New Electro-Optic Effect in a Room-Temperature Nematic Liquid Crystal*

W. Haas, J. Adams, and J. B. Flannery Xerox Research Laboratories, Webster, New York 14580 (Received 19 October 1970)

The influence of electric dc fields on spontaneously aligned doped films of the nematic liquid crystal anisylidene-p-n-butylaniline was investigated. Prior to the application of the field films were uniaxial with the optic axis normal to the substrate; under the in-fluence of a field applied perpendicular to the optic axis films became biaxial. The magnitude of the induced retardation was measured as a function of field strength, and found to increase linearly with E^2 .

Several electro-optic effects in nematic liquid crystals are described in the literature.¹⁻⁴ Thin layers of anisylidene-p-n-butylaniline (ABUTA) doped with small amounts of polyamide resin⁵ (0.5% by weight) have a tendency to become spontaneously aligned between glass plates with the optic axis normal to the substrate. It was found that the effect of electric fields applied normal to the optic axis of spontaneously aligned films of ABUTA,^{6,7} is to induce optical biaxiality.

The liquid crystal was held by capillary action between standard microscope and cover slides; the electric field was applied parallel to the substrate with the help of two aluminum foil strips which also acted as spacers. The gap between the electrodes was varied from 1 to 4 mm and the thickness of the aluminum strips used in the measurements was 5-20 μ m.

The preparation adopted the homoeotropic texture,⁸ resulting in an optic axis which was uniformly normal to the substrate. Under the microscope between crossed polarizers and in parallel light the sample was dark in all stage positions and in convergent light the conoscopic figure was a uniaxial cross, Fig. 1(a). The optic sign was positive.

After application of a dc field the sample started to behave like a crystal section cut nor-



FIG. 1. (a) Uniaxial conoscopic figure of homoeotropic texture in ABUTA. (b) Biaxial conoscopic figure in 45° position obtained with a dc field applied perpendicular to the optic axis.

mal to the acute bisectrix. The following observations were made in parallel white light between crossed polarizers: Prior to the application of the field, as said before, the field of view was extinguished for all positions of the stage: after application of the field, extinction occurred only if the direction of the field was parallel to the direction of vibration of either polarizer or analyzer, i.e., extinction occurred four times when the stage was rotated through 360°. Maximum transmission occurred if the field direction was at an angle of 45° from the direction of vibration of the polarizer (or analyzer). The sample transmitted light uniformly and transmission increased with field. Initially, the color of the transmitted light was white but as the field strength was increased uniform interference hues became visible. Examination with a "red of first-order plate" showed that the red changed to yellow if the direction of the field was perpendicular to n_{ν} of the red plate (slow direction); this means that light vibrating parallel to the field propagated with the larger index. Field reversal did not affect this result. The samples were quite uniform with the exception of two very narrow margins which were bright prior to the application of the field, because interaction with the aluminum foil electrodes resulted in loss of alignment. When the electric field strength exceeded 1500 V/cm (cell thickness 5 μ m) sample uniformity was lost; at still higher fields (3500 V/cm), dynamic scattering was observed.

As said before, in convergent light the conoscopic figure was clearly uniaxial before application of the field. As a matter of fact, the interference figure is exceptionally sharp and beautiful. The application of a dc field resulted in breaking of the uniaxial figure, and when the film was observed in the 45° position, two hyperbolic isogyres could be seen, the separation of which increased with field strength. The resulting acute bisectrix figure in a thin film is illustrated in Fig. 1(b). Very occasionally samples



FIG. 2. Retardation versus E^2 .

are not perfectly aligned and one sees brighter regions which are slightly biaxial. Under the influence of the electric field, they first become uniaxial and then, at higher field strengths, again biaxial.

The induced birefringence in well aligned films was measured with a Brace-Kohler compensator for small values and by the Senarmont compensation method for larger retardations. The retardation is plotted versus E^2 in Fig. 2. The refractive-index changes are extremely large compared with the changes normally obtainable with Pockels or Kerr materials where similar retardations are only observed with high fields and long light paths.

The role of the polyamide additive is not clear. However, it does not appear unreasonable to speculate that the surfactant properties of the resin molecules help to foster an alignment in which the elongated axis is normal to the substrate. In some cases especially with very thin evaporated electrodes we obtained small homoeotropic areas with pure ABUTA and the electrooptic effect observed was empirically identical. This indicates that the dopant is not germane to the electro-optic effect but performs a very valuable function by fostering "thick" homoeotropic textures which can be easily measured. Spontaneous homoeotropic alignments have also been described earlier by Chatelain for p-azoxyanisole;⁹ that author used special chemical or physical cleaning procedures for the substrate.

The authors gratefully acknowledge the technical assistance of Mr. Bela Mechlowitz.

*Parts of this Letter were presented at the Third International Liquid Crystal Conference, West Berlin, Germany, August, 1970 (unpublished).

- $^1\mathrm{H.}$ Zocher and V. Birstein, Z. Phys. Chem., Abt. A 142, 186 (1929).
 - ²V. Naggiar, Ann. Phys. (Paris) <u>18</u>, 5 (1943).
 - ³R. Williams, J. Chem. Phys., <u>50</u>, 1324 (1969).

⁴G. H. Heilmeier, L. A. Zanoni, and L. A. Barton, Proc. IEEE <u>56</u>, 1162 (1968).

^bSold under the name of Versamid 100 by General Mills, Kankakee, Ill.

⁶H. Kelker and B. Scheurle, Angew. Chem., Int. Ed. Engl. 8, 884, (1969).

⁷W. Haas, J. Adams, and J. B. Flannery, Phys. Rev. Lett. <u>24</u>, 577 (1969).

⁸G. W. Gray, *Molecular Structure and the Properties* of *Liquid Crystals*, (Academic, New York, 1962).

⁹P. Chatelain, Bull. Soc. Fr. Mineral. Cristallogr. <u>66</u>, 105 (1962).

Self-Diffusion and Molecular Order in Lyotropic Liquid Crystals

R. Blinc, K. Easwaran, J. Pirš, M. Volfan, and I. Zupančič Institute "J. Stefan," University of Ljubljana, Ljubljana, Yugoslavia (Received 28 August 1970)

The translational self-diffusion coefficients of the H_2O molecules in the water channels of both hexagonal and lamellar lyotropic liquid crystals have been measured by the variable field-gradient proton spin-echo method, and the temperature dependence of the ordering of D_2O and H_2O molecules was studied by quadrupole perturbed deuteron NMR and proton spin-lattice relaxation measurements.

Recent x-ray studies have greatly enhanced^{1,2} our knowledge of the structure of the two most common phases—neat and middle—of lyotropic liquid crystals. These systems, which are formed by addition of water to various amphiphilic materials, seem to play an important role in many biological systems including cell membranes. The liquid-crystalline phases are limited by an upper temperature at which the transition to the isotropic liquid occurs, and a lower



FIG. 1. (a) Uniaxial conoscopic figure of homoeotropic texture in ABUTA. (b) Biaxial conoscopic figure in 45° position obtained with a dc field applied perpendicular to the optic axis.