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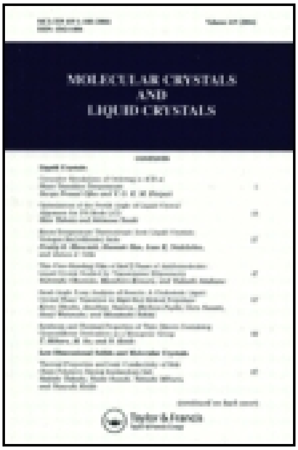

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The Dielectric Constant of a Cy Anophenyl-Thiobenzoate

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THE DIELECTRIC CONSTANT OF A CYANOPHENYL-THIOBENZOATE

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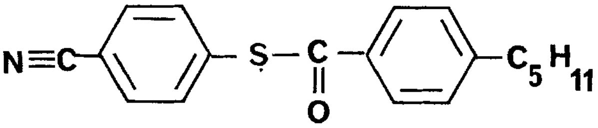
ABSTRACT

We have measured the dielectric constants of S-(4-cyanophenyl)4-pentyl (this benzoate) [5CTB] using a simple but novel technique. We find the dielectric anisotropy of 5CTB to be 70% less than the value expected from a linear extrapolation of dielectric constant measurements of 5CTB in solution with Nematic Phase 5. This is understood in terms of the pairing hypothesis of Cladis et al.

(Submitted for Publication December 28, 1981)

I. INTRODUCTION

The purpose of this paper is to report measurements of the dielectric constants of S-(4-cyanophenyl)4-pentyl (thiobenzoate)$^{(1)}$ or 5CTB

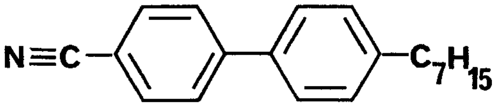


$$\text{crystal} \underset{66^\circ\text{C}}{\overset{76^\circ\text{C}}{\rightleftarrows}} \text{nematic} \overset{98^\circ\text{C}}{\longleftrightarrow} \text{isotropic}$$

using a novel but simple technique. Prior to our measurements, the dielectric anisotropy, $\Delta\epsilon$ ($= \epsilon_{\parallel} - \epsilon_{\perp}$, the difference between the dielectric constant parallel to the director and perpendicular to it) of this material was estimated by extrapolating dielectric constant measurements of dilute solutions (less than 20%) of 5CTB in the nematic mixture known as Nematic Phase 5.$^{(1)}$ Nematic Phase 5 is a eutectic mixture of 4-ethyl-4′-methoxyazoxybenzene and 4-butyl-4′-methoxyazoxybenzene. These molecules are relatively symmetric compared to 5CTB. On the basis of this extrapolation, $\Delta\epsilon$ for pure 5CTB should be about

33. The maximum value we measured is 19.7 or nearly 70% smaller than expected. A possible reason for this discrepancy is that concentrated solutions of 5CTB form dimers as do the cyanobiphenyls.(2) Such molecular associations neutralize the strong longitudinal dipoles of the cyanoaromatic moiety. The permanent dipole associated with a dimer is zero. Effects which arise exclusively from a dipole-dipole interaction will be non-existent in a population of dimers and very important in a monomer population. Consequently, a linear extrapolation of data found in the dilute limit where there are only monomers need not be relevant in the neat limit where there are predominantly dimers — as we have found.

Since our measurements were performed using a novel technique, we first tested it on 7CB (cyano-heptylbiphenyl)



$$\text{crystal} \xrightarrow{30^{\circ}\mathrm{C}} \text{nematic} \xleftrightarrow{42.8^{\circ}\mathrm{C}} \text{isotropic}$$

for which careful dielectric measurements had already been made.(3)

II. EXPERIMENT

A. Sample Preparation

Parallel plate capacitors were made from 1 inch square glass microscope slides with evaporated InO_3 electrodes etched to a 1 cm^2 pattern with a single lead extending from one of the square sides. Two plates were epoxied together with 100 μ mylar spacers between them so that the square electrodes were in register and the leads extended in opposite directions from the registered squares. The cell thickness was determined using a section microscope.

Chloroform was used to calibrate the capacitor. After calibration, the cell was flushed with acetone and water, then refilled with the liquid crystals 1) 7CB and 2) 5CTB. A final calibration check was again made at the end of this

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experiment.

B. Measuring Circuit

Figure 1 shows the circuit used to measure the dielectric constants of the material in the capacitor. The circuit consists of a buffer amplifier in a follower configuration that permits a high input impedance.(4) The amplifier output provides a low impedance image of the voltage across the liquid crystal cell capacitor. The output is also used to supply a guard potential to a copper foil placed around the exterior of the cell as well as to a coaxial shield around the cable connecting the cell to the amplifier circuit. This guard minimizes stray capacitive effects.

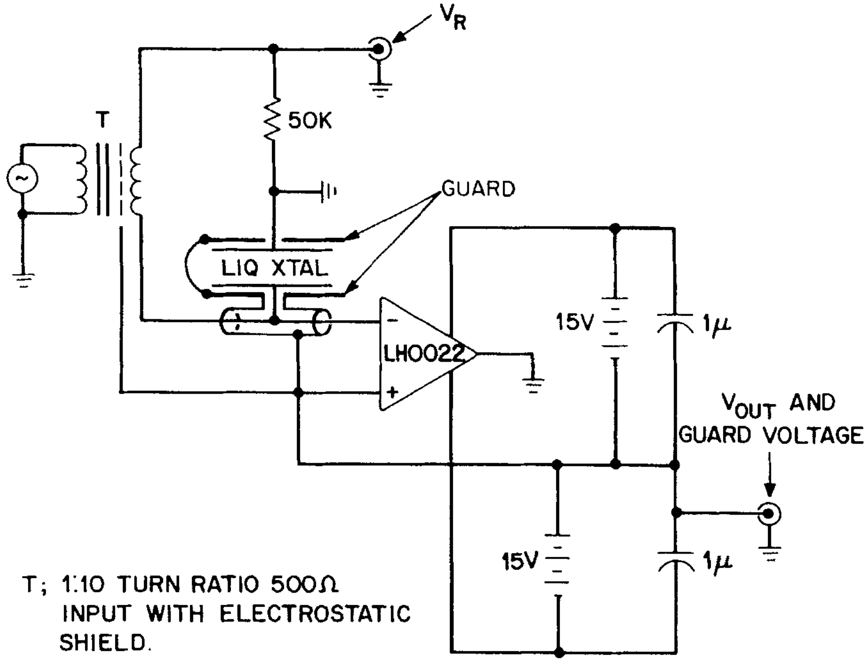

Figure 1 Circuit used to measure the dielectric constants. This configuration combines high A.C. impedance with minimal experimental complexity.

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The voltage across the 50 K resistor was used as a measure of the current flowing through the cell. The phases of the voltage across both the resistor and the cell were monitored to be sure that they were, in fact, exactly 90° out of phase. The input capacitance of the empty cell was 7pfs. Capacitance measurements to better than 1% were obtained with this circuit.

C. Method

In order to measure the dielectric constant of chloroform, one need only determine the cell capacitance at room temperature. For the liquid crystal measurements, the cell was loaded in a Mettler FP52 hot-stage and positioned between the poles of an electro-magnet whose maximum field is 11 kilogauss. To measure $\epsilon_{\parallel}$, the hot stage and sample were rotated in the field until the voltage across the 50K resistor was maximum. To measure $\epsilon_{\perp}$, it was turned 90° to this position then fine tuned by slowly rotating to find the minimum voltage. Knowing the cell calibration, it is then straightforward to deduce the dielectric constants.

With a 100 μ sample, a 7 kilogauss field was observed to be sufficient to produce saturation in the resistor voltage.

Because of the large heat leaks from the copper shields surrounding the sample in the Mettler oven, the absolute accuracy of the temperature read out was changed by 1 or 2 degrees. Therefore, we monitored the temperature of the sample with a thermocouple.

III. RESULTS

Figure 2 shows a comparison of the dielectric constants of 7CB versus reduced temperature found using this method with previous measurements of Schad et al.(3) Far from the isotropic transition, the $\epsilon_{\perp}$ measurements are seen to agree exactly but our $\epsilon_{\parallel}$ is about 7% less than the value they found. Our value for ϵ just in the isotropic phase is also 7% smaller than their value.

Figure 3 shows the dielectric constants we found for 5CTB. The cross hatched region is a temperature range where both rematic and isotropic phases co-existed. Here, the voltage across the capacitor fluctuated too much to allow ϵ to be deduced. The maximum value of $\Delta\epsilon$ is 19.7 just before the sample crystallized. Both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are larger than in 7CB. Also, the average $\epsilon_i = (\epsilon_{\parallel}+2\epsilon_{\perp})/3$ is somewhat less than the value found for ϵ in the isotropic phase in agreement with similar results of Ratna and Shashidhar(5) for the cyanobiphenyls. However, they interpreted this as being due to an ***enhancement*** of the short-range or nearest neighbor anti-parallel correlations because of the strong longitudinal dipoles.

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As we discuss next, our interpretation is that this is due to dimer formation which has the effect of *weakening* the anti-parallel short-range correlations.

IV. DISCUSSION

Two of the factors which contribute to the magnitude of the dielectric constant are 1) the polarizability of the molecular electron cloud by external fields and 2) the permanent dipole associated with a molecular species.

The polarizability of a molecule depends on the number of electrons interacting with the external field: the more electrons, the more polarizable and the larger the dielectric constant. Although $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ is larger for 5CTB than it is for 7CB, $\Delta\epsilon/\epsilon_i$ is comparable. For example, at reduced temperature, $t = T/T_{NI} = 0.975$, with T_{NI} the clearing temperature, $\Delta\epsilon/\epsilon_i = 1.1$ for 5CTB and 1.05 for 7CB. This suggests that the larger values for the dielectric constants of 5CTB arise simply from the larger number of electrons associated with the thio-ester link contributing equally to $\epsilon_{\parallel}$ and $\epsilon_{\perp}$: i.e., the sulfur electrons contribute equally to an increase in polarizability along and perpendicular to the molecular long axis. In addition, conjugation of the ketonic group with the pentyl substituted benzene ring allows withdrawal of π-electrons from the benzene ring by mesomeric relay resulting in a permanent dipole oriented at an angle to the molecular long axis making a contribution to both components of the permanent dipole.

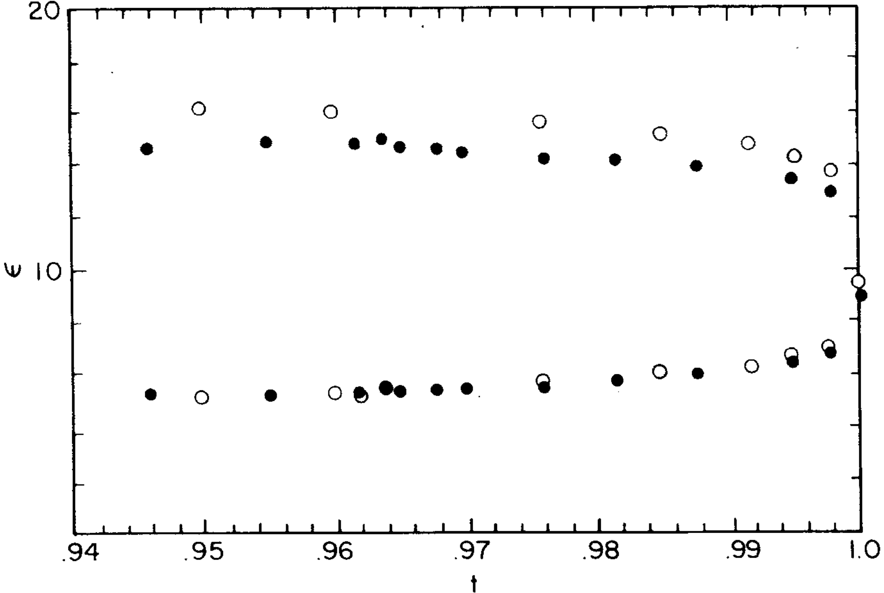

Figure 2 The dielectric constants of 7CB as found by this method (○) and by Schad et al.[3] (●).

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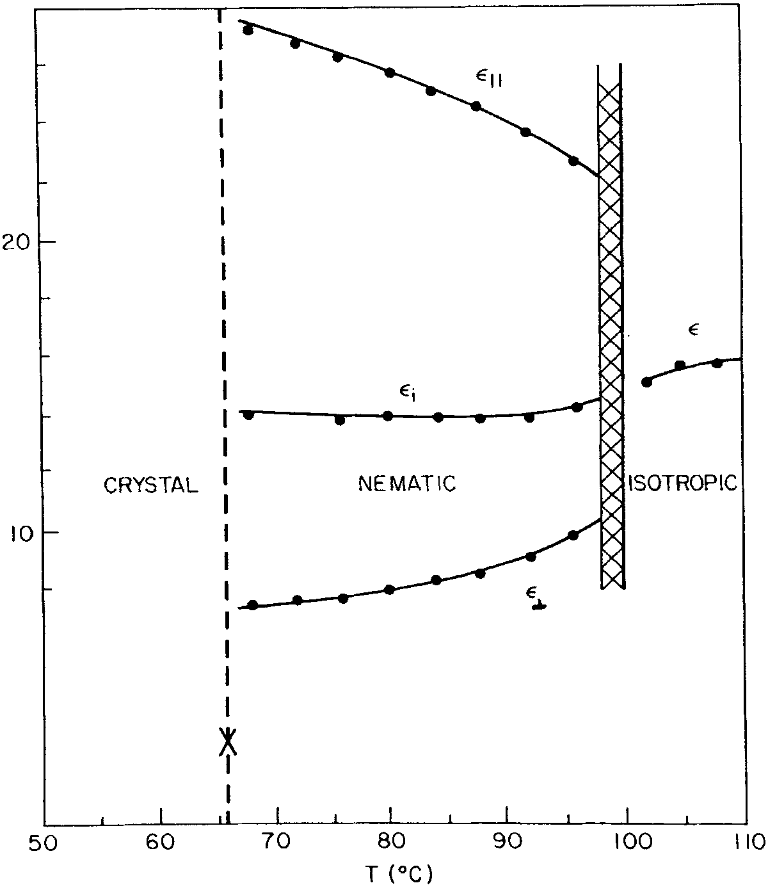

Figure 3 The dielectric constants of 5CTB. $\epsilon_i = (\epsilon_{\parallel}+2\epsilon_{\perp})/3$.

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$\epsilon_{\parallel}$ is less than one expects from an extrapolation of measurements made in a dilute solution of 5CTB in Nematic Phase 5 because 5CTB forms dimers when concentrated enough (and Nematic Phase 5 does not). The permanent dipole associated with a dimer is much less than it is for two monomers. In 5CTB and 7CB, both monomers and dimers are present. We expect the short range anti-parallel correlations calculated by Madhusadana and Chandrasekhar$^{(6)}$ for a system of interacting dipoles (and not to be confused with dimer formation) to be weaker in a system of dimers (i.e. nearest neighbors are also dimers) which have no permanent dipoles than in a system of monomers with large longitudinal dipoles. The weakening of the anti-parallel short range correlations with increasing dimer population decreases the long range orientational order.$^{(6)}$ In compounds with smectic A phases, this effect could lead to re-entrant nematic behavior.$^{(7)}$

V. CONCLUSION

We have measured the dielectric constant of 5CTB using a novel but simple technique. We found that the dielectric anisotropy of 5CTB is much smaller in the pure state than one would expect from an extrapolation of dilute solution data. We attribute this to dimer formation of 5CTB. Dimer formation implies a decrease in short-range anti-parallel correlations compared to a system of monomers with large longitudinal dipoles. A decrease in short-range anti-parallel correlations in turn has been shown$^{(6)}$ to correlate with a decrease in the long-range nematic ordering.

Acknowledgements

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REFERENCES

[1] All chemicals were purchased from E. Merck and used without further purification. The extrapolated value for $\Delta\epsilon$ referred to here for 5CTB is from the Merck Catalogue, July 1977.

[2] P. E. Cladis, R. K. Bogardus and D. Aadsen, Phys. Reo. **A18**, 2292 (1978).

[3] Hp. Schad and M. Ossman, J. Chem. Phys. **75**, 880 (1981).

[4] "Applications of Operational Amplifiers: Third Generation Techniques" by Jerald G. Graeme, McGraw Hill, New York (1973).

[5] B. R. Ratna and R. Shashidhar, Mol. Cryst. Lig. Cryst. **42**, 113 (1977); **45**, 103 (1978). B. R. Ratna, M. S. Vijaya, R. Shashidhar and B. K. Sadashiua, Pramana, Suppl. No. 1, 69 (1975).

[6] N. Y. Madhusudana and S. Chandrasekhar, Pramana, Suppl. No. 1, 57 (1975).

[7] P. E. Cladis, Molecular Crystals. Liquid Crystals **67**, 177 (1981).