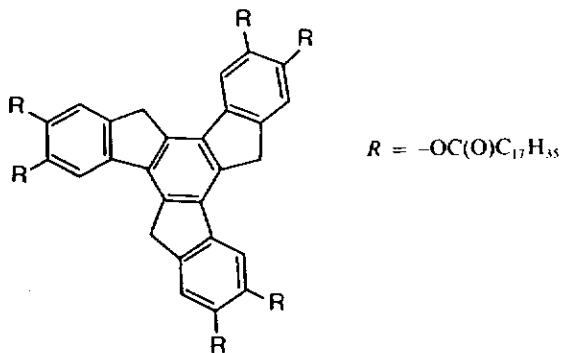


Figure 1. Structure of 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene.

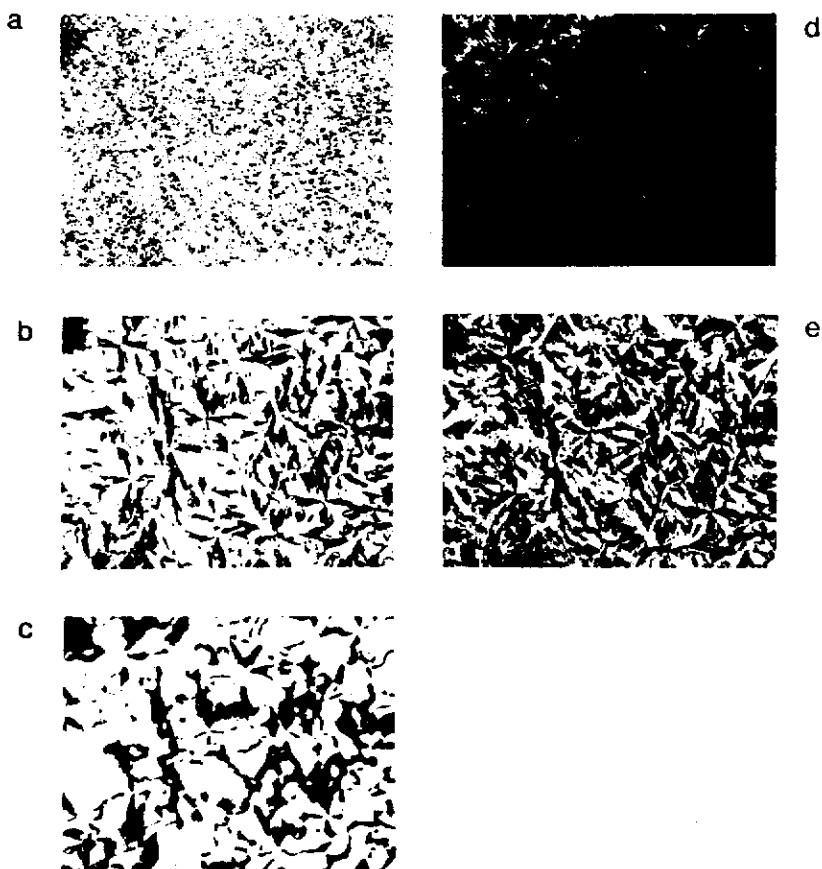


Figure 2. Optical textures observed with 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene. (a) Crystalline phase at 47°C. (b) Columnar phase at 61°C. (c) Nematic phase at 77°C. (d) Isotropic phase at 82°C. (e) Columnar phase at 109°C.

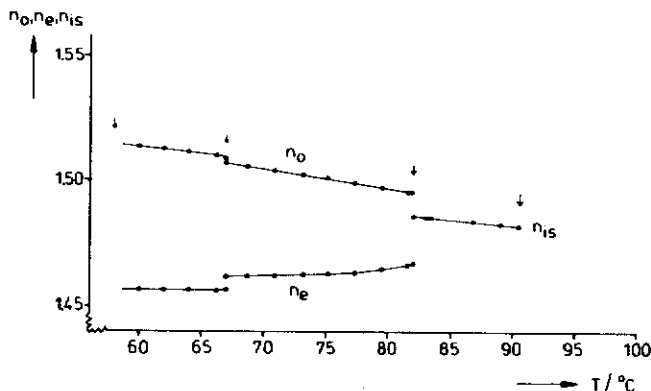
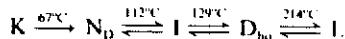


Figure 3. Refractive indices of 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene as a function of temperature. Phase transition temperatures are indicated by the arrows.

this nematic phase goes over into a columnar phase (D') (cf. figure 2(b)). The optical texture of this phase shows a great resemblance with the high temperature columnar phase D (cf. figure 2(e)), so this might also be a re-entrant phase. On further cooling the material crystallizes at 50°C (cf. figure 2(a)).

The occurrence of an isotropic phase between a nematic and a columnar phase is analogous to what is observed for a mixture of 87 per cent of 2,3,7,8,12,13-hexa-(tetradecanoyloxy)truxene and 13 per cent of 2,3,7,8,12,13-hexa(4-*n*-dodecyloxy-benzoyloxy)truxene, which shows the following sequence [6]:



Of course, there is the possibility that the optically isotropic phase is not a true re-entrant isotropic liquid phase, but some kind of cubic phase analogous to the 'smectic' D phase in rod-like liquid crystals [8]. However, no birefringence could be detected by rotating the sample or by inducing shear flow by moving the upper glass slide. In addition the fluidity of this optically isotropic phase is much greater than the fluidity of the columnar phases and rather resembles the fluidity of the nematic phase. These observations suggest that we are dealing with a normal isotropic liquid phase and make it less likely that it is some kind of cubic phase.

In addition to the observations made using a polarizing microscope, we also measured the refractive indices of this material as a function of temperature. The results of these measurements, using a temperature controlled Abbé refractometer, are represented in figure 3. We can clearly detect the birefringence in the nematic phase (67 – 82°C). On cooling we see a change in the refractive indices at 67°C , indicating the phase transition to the columnar phase D' . Above 82°C the birefringence disappears and we detect only one refractive index, indicating an isotropic phase. Note that at the nematic-isotropic transition the change in the refractive indices is in agreement with $n_{is} = (2n_o + n_e)/3$, where n_{is} is the isotropic refractive index and n_o and n_e indicate the ordinary and extraordinary refractive index, respectively. Note also that, contrary to what is commonly observed in rod-like liquid crystals, the optical anisotropy $\Delta n = n_e - n_o$, is negative, as is to be expected for a flat polyaromatic molecule. Below 58°C and above 90°C we could not clearly detect any refractive indices, due to the disappearance of a sharp boundary line.

Summarizing, both optical observation with a polarizing microscope and the refractive index measurements support the existence of a re-entrant isotropic phase in this new mesogenic compound. Further experiments are in progress to study the nature of this re-entrant isotropic liquid phase.

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