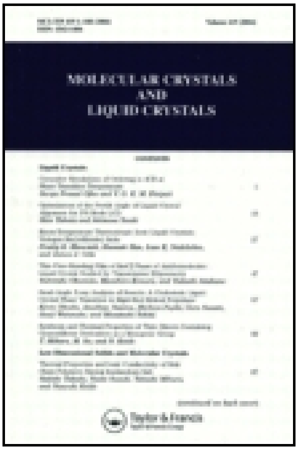

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Molecular Relaxation in hi Ghly Ordered Orthogonal Smectic S_A, S_B and S_E Phases

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MOLECULAR RELAXATION IN HIGHLY ORDERED ORTHOGONAL SMECTIC S_A, S_B AND S_E PHASES

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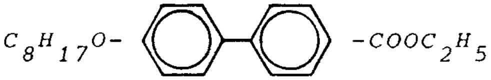
ABSTRACT: Dielectric relaxation and calorimetric investigations were performed on different smectic phases. Discontinuities of the critical frequency were found at both S_A-S_B *and* S_B-S_E *phase transitions.* S_A *and* S_E *structures can be regarded as two-dimensional liquid and two-dimensional crystal, respectively. The low frequency dielectric dispersion presented here demonstrates the difference between the* S_E *and a three-dimensional crystal where this phenomena is absent.*

INTRODUCTION.- The characteristic low frequency dielectric relaxation phenomenon is well known in nematic liquid crystals appearing as a consequence of the long range orientational ordering of the molecular long axes and disappearing in the isotropic liquid and solid state. This relaxation process is connected with the rotational motion of the molecules around their short axes[1]*. It was found*[2-4] *that this low frequency dielectric dispersion is present in some smectic liquid crystals, such as* S_A *where the elongated molecules oriented parallel to each other form layers but the structure is liquid-like inside the layer;* S_B *which is characterized by a hexagonal pattern of the* *centres of gravity of the molecules with a free rotation around the molecular axis.*

In the present communication we concentrate on the S_E *phase, which represents a two-dimensional crystal with a herring-bone structure formed by the planes of the molecules (see Fig. 2). The question arises about the difference between the molecular dynamics in the* S_B *and* S_E *phases.*

EXPERIMENTAL.- Experiments were carried out on ethyl-4'-n-octyloxybiphenyl-4-carboxylate, viz.[6]



which has

$$Cr \xrightarrow{348\ K} S_E \xrightarrow{356\ K} S_B \xrightarrow{367\ K} S_A \xrightarrow{383\ K} I$$

phases and was synthesized in our laboratory. The thermal properties were studied by polarizing microscope and a Perkin-Elmer DSC-2 calorimeter. The dielectric relaxation was measured in a wide frequency range up to 250 MHz. The calorimetric run is shown in Fig. 1 from which the high peak at the S_A *- isotropic transition is easily apparent. The measured transition heats are* $\Delta H_{AI} = 9.65 \pm 0.18$ *kJ/mole,* $\Delta H_{BA} = 1.56 \pm 0.28$ *kJ/mole and* $\Delta H_{EB} = 2.45 \pm 0.18$ *kJ/mole for the* S_A *- Iso,* S_B *-* S_A *and* S_E *-* S_B *phase transitions respectively.*

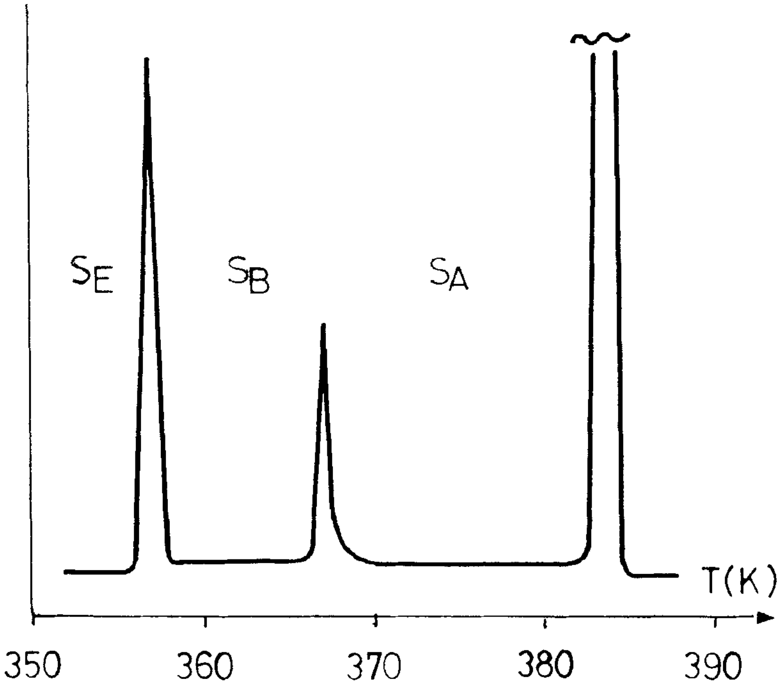


FIGURE 1 DSC trace of the compound

The dielectric critical frequencies connected with the rotational motion of the molecule around its short axis are shown in Fig. 2.

Apart from the jump about a factor of 3 in f_c *at the* S_A - S_B *transition (which is less pronounced than the effect registered in*[2]*) there appears a very intensive change (x20) at the* S_B - S_E *transition which was not observed in*[5]*. Contrary to the usual decrease towards the more ordered phases we found a strong increase in the activation energy from* S_A *to* S_B*.*

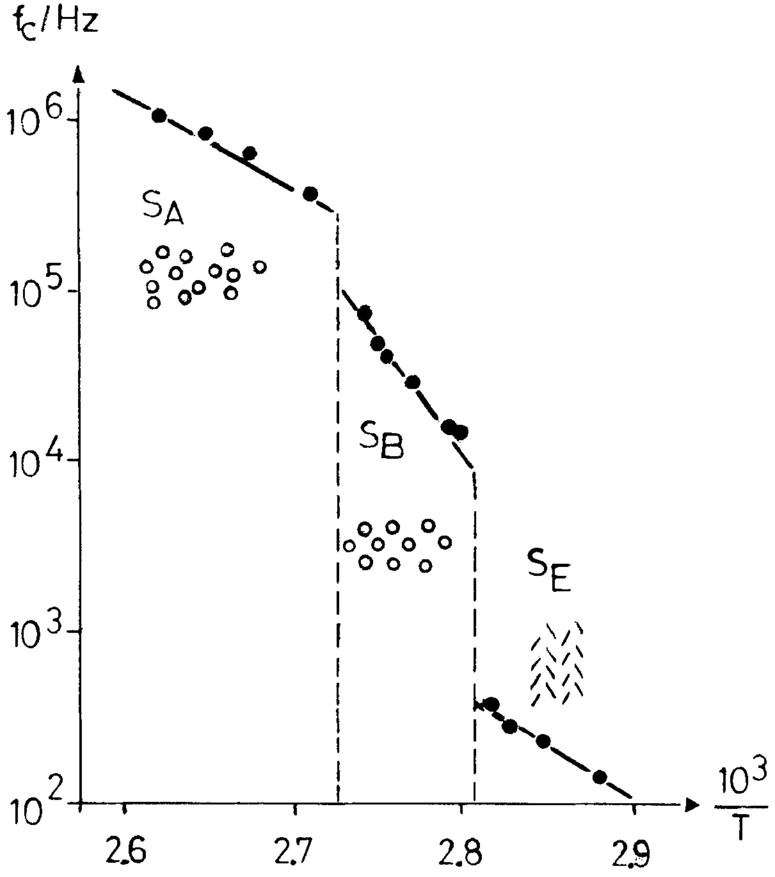


FIGURE 2 Arrhenius plot of the critical frequency
● experimental points;
—— mean square fit

DISCUSSION.- The measured high values of the transition enthalpies show that both $S_A - S_B$ and $S_B - S_E$ transitions are of first order. Discontinuities in the critical frequency indicate a hindrance increasing by steps of the rotational motion. Decrease of f_c by a step at the $S_A - S_B$ phase transition was interpreted by the appearance *of a collective libration in the two-dimensional hexagonal layer*[3]*. The further decrease of* f_C *found at the* S_B - S_E *transition is connected with the creation of the herring-bone structure. Whereas in the* S_B *phase librational waves can be created in any direction in the layers, in* S_E *this collective motion becomes anisotropic due to the structure formed by the planes of the molecules.*

X-ray investigations show a close similarity between the S_E *and crystalline phases. The measured here relaxation times in* S_E ($\tau = 1/2\pi f_C$) *show a prominent difference between them. This relaxation phenomena is frozen in solid phase.*

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