[4] C. V. Heer and R. H. Kohl, Phys. Rev. A 1, 693 (1970).

[5] A. Compaan and I. D. Abella, Phys. Rev. Lett. **27**, 23 (1971); L. Q. Lambert, A. Compaan, and I. D. Abella, Phys. Lett. A **30**, 153 (1969).

[6] A. Compaan, Phys. Rev. B **5**, 4450 (1972).

[7] E. L. Hahn, N. S. Shiren, and S. L. McCall, Phys. Lett. A **37**, 265 (1971); R. Friedberg and S. R. Hartman, Phys. Lett. A **37**, 285 (1971).

[8] R. L. Shoemaker and R. G. Brewer, Phys. Rev. Lett. **27**, 631 (1971).

[9] C. V. Heer, *Statistical Mechanics, Kinetic Theory, and Stochastic Processes* (Academic, New York, 1972), p. 508.

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Molecular Alignment Owing to Electric and High Magnetic Fields in the Liquid Crystal *p*-*n*-Nonyloxybenzoic Acid*

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An anomalous effect owing to electric fields has been found in the nematic phase of a liquid crystal exhibiting positive dielectric and negative conductivity anisotropies. The preferred direction for the long axes of the molecules is perpendicular to a dc or very low-frequency ac electric field but parallel to a field for frequencies of a few thousand Hz. A sizable change in the average value of the dielectric loss was observed at the nematic-liquid transition temperature. This is explained by assuming that the nematic phase, which is believed to be a doubly-hydrogen-bonded dimer, contains a small percentage of monomer or dimer with one hydrogen bond broken. A small change in the percentage of normal dimer at the transition temperature could account for the change in loss. The effect of magnetic fields up to 68 000 G on the molecular alignment in the smectic *C* phase is discussed.

The liquid crystal *p*-*n*-nonyloxybenzoic acid[1,2] (NOBA) exhibits a smectic *C* phase (94–117 °C) and a nematic phase (117–143 °C). Measurements of the dielectric loss at microwave frequencies have been made in NOBA in the presence of magnetic fields up to 68 kG. The experimental techniques were similar to those reported earlier,[3] except the temperature bath was replaced with a copper block which was uniformly wound with heater wire. The samples of NOBA were purified by recrystallization and chromatographic methods.

Figure 1 shows the temperature dependence of the dielectric loss at a microwave frequency of 24.5 GHz. An external magnetic field of 10 kG is applied parallel and perpendicular to the polarized microwave electric field. A magnetic field of 68 kG

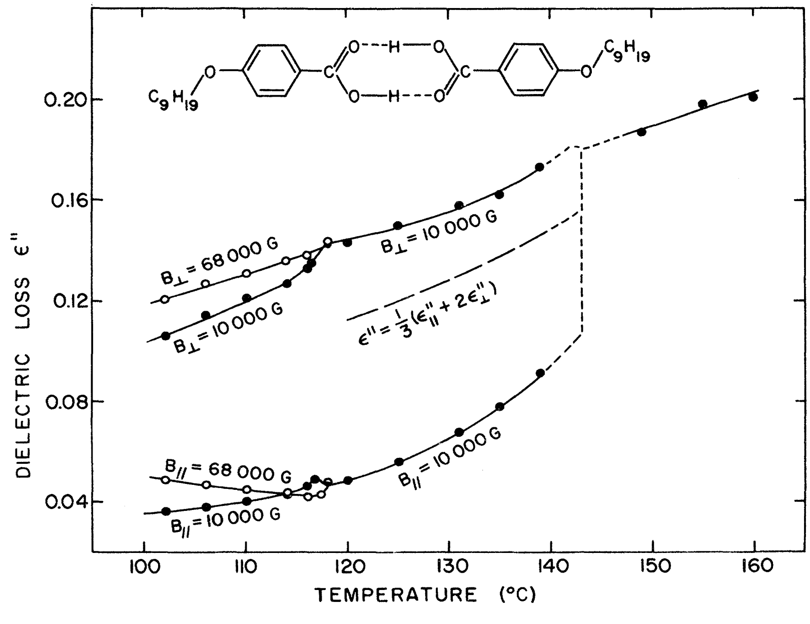

FIG. 1. Temperature dependence of the dielectric loss at a frequency of 24.5 GHz in magnetic fields of 10 and 68 kG parallel and perpendicular to the microwave electric field in *p*-*n*-nonyloxybenzoic acid.

was also used for the smectic *C* phase. All measurements of the loss in the smectic phase were made by cooling from the nematic phase in the presence of the field. Increasing the field above 10 kG in the nematic phase did not change the results. In fact, a field of 2 or 3 kG gave results comparable to the 10-kG field.

The effect of the magnetic field in the smectic phase is a little difficult to understand. Since the maximum value of the dielectric loss in the nematic phase is observed when the preferred direction of the long axes of the molecules is perpendicular to the microwave electric field, it is reasonable to assume that this is also true for the smectic phase. With this assumption, the 68-kG field is a little more effective in ordering the long axes of the molecules when applied perpendicular to the microwave field. For the case where the magnetic fields are applied parallel to the microwave field, the 10-kG field appears to be more effective in the smectic *C* phase because the lowest value of the loss indicates the highest degree of ordering for this orientation. The drop in the loss in the transition region for the 68-kG field indicated good alignment of the molecules in this region, but it might also mean that the planes which are associated with the smectic *C* structure become entangled, and a small change in tilt angle (angle between long molecular axis and normal to the plane) may account for the difference. The increase in absorption in the transition region for the 10-kG field indicates a little more freedom, and an ordering may take place which is more favorable when considering the planes. Results employing a 40-kG field were comparable to those for 68 kG. It should be pointed out that the changes referred to here were very small, and the only reason they were able to be observed is that relative measurements of the transmitted power were being made as the temperature was changing. Any suggestions concerning the behavior of the sample in the smectic *C* phase when the magnetic field is applied parallel to the microwave field must be made with a great deal of caution. The absorption was very low and the space in the magnetic field was limited. This allowed for multiple reflections of the microwave beam and added to the uncertainty of the measurements.

Attempts were made to change the molecular alignment in the smectic phase employing high magnetic fields. The sample was first cooled from the nematic phase to 110 °C in the presence of a 68-kG field perpendicular to the microwave electric field. The field was turned off, then applied parallel to the microwave electric field. A field of 10 kG produced a change of approximately 60% of the difference in dielectric loss between the parallel and perpendicular orientations with respect to the microwave electric field. A 40-kG field produced approximately a 75% change. The 40-kG field was slightly more effective than 20 kG but its effect was comparable to that of the 68-kG field. The changes at 10 kG may be due to a reorientation of the molecules in a cone with the tilt angle remaining constant, but the changes at 40 kG and up may also involve the planes.

If it is assumed that the average value of the loss in the nematic phase can be represented by $\frac{1}{3}(\epsilon_{\parallel}''+2\epsilon_{\perp}'')$, Fig. 1 shows a sizable change in absorption at the nematic-liquid transition temperature. An idea which was discussed earlier[4] and used to explain similar results[5] for *p*-*n*-butyloxybenzoic acid assumes that the nematic phase, which is believed to be predominately a dimer, contains a small percentage of monomer or a dimer with one hydrogen bond broken. Work by Delodre and Cabane[6] also supports the idea that in the nematic phase it is not 100% dimer with both hydrogen bonds. In order to explain the abrupt change in loss one has to further assume that the percentage of monomer or dimer with one broken bond must change abruptly at the transition temperature. This would allow for a small change in the average dipole moment and also a small change in the characteristic relaxation time.

Anomalous alignment due to electric fields has been observed in nematic phases which exhibit negative dielectric and positive conductivity anisotropies,[7,8] negative dielectric and negative conductivity anisotropies,[9] and positive dielectric and positive conductivity anisotropies.[5] Positive means a maximum value in a direction preferred by the

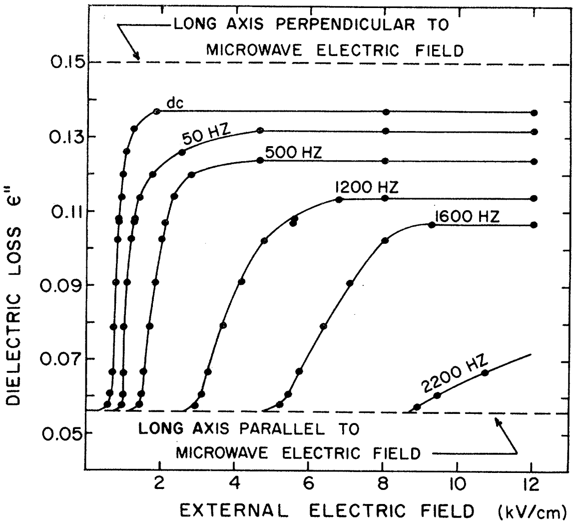

FIG. 2. Dielectric loss in *p*-*n*-nonyloxybenzoic acid at a microwave frequency of 24.5 GHz as a function of an externally applied electric field. The individual curves are for various frequencies of the electric field applied parallel to a 2000-G magnetic field. The temperature was 125 °C.

long molecular axes in a completely ordered sample. Figure 2 shows the effect of electric fields on the molecular alignment in the nematic phase of NOBA. The experimental techniques employed here were similar to those reported earlier.[10] The effect of the electric field on the molecular alignment is indicated by measurements of the dielectric loss at a constant temperature of 125 °C. A change in the dielectric loss from that indicated by the lower dotted line in Fig. 2 to the upper dotted line corresponds to a change of the preferred direction for the long molecular axes from parallel to perpendicular to the microwave field as can be seen from Fig. 1.

Figure 2 shows the effect of electric fields that are applied parallel to an external magnetic field of 2 kG. The magnetic field initially aligns the preferred direction for the long molecular axes parallel to the microwave electric field. As an external dc field is increased, a value is reached such that the absorption increases. This indicates that the preferred direction of the long axes is perpendicular to the electric field. Similar curves are shown for ac electric fields. As the frequency is increased the effect of the electric field in realigning the molecules decreases. For a frequency of a few thousand hertz, the preferred direction for the long molecular axes is parallel to the field. This implies that the dielectric anisotropy is positive and that the effect at a few hundred hertz or less is anomalous.

Measurements of the resistivity of NOBA, which was the order of 10^9 Ω cm, showed that the conductivity was approximately 1.3 times greater perpendicular to a direction preferred by the long molecular axes than in a parallel direction. The negative conductivity and positive dielectric anisotropies can be used in conjunction with a model[8] that was discussed earlier. This model can be used to explain the behavior in NOBA. This is a crude model but it does illustrate the counter action of the dielectric and conductivity anisotropy. This model assumes that a misaligned region will possess positive and negative space charges due to the conductivity anisotropy which can interact with the external field. By interchanging the sign of the charges in the model discussed earlier[8] the counter action of the two mechanisms can be explained for NOBA. Including the work reported here, anomalous alignment has now been observed in nematic phases with all possible combinations of the dielectric and the conductivity anisotropies. In all cases the preferred alignment due to this new mechanism is such that the direction of maximum conductivity is parallel to the electric field. This supports the idea presented earlier.[9,10] In both cases when the conductivity anisotropy was negative, the nematic phase was followed by a smectic *C* phase as the temperature was lowered. The structure for this combination has been discussed by deVries.[11]

When NOBA was cooled in a 5-KHz electric field (5000 V/cm), the preferred direction for the long axes of the molecules changed from parallel to the field in the nematic to perpendicular in the smectic phase. This implies that the dielectric anisotropy changes sign. This is a small change and could be associated with small changes in the percentage of pure dimer at the transition. A mechanism reported by Maier and Meier[12] and recently discussed by Martin, Meier, and Saupe[13] may also be needed to allow for a dispersion involving a small percentage of monomer. This involves a rotation about an axis perpendicular to the long molecular axis.

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[1] C. Weyland and R. Gabler, Z. Phys. Chem. B **46**, 270 (1940).

[2] T. R. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Lett. **24**, 359 (1970).

[3] E. F. Carr and R. D. Spence, J. Chem. Phys. **22**, 1481 (1954).

[4] E. F. Carr, in Gordon Conference on Dielectric Phenomena, 1972 (unpublished).

[5] W. T. Flint and E. F. Carr, in Fourth International Liquid Crystal Conference, Kent, Ohio, 1972 (unpublished).

[6] B. Delodre and B. Cabane, Mol. Cryst. Liq. Cryst. **19**, 25 (1972).

[7] R. P. Twitchell and E. F. Carr, J. Chem. Phys. **46**, 2765 (1967).

[8] E. F. Carr, Mol. Cryst. Liq. Cryst. **7**, 253 (1969).

[9] D. P. McLemore and E. F. Carr, J. Chem. Phys. **57**, 3245 (1972).

[10] E. F. Carr, Adv. Chem. Ser. **63**, 76 (1967).

[11] A. deVries, Mol. Cryst. Liq. Cryst. **10**, 219 (1970).

[12] W. Maier and G. Meier, Z. Naturforsch. A **16**, 1200 (1961).

[13] Anna J. Martin, G. Meier, and A. Saupe, Symposium of the Faraday Society, No. (5), 119 (1971).