

Luban for letting us know the results of his work prior to publication. This helped to stimulate our interest in the problems dealt with in this paper. We would also like to thank Professor S. Alexander and Dr. J. Grunzweig-Genossar for helpful discussions. We would like to thank Dr. E. Litov for bringing to our attention the recent results of Garland and Weiner.¹²

* Part of this work was done while L. G. was visiting Tel-Aviv University.

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¹O. K. Rice, *J. Chem. Phys.* **22**, 1535 (1954).

²C. Domb, *J. Chem. Phys.* **25**, 783 (1956).

³C. W. Garland and R. Renard, in *Critical Phenomena, Proceedings of a Conference, Washington, D. C., 1965*, edited by M. S. Green and J. V. Sengers, National Bureau of Standards Miscellaneous Publication No. 273 (U. S. GPO, Washington, D. C., 1966).

⁴C. W. Garland and R. Renard, *J. Chem. Phys.* **44**, 1120, 1125, 1130 (1966).

⁵C. Domb, *Proc. Phys. Soc.*, London **88**, 260 (1966).

⁶M. E. Fisher, *Phys. Rev.* **176**, 257 (1968).

⁷G. A. Baker, Jr., and J. W. Essam, *Phys. Rev. Lett.* **24**, 447 (1970).

⁸We have been recently informed by Essam (to whom we are very grateful for his communication to us) that he and Baker have solved exactly a compressible Ising model with infinite shear forces which exhibits a first-order transition at all pressures. (See Ref. 14 for related comments.) The latest BE work will be published

in Proceedings of the International Conference on Magnetism, Grenoble, France, September 1970 [*J. Phys. (Paris) Suppl.*, to be published].

⁹This fact, though completely obvious from Eq. (11) of BE, was first noted by L. A. Coplan and M. Dresden, *Phys. Rev. Lett.* **25**, 785 (1970). They realized that "the thermodynamic instability... might well have observable consequences." We have confirmed this conjecture, demonstrating moreover that the system undergoes a first-order phase transition. Coplan and Dresden also dealt with the effect of "boundary conditions" and quadratic $J(x)$.

¹⁰While negative pressure cannot occur in equilibrium states of real systems, in this model it is perfectly all right because of the peculiar and nonphysical property of the interparticle forces, namely, that they become more and more attractive and grow without limit as the interparticle distance increases.

¹¹The results we find are essentially the same for the BE model in three dimensions and when $\varphi(x)$ and $J(x)$ are arbitrary functions. This generalization as well as the independence of our results on the ensemble will be discussed elsewhere.

¹²C. W. Garland and B. B. Weiner, *Phys. Rev. B* **3**, 1634 (1971).

¹³We would like to emphasize that this conclusion differs entirely from what was obtained in Refs. 1–5 by approximate methods.

¹⁴We expect that the special role played by $P=0$ as the dividing point between the region of renormalization and the region of the first-order transition is an artifact of the special model we have treated. Use of a more realistic model, including, for example, shear forces between the lattice points, would hopefully move this point to some positive value of the pressure.

Birefringence of Nematogenic Liquids Caused by Electrical Conduction

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Experiments are reported which show that the electrical birefringence of the isotropic phase of two nematic liquid crystals depends on electrical conductivity. It is argued that the conduction-induced alignment is due to local conduction anisotropy.

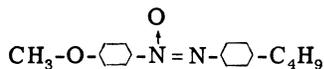
The alignment of nematic liquid crystals in electric fields is known to be strongly influenced by electrical conduction. Simple dielectric alignment is often prevented by electrohydrodynamic flow if the conductance of the sample is large enough. There seems to be essentially two mechanisms of such flow. One operates in isotropic and anisotropic liquids and requires injected space charge.¹ The other is based on conduction anisotropy and is usually ascribed to an intrinsic conductivity (but may also work with injected

charge).² The second mechanism seems by definition restricted to liquid crystals. However, a similar aligning effect appears possible in the isotropic phase of nematogenic liquids at temperatures not too far above the clearing point.

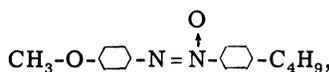
If a liquid crystal is heated into the isotropic state, the long-range order breaks down, but the parallel ordering of the rodlike molecules is preserved on a smaller scale. The existence of "swarms"³ of parallel molecules may be inferred, for instance, from measurements of the bire-

fringence in electric⁴ and magnetic⁵ fields and under shear.⁵ The induced optical anisotropies tend to be huge near the clearing point and then tend to drop over an interval of a few tens of degrees centigrade to values typical of normal organic isotropic liquids. The preferential alignment of large swarms in an electric field may be controlled not only by their dielectric anisotropy but also by anisotropic conduction. In the following we wish to report and interpret experiments which seem to confirm this expectation.

The materials studied were *p*-azoxyanisole (PAA) and a mixture of about 60%



and 40%



henceforth called Merck IV.⁶ The clearing points were 134.8 and 75.7°C, respectively, for the purified substances. The conductivities and thus the ion concentrations were varied by doping with tetrabutyl-ammonium chloride which strongly dissociates in organic solvents. To be able to start at low conduction we deionized both liquids prior to doping. The conductivity of Merck IV could be reduced to $10^{-12} \Omega^{-1} \text{cm}^{-1}$ by means of electrodiagnosis.⁷ PAA was purified with active carbon, which resulted in a conductivity of ca. $10^{-10} \Omega^{-1} \text{cm}^{-1}$.

For measuring the electrical birefringence we used a polarizing microscope with a built-in photomultiplier tube to detect small changes of light intensity. The electro-optical cell was made up of two parallel metal bars between glass plates. The bars served as spacers and electrodes and held the sample in place. Their height, i.e., the light path, was 1 mm and their distance about 0.1 mm. The difference Δn between the two principal refractive indices could be measured with an accuracy of $\Delta n \approx 10^{-7}$ by means of an elliptical compensator ($\lambda/10$). The cell was mounted in a Mettler heating stage permitting temperature stabilization within $\pm 0.02^\circ\text{C}$.

Measurements of the electrical birefringence Δn versus the electric field F showed a quadratic dependence $\Delta n \propto F^2$ at all conductivities, the fields ranging between $3 \times 10^3 \text{ V cm}^{-1}$ and $8 \times 10^4 \text{ V cm}^{-1}$. The birefringence as a function of conductivity is plotted in Fig. 1. The field strength and the difference $(T - T_{cl})$ between the actual temperature T and the clearing point T_{cl} were the

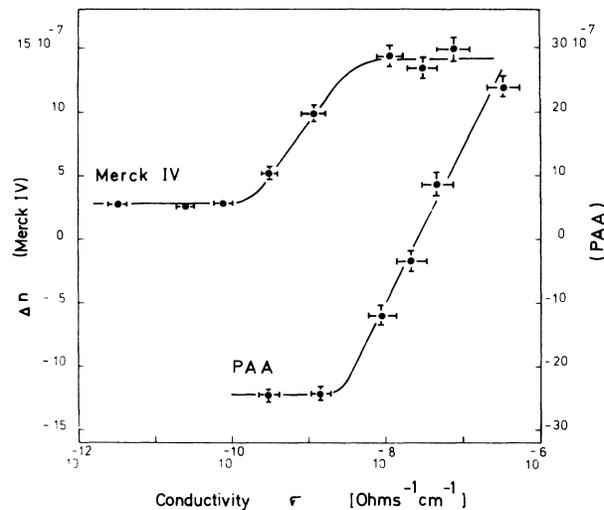


FIG. 1. Birefringence Δn as function of conductivity σ , measured at constant electric field $F = 3 \times 10^4 \text{ V cm}^{-1}$ and constant temperature difference $T - T_{cl} = 0.1^\circ\text{C}$.

same in all these measurements. It should be noted that T_{cl} is not constant but decreases with impurity content (up to 3°C in our experiments). Very similar results (to the eye) were obtained under ac (50-Hz) and dc operation.⁸ However, single pulses of 50 msec duration had to be used at the largest conductivities to avoid heating of the sample and, as a result, a spurious birefringence caused by thermal strain of the glass plates. The conductivities were measured with both ac and dc wherever possible. The agreement was good, apart from the fact that the current tended to drop with time when a dc voltage was applied. (This explains the large errors of the conductivity in Fig. 1.)

Strongly conducting samples decomposed rapidly in high fields, especially with dc. Another side effect, also larger with dc, was material flow such as vortices and turbulence. They seemed to have lower thresholds and to be more pronounced in the purer samples. Flow birefringence was occasionally noticed, but on the whole it appeared to be negligible as is evidenced, e.g., by the similarity of ac and dc results.

The measurements show a significant influence of conduction on electrical birefringence. The conduction-induced alignment is of the same type as in the nematic phase of these materials, i.e., it tends to turn the long axes of the molecules into the direction of the field. The electrical birefringence of PAA immediately above T_{cl} is negative in the insulating state, in agreement with the negative dielectric anisotropy ($\epsilon_{\parallel} < \epsilon_{\perp}$) of nematic

PAA, and changes sign at a certain conductivity.⁹ It is perhaps surprising that the dielectric birefringence of Merck IV is positive while the dielectric anisotropy of the liquid crystal, also measured by us, seems to be negative up to the clearing point. However, both are exceptionally weak.

Conduction-induced birefringence displays saturation at large ion concentrations. This is clearly seen in Fig. 1 with Merck IV; it also becomes visible with PAA if a linear scale is used for the conductivity. The saturation indicates that the conduction-induced alignment is linked with the formation of space charge. If there is overall charge neutrality, as is likely under ac operation, space charges may be expected to arise from a segregation of positive and negative ions because of local conduction anisotropy. The sign and density of the space charge would be a function of the spatial variation of molecular orientation. The interaction of such space charges with the electric field leads to shear which could have an aligning influence on the swarms.

Clearly, our interpretation resembles the above-mentioned theory of electrohydrodynamic alignment of nematic liquid crystals by anisotropic conduction.² However, because of the long-range disorder in the isotropic phase it cannot readily be given a quantitative form. Different swarms, except neighbors, align independently (although a spatially varying alignment is essential to the model). The aligning effect of the electric field is relatively weak in the isotropic state despite the existence of swarms. Even at the highest fields used, dielectric birefringence (the Kerr effect) and conduction-induced birefringence were much smaller than the optical anisotropy of the liquid crystal.

The following predictions may be made, in accordance with Ref. 2, if our picture is correct. Saturation should be attained if there are more than a pair of ions per swarm and if diffusive currents are negligible. Cases are conceivable where the second condition is satisfied at lower ion concentrations than is the first. We may speculate that this would result in a peak of electrical birefringence at a certain conductivity, followed by a drop to the saturation value. The hypothesis may be verifiable, with more sensitive apparatus than ours, by going to higher temperatures where the swarms are smaller. Conduction-induced alignment of swarms should also be possible with unipolar injection currents. Instead of charge segregation there would be a variable density of charge of one sign.

Let us attempt an estimate of the swarm size using the saturation point σ_{sat} of conduction birefringence. Choosing Merck IV we take from Fig. 1 $\sigma_{\text{sat}} \approx 3 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$. With an estimated mobility¹⁰ of $10^{-5} \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ one calculates $n = 2 \times 10^{15} \text{cm}^{-3}$ for the total ion concentration n . We regard the swarms as roughly spherical. Then their average diameter d should be

$$d > 1 \times 10^{-5} \text{cm},$$

if one demands at least one pair of ions for each swarm. The diffusive contribution to the current is negligible for

$$R = \epsilon kT q^2 / 4\pi e_0^2 n \ll 1,$$

where q is the wave vector of a periodic alignment perturbation, e_0 is the elementary charge, and ϵ is the dielectric constant. The inequality holds for singly charged ions and was derived for the nematic state.² It may also be applied as an approximation to the isotropic phase if q is replaced by π/d . At the saturation point one should have $R \approx 1$. Insertion of $kT = 0.03 \text{eV}$, $\epsilon = 5$, and $n = 2 \times 10^{15}$ in this equation yields

$$d \approx 2 \times 10^{-5} \text{cm}.$$

A swarm diameter of this magnitude appears reasonable close to T_{cl} . There would be of the order of ten ion pairs per swarm at the saturation point. However, the validity of the numerical results may be questioned as the swarm model is vague and the ionic mobility not exactly known.

It should be mentioned that there are at least two other mechanisms which may be invoked to interpret our experimental results. The dependence of the electrical birefringence on conductivity might be attributed to a change of the dielectric properties or the size of the swarms. However, such an effect is unlikely to reach saturation at an ion concentration apparently much smaller than the molecular density. Another explanation which is implausible for the same reason is flow alignment in the local shear caused by ion transport. Besides, if flow alignment by transported ions would be important, it should also show in the nematic phase where it has never been observed.

¹J. M. Schneider and P. K. Watson, *Phys. Fluids* **13**, 1948 (1970); P. Atten and R. Moreau, *C. R. Acad. Sci., Ser. A* **270**, 415 (1970).

²W. Helfrich, *J. Chem. Phys.* **51**, 4092 (1969).

³These swarms are a visualization of the orientational correlation length and thus unlikely to have

sharp boundaries. They are similar to the swarms of the defunct "swarm theory" of nematic liquid crystals.

⁴V. N. Tsvetkov and E. I. Ryumtsev, *Kristallografiya* **13**, 290 (1968) [*Sov. Phys. Crystallogr.* **13**, 225 (1968)].

⁵V. N. Tsvetkov, *Acta Physicochim. U.R.S.S.* **19**, 86 (1944).

⁶Prepared by H. Scherrer of our laboratories according to H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *Angew. Chemie* **82**, 984 (1970). The composition is very similar to a mixture available from Merck under the trade name "Nematische Phase IV Licristal," as recently disclosed by R. Steinr asser and L. Pohl, *Tetrahedron Lett.* **22**, 1921 (1971).

⁷G. Bri ere and N. F elici, *C. R. Acad. Sci., Ser. C*

259, 3237 (1964).

⁸The orientational relaxation time of the swarms could not be measured with our equipment, but it was checked to be shorter than 10^{-4} sec.

⁹The dielectric birefringence (Kerr effect) of PAA changes sign with temperature at 5°C above T_{c1} (Ref. 4). This effect is connected with the decrease of the swarm size with temperature; it is unrelated to ours.

¹⁰Our estimate is based on measurements with the room-temperature nematic *p*-methoxy-benzylidene, *p-n* butyl-aniline by Groupe d'Etudes des Cristaux Liquides LETI-Centre National de la Recherche Scientifique, in Proceedings of the Third International Conference on Liquid Crystals, Berlin, West Germany, August 1970 (to be published).

Helical Twisting Power in Mixtures of Nematic and Cholesteric Liquid Crystals*

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The helical twisting power in nematic (methoxybenzylidene *p*-aminophenyl acetate)-cholesteric (cholesteryl propionate) mixtures as a function of cholesteric material concentration is studied by measuring the circular dichroism, the wavelength of selective reflection, and the Grandjean fringes. It is found that as the cholesteric material concentration increases, the twisting power of the mixtures increases linearly up to a certain concentration, beyond which, however, it increases more slowly, taking a maximum value at some specific concentration which normally falls in the high-concentration region.

The cholesteric phase may be regarded as a special case of the nematic phase since it forms a molecular structure having twisted nematic layers; each layer forms a two-dimensional nematic ordering, subsequent layers being twisted by a small angle.¹ If a small amount of optically active substance is added to the normally nematic substance, the mesophase is easily transformed into cholesteric mesophase.² The helical twist angle of such mixtures has been shown to be a linear function of the cholesteric material concentration in some limited range of low concentration.^{3,4}

It is the purpose of this Letter to report results of investigation on twisting power as a

function of the concentration of active cholesteric material over the whole range of concentration ($0.02 \leq C_2 \leq 1.0$) in nematic-cholesteric mixtures. The samples investigated were nematic-cholesteric mixtures consisting of the nematic *p*-methoxybenzylidenyl acetate (MBA) and the cholesteric cholesteryl propionate (CP). The CP, which is a levorotatory and enantiotropic cholesteric liquid crystal, has no smectic phase at low temperature in its mesophase.⁵ All mixtures were assured to be levorotatory.

Many properties of the cholesteric phase can be derived from the mean refractive index n of the birefringent layers, the pitch p , and the sense of helix. In thermotropic liquid crystals,