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The Polymorphism of the Smectic Liquid Crystal‡

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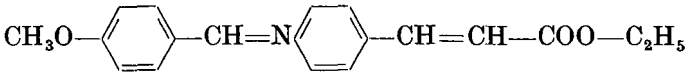
Abstract—The presence of one nematic and two smectic mesophases of *p*-anisolaminocinnamate has been confirmed by the methods of differential, thermal and X-ray analysis.

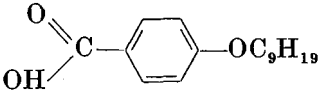
The scheme of phase changes is similar to the scheme of H. Arnold and H. Sackmann. Some difference lies in the anticoincidence of temperature of the transformation of the smectic phase *B* into solid.

Information about the presence of several polymorphic varieties of thermotropic smectic mesophases can be found in papers by Vorländer,[1] Weygand,[2] Gray[3] and Herrmann.[4] The systematic researches in this field were made by German investigators. The statement of the problem, the review of their papers and the papers of other authors are available in the articles by Arnold and Sackmann[5] and by Sackmann and Demus.[6]

In this paper, the data of X-ray analysis, of differential-thermal analysis and of microscopic analysis using polarized light are presented for ethyl-(*p*-anisolamino)-cinnamate[7].

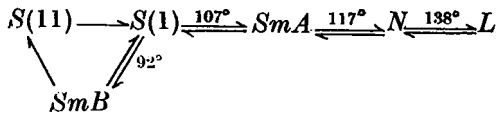


and *p*-nonyloxybenzoic acid[9,10]



‡ Paper presented by title at the Second International Liquid Crystal Conference.

Differential thermal analysis of ethyl-(*p*-anisolamino)-cinnamate and the microscopic determination with polarized light of the point of phase transformations confirmed the findings of Demus and Sackmann and may be represented as follows:



Ethyl-(*p*-anisolamino)-cinnamate produces three mesophases: one nematic and two smectic (*A* and *B* type according to Demus and Sackmann). The smectic modification *B* is monotropic and it only appears as the supercooled smectic *B* modification.

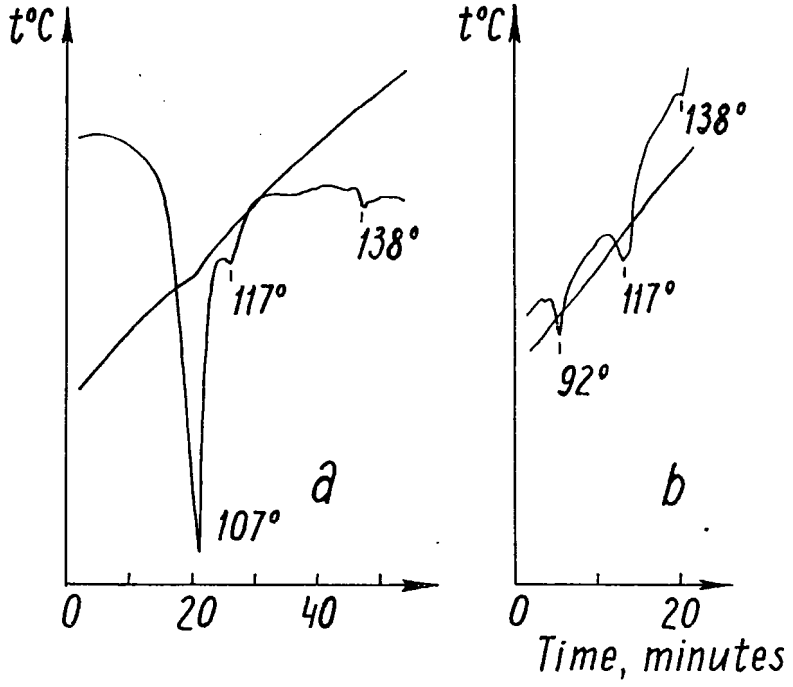


Figure 1. Thermogram of ethyl-(*p*-anisolamino)-cinnamate in heating cycle (a) and the thermogram of heating of supercooled substance (b).

Thermograms of the heating cycle (Fig. 1a) produce three endothermal peaks which indicate accordingly the melting point of the solid (107 °C), the transformation of smectic modification *A* into the nematic phase (117 °C) and the melting of the nematic into isotropic phase.

The thermogram of the heating of the supercooled substance is shown in Fig. 1b. The clear-cut peak at 92 °C indicates the transformation of the smectic modification *B* into modification *A*. The intensity of this peak is equal to the one at 117 °C, which corresponds to the transition of the smectic modification *A* into nematic liquid crystal.

At 92 °C there is a change in the texture of the sample. The number of conic focal domains in smectic modification *A* (Fig. 2a) increases in comparison to those found in smectic modification *B* (Fig. 2b). The X-ray diagrams of the mesomorphic phases differ greatly from one another. In Fig. 3 the X-ray diagrams of nematic, smectic *A* and smectic *B* phases are shown accordingly. In the upper row of Fig. 3 the X-ray diagrams represent, from left to right, the nematic, smectic *A* and smectic *B* in the absence of an electric field. In the lower row are the corresponding X-ray diagrams with the phases under the influence of an electric field of 10 kv/cm. X-ray diagrams in the absence of an electric field are sufficient to recognize hexagonal packing in the smectic plane in modification *B*. The reflection in the X-ray diagram of phase *B* is more clear-cut than the reflection in the X-ray diagram of phase *A*. In the latter, however, there are only two orders of reflection which can be detected from the smectic planes, while the *B* modification indicates four orders. Another interesting example of a smectic modification can be observed in *p*-nonyloxybenzoic acid. The acid possesses both the nematic and smectic mesophases. The X-ray diagrams of the acid in a permanent electric field is shown in Fig. 4a, b. In the smectic phase the align is along the field (principal axis of texture is normal to the field). On transition into the nematic phase, the X-ray diagram changes with the axis becoming parallel to the field. The X-ray diagram of the smectic phase indicates the molecules in planes have a concerted incline.

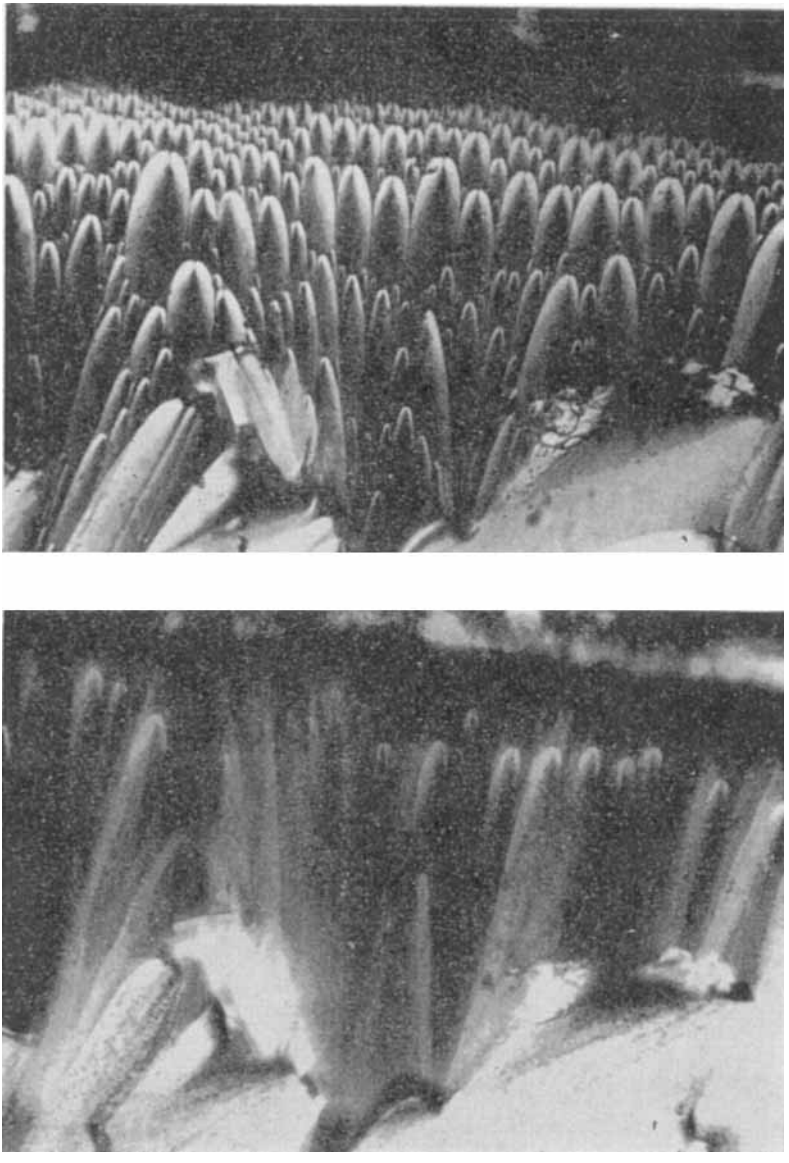


Figure 2. The texture of smectic modification *A* (above) and modification *B* (below).

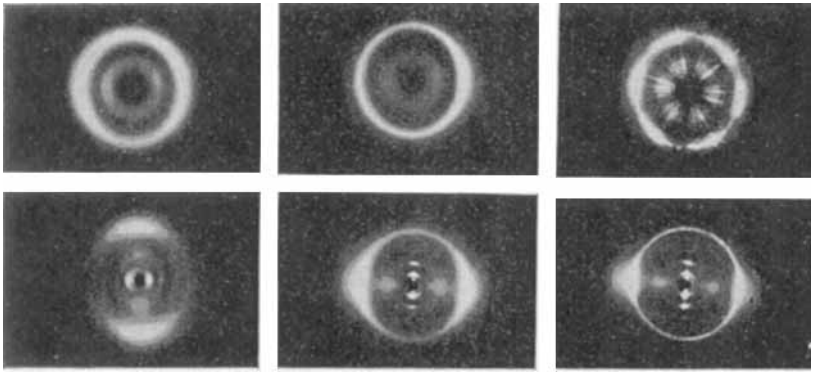


Figure 3. The X-ray diagrams of ethyl-(*p*-anisolamino)-cinnamate. The upper row: without the electric field. The lower row: with the electric field. From left to right: nematic, smectic *A*, smectic *B*.

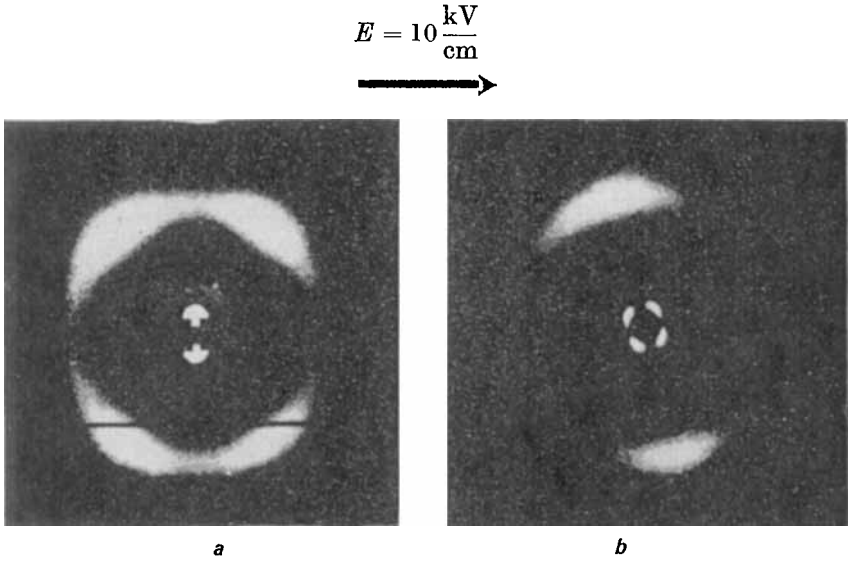
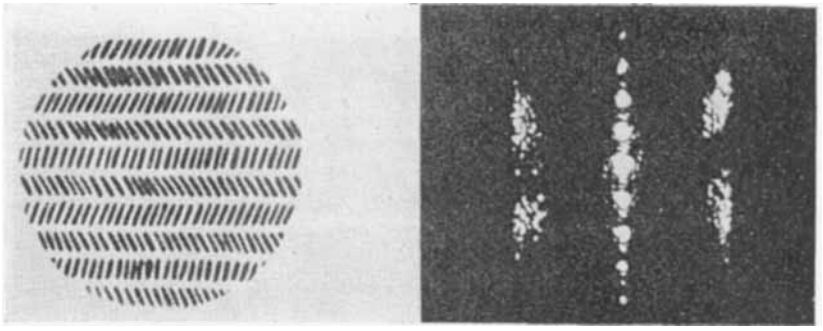


Figure 4. The X-ray diagrams of *n*-nonyloxybenzoic acid, (a) smectic phase, (b) nematic phase.



a b

Figure 5. The probable model of smectic structure (a) and the optical diffraction on the mode of the structure.

This conclusion was proven by the optical diffraction on a model of the structure (Fig. 5a). Another variant of the structure is certainly possible. Nevertheless, we have a new type of smectic mesophase here.

One should think that it corresponds to the mesophase which Sackmann and Demus refer to as a C-type.

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