Ferroelectricity in ester-group liquid crystal

M. V. Loseva, B. I. Ostrovskiĭ, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova

All-Union Research Institute of Optical-Physics Measurements

Spontaneous polarization and ferroelectric properties were observed in the smectic-c phase of a new chemically stable chiral liquid crystal.

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Although ferroelectric liquid crystals have been investigated by only a few workers for more than three years, the accumulated experimental data already lead to certain conclusions concerning the features of dipole ordering in this system.[1–3]
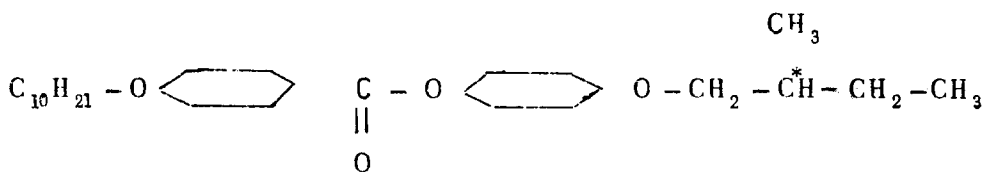
The ferroelectric ordering in liquid crystals, as is well known, is realized in the smectic-C phase made up of chiral molecules (C*). The tilt of the molecule by an angle θ on going from the high-temperature smectic A (A*) into the C* phase can be regarded as a certain deformation that leads, by virtue of the asymmetry of the molecule shape, to a preferred orientation of their constant transverse dipoles in the smectic layers. As indicated in Ref. 2, the physical cause of the ordering of the dipoles may be also the spontaneous flexoelectric effect, which is allowed by the C* symmetry and which is due to the helicoidal twisting (deformation) of C*.

The spontaneous polarization, measured by a direct method, in the liquid-crystal ferroelectric D-p decyloxybenzilidene-p'-amino-2-methylbutylcinnamate (DOBAMBC) and its homologs[4,5] turned out to be smaller by a factor 10^2–10^3 than in ordinary ferroelectrics; referred to a single molecule, this amounts to 10^{-2} of its constant dipole amount. This indicates that the character of the molecular motion in the smectic-C* phase changes insignificantly in comparison with the nonpolar smectic-A* phase, and the onset of polarization, in accord with the foregoing, is the result of the weak spontaneous deformation of the C*. In this case one should expect a universal behavior of the different physical properties near the A*→C* phase transition, determined by the orientational ordering of the C* molecules. The available experimental

data, however, suffer from the shortcoming that the effects of the dipole ordering were investigated in componds belonging only to the azomethine class.[6] In addition, the low hydrolytic stability of the azomethine compounds causes the investigated substances to be contaminated by the hydrolysis products and leads to a change in the temperature of the phase transitions; this is inconvenient both for the performance of the experiments and for the practical utilization of the C^*. In view of the foregoing, a search was made for liquid-crystal ferroelectrics among other chemical classes of compounds, including those that are more stable.
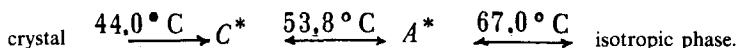
In this paper we report observation of ferroelectric properties in a liquid crystal compound belonging to the ester group.

d-4-(2-methylbutoxy)phenyl ester of 4-desoxybenzoic acid

$$C_{10}H_{21} - O \left< \right> \overset{\displaystyle C}{\underset{\displaystyle O}{\|}} - O \left< \right> O - CH_2 - \overset{*}{C}H - CH_2 - CH_3 \quad (CH_3)$$

was obtained by acylating 4-(2-methylbutoxy)phenyl with chloro-anhydride of 4-desoxybenzoic acid in dry pyridine at room temperature. The purity of the compound was verified chromatographically. The asymmetric position of the carbon atom C^* ensures chirality of the molecule, and the transverse moment is formed by the $C = O$ bond in the connection bridge of the benzene rings.

The scheme of the phase transitions observed by studing the texture transformations in a thin layer of the investigated substance with the aid of a polarization microscope is:

crystal $\xrightarrow{\;44.0\,^\bullet C\;}$ C^* $\xleftrightarrow{\;53.8\,^\circ C\;}$ A^* $\xleftrightarrow{\;67.0\,^\circ C\;}$ isotropic phase.

In the C^* phase, a characteristic helicoidal arrangement of the long axis of the molecules over the smectic planes is observed, and the pitch of the helix amounts to ≈ 6 μm. In a constant electric field of definite magnitude, an "untwisting" of the helicoid takes place, and the orientation of the director n in the untwisted state depends on the sign of the field E, i.e., a linear electro-optical effect typical of ferroelectric C^* is observed and is due to the interaction of the field with the ensemble of the constant dipoles of the molecules.

To measure the spontaneous polarization (P_s) and its temperature dependence, we used a scheme[7] that made it possible to compensate, via reversal of the polarization with a sinusoidal voltage, the linear components of the sample impedance; this increased the measurement accuracy. The measurements were made on samples prepared in plane-parallel glass cells with transparent conducting electrodes. The production of the planar orientation and the monitoring of the polarization-reversal process were carried out by the method indicated in Ref. 5.

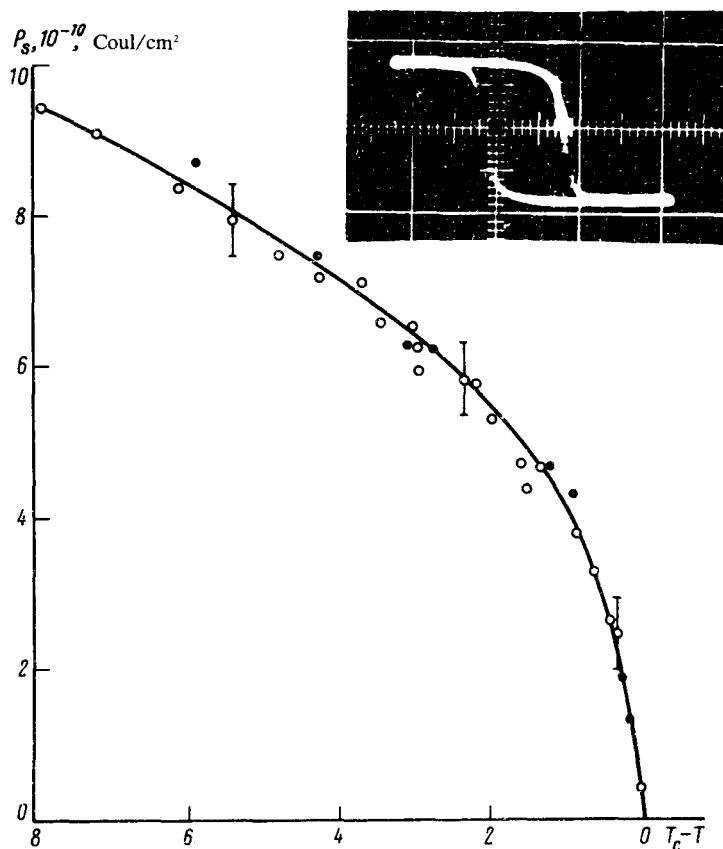The dependence of P_s on the temperature in the C^* phase, measured at 20 Hz, is

FIG. 1. Temperature dependence of the spontaneous polarization in the vicinity of the C^*–A^* phase transition. In the upper right corner is shown a typical oscillogram of the polarization reversal of C^*, on the basis of which P_s is determined; $T_c = 53.8\,°C$.

shown in Figs. 1 and 2, and is approximated by the expression $P_s \sim (T_c - T)^{0.43 \pm 0.05}$. Characteristically, the spontaneous polarization in the investigated ferroelectric is smaller by approximately one order of magnitude than that of the homologs of the azomethine series.[4,5] The phase transition from the ferroelectric C^* phase to the non-polar A^* phase, just as in the previously investigated DOBAMBC liquid crystal,[5] is of second order.

The temperature dependence of the inclination angle θ of the long axis of the molecules to the normal of the smetic layers, an angle which is a parameter of the C^*–A^* phase transition (Fig. 2), takes a form typical of systems with short-range interaction: $\theta (T_c - T)^{0.35 \pm 0.06}$.

It is confirmed, as was previously established for DOBAMBC, that the critical exponent for the spontaneous polarization P_s exceeds systematically (as obtained for different samples) the critical exponent for θ; this agrees with the arguments advanced in Ref. 2 that the flexoelectric effect plays a substantial role in the production of the spontaneous polarization in C^*.
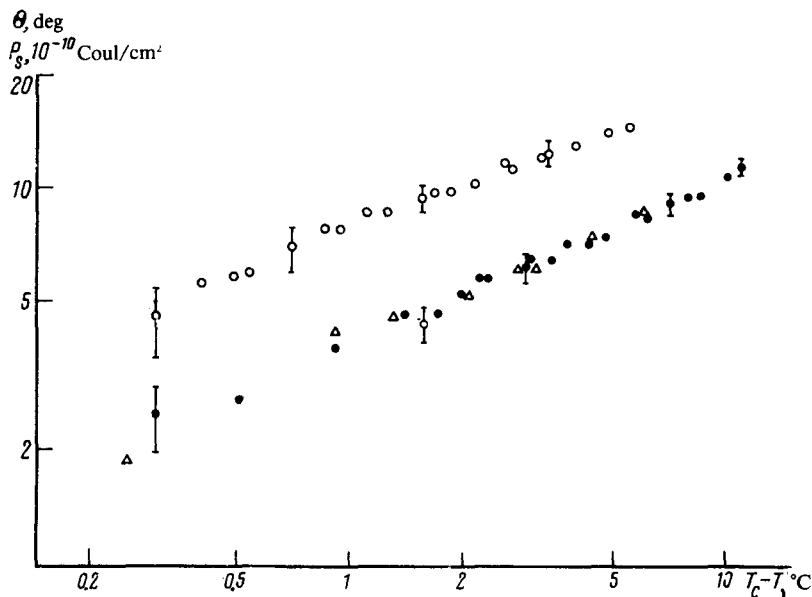
FIG. 2. Temperature dependences of the angle of inclination θ of the molecules in smectic layers (O) and of the spontaneous polarization P_s (● and △–different measurement runs) in a log–log scale.

The expression for the polarization, with allowance for the flexoelectric effect, takes according to Ref. 2 the form

$$P_s \sim \mid \mu_1 - \mu_2 q \mid \theta,$$

where μ_1 and μ_2 are coefficients corresponding respectively to the linear (piezoelectric) and flexural (flexoelectric) effects, and q is the "wave" number connected with the pitch of the helix p by the relation $q = 2\pi/p$.

The weak temperature dependence of $q = q(T_c - T)$, observed, for example, in DOBAMBC,[3,8] actually leads to a small difference between the temperature dependences of θ and P_s and to a renormalization of the critical exponent for P_s.

Thus, the results point on the whole to a common character of the $C*$–$A*$ phase transition and the dipole ordering in liquid crystals belonging to different chemical classes of compounds, and confirm by the same token the orientational treatment of the onset of P_s in chiral smectic-C liquid crystals.

We note in conclusion that the phase-transition point T_c, determined from the temperature dependences of P_s and θ, remains practically unchanged in numerous measurements performed on samples that are not hermetically sealed. This circumstance attests to the high stability of the new ferroelectric liquid crystal and, in conjunction with the rather low value of T_c, makes it possible to regard this crystal as a convenient object for experimental investigations and practical developments.

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