Comments and Addenda

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Conductivity anisotropy in *p*-*n*-nonyloxybenzoic acid*

E. F. Carr
Physics Department, University of Maine, Orono, Maine 04473
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Ionic conduction in the nematic phase of *p*-*n*-nonyloxybenzoic acid can be a maximum in a direction parallel (positive conductivity anisotropy) or perpendicular (negative anisotropy) to the nematic director. The presence of acetone can change a sample which exhibits a positive conductivity anisotropy to negative anisotropy. Experimental evidence indicates that there are many other dopants that can change the sign of anisotropy. It is suggested that the dopant may disrupt one of the hydrogen bonds of the dimer in some of the molecules, which makes it easier for trimers and higher polymers to form. This process should favor a smecticlike structure.

Molecular alignment in a liquid crystal exhibiting positive dielectric and negative conductivity anisotropies was reported earlier.[1] The material investigated was *p*-*n*-nonyloxybenzoic acid (NOBA), in which the maximum value of the static dielectric constant was parallel to the nematic director (positive anisotropy) and the maximum value of the conductivity was in a direction perpendicular to the director in the nematic phase. Recent results have indicated that pure NOBA probably exhibits a positive conductivity anisotropy, and the observed negative conductivity may be due to the presence of dopants which remained after purification. This should not affect the significance of the results, because if they can be controlled by doping pure samples with known materials, interesting studies should result.

Samples of NOBA that have been purified by recrystallization and zone refining showed resistivities which were the order of $10^{10}\,\Omega\,\mathrm{cm}$. These materials exhibited positive dielectric and positive conductivity anisotropies. However, the presence of acetone (spectranalyzed) can change the conductivity anisotropy from positive to negative. This was accomplished by adding approximately 2 ml of acetone to 0.1 g of NOBA and boiling off the acetone. Samples which originally exhibited a positive conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp} \approx 1.4$ at 125° C) showed negative conductivity anisotropy in the nematic phase. After heating for approximately 20 min at 160° C, they then showed a positive conductivity anisotropy in the nematic phase. This process can be repeated with the same sample. These results imply that most of the acetone is boiled off but some is trapped in the NOBA giving rise to the negative anisotropy. After heating at a high temperature some of the trapped acetone is probably boiled off giving a positive anisotropy, and the process can be repeated by adding more acetone. After adding the acetone the ratio of the conductivities $\sigma_{\parallel}/\sigma_{\perp}$ normally dropped to between 0.95 and 0.96 at 125° C. At lower temperatures it was often less. Although there is some variation of $\sigma_{\parallel}/\sigma_{\perp}$, successive measurements that were made within a period of a few minutes did not normally vary by more than 2% with the techniques employed. As the ratio of $\sigma_{\parallel}/\sigma_{\perp}$ approached 1, the variation was less than 1%. When adding a dopant to any liquid crystal, one must be aware of the fact that complete mixing does not always take place immediately. This is also the case when doping a fresh sample of NOBA with acetone. Because of mixing problems and evaporation of the acetone, the values of $\sigma_{\parallel}/\sigma_{\perp}$ will vary. After most of the trapped acetone was boiled off at 160° C, the ratio of the conductivities $\sigma_{\parallel}/\sigma_{\perp}$ returned to approximately 1.4.

The conductivity anisotropy was determined from dc measurements of the resistance of the sample which was aligned with a 2500-G mag-

netic field. Although dc measurements are not always satisfactory for measuring the magnitude of the conductivity, they can often be used for measurements of $\sigma_{\parallel}/\sigma_{\perp}$. When some dc measurements of $\sigma_{\parallel}/\sigma_{\perp}$ were compared with those employing an ac bridge, the comparison indicated that the dc measurements were adequate for the work reported here. The dc voltages applied across the sample were normally between 1 and 10 V. The cell was constructed so that the sample could be easily rotated in the magnetic field. This meant that the measurements of $\sigma_{\parallel}/\sigma_{\perp}$ could be made within seconds, and most of the measurements were checked many times.

From x-ray studies de Vries[2] has suggested a cybotactic structure for the nematic phase of some liquid crystals like NOBA that also exhibit a smectic phase. If one imagines a mixture of smecticlike and nematiclike regions, it might be possible for certain ions to exhibit a positive conductivity anisotropy while other ions exhibit a negative anisotropy. Svedberg[3] showed that the conductivity anisotropy in liquid crystals could vary considerably with the type of dopant. If an ion exhibits a large anisotropy in the smecticlike regions and a small anisotropy in the nematiclike regions, it could show a negative conductivity anisotropy, whereas an ion exhibiting a large anisotropy in a nematic region and a small anisotropy in the smectic region might show a positive anisotropy in the same sample. Although the change in the anisotropies due to various dopants would have to be considered in any detailed analysis of this problem, a change in structure which is due to a dopant should also be considered. For a dopant to change a smecticlike region to a nematiclike region is not unexpected, but a change from a nematiclike to a smecticlike region is unusual.

Earlier work[4,5] on the *p*-alkoxybenzoic acids, which showed changes in the sign of the conductivity anisotropy at given temperatures in the nematic range, implies that the change in sign was due to a structural change in the material. The investigation of molecular alignment in NOBA[4,6] has shown that low-frequency electric fields (conduction regime) are very effective in producing alignment and that the preferred direction for the nematic director is different for positive and negative conductivity anisotropies. These results suggest possible changes in the shear torque coefficients which also imply a change in structure.

If one imagines a mixture of nematiclike and smecticlike regions, the material may appear to behave like a nematic or smectic material. If it behaves like a nematic, in might be changed to a smectic by slightly increasing the number and size of the smecticlike regions. It has been suggested[4] that NOBA may tend to polymerize by hydrogen bonding and give rise to a smecticlike structure. A polymerization process would have to be initiated by an open dimer, but entropy considerations favor the reformation of dimers over trimers or higher polymers. However, if one of the hydrogen bonds of the NOBA dimer was disrupted by ionization of the hydrogen atom of the carboxyl group or interaction with some other chemical unit, the formation of trimers and higher polymers would then be a possibility. The formation of trimers and higher polymers could aid in increasing the number and sizes of the smecticlike regions.

Although acetone is an example of a material that can affect the conductivity anisotropy of NOBA, results from this investigation have indicated that there are other materials that can alter the anisotropy. Methyl *p*-hydroxybenzoate is an example of a material that appears to be effective in changing smecticlike to nematiclike structure. Normal samples probably contain impurities of both types, and the behavior of a particular sample depends on the concentration and types of impurities. This implies that further studies should be very concerned with the purification of NOBA, and the purest compounds should be checked to see if they exhibit positive or negative anisotropy. Although the samples used in this work appeared to be quite pure, the primary objective is to point out that the sign of the anisotropy can be changed by dopants. The presence of impurities may explain some of the reversible processes[4] which are associated with solidification. Materials that affect the structure may tend to separate from the NOBA when it becomes a solid and redissolve after melting. The redissolving process could allow for time-dependent behavior. It should be emphasized that measurements involving the effect of dopants may be time dependent. Some measurements can be made quickly, while others may require a waiting period of hours.

The purest samples of NOBA (resistivity $10^{10}\,\Omega$ cm) did not exhibit domain formation or dynamic scattering due to electric fields when placed in a cell similar to that described by Williams[7]. This is consistent with the behavior of other nematic materials with a very high resistivity. A sample which was doped with acetone showed some loop domains and light scattering with a cutoff frequency in the audio region. This was consistent with results on other samples of NOBA[6] which exhibited a negative conductivity anisotropy. A doped sample

of NOBA with a positive anisotropy exhibited light scattering, but loop domains or Williams domains were not observed. The threshold voltage for light scattering appears to be higher than in most other nematic materials.

Preliminary measurements have indicated that the smectic *C* phase of NOBA is also affected by dopants. Recent results[8] have indicated that *p-n*-octyloxybenzoic acid and *p-n*-hepyloxybenzoic acid exhibit a behavior similar to that of NOBA; so similar effects may be observed in other liquid crystals.

Although the presence of impurities appears to make an investigation of NOBA complicated, earlier work on NOBA has shown that the mechanism which is responsible for molecular alignment due to ionic conduction is a well-behaved process. A better understanding of the effect of dopants in NOBA should provide investigators with materials for some interesting studies in electrohydrodynamics. An investigation of materials like NOBA should aid in understanding electrohydrodynamic phenomena in smectic[9] liquid crystals.

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