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DIELECTRIC AND CONDUCTIVITY ANISOTROPY OF THE TWO ISOMERIC N-PENTYLPHENYL CYANO-THIOBENZOATE LIQUID CRYSTALS

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ABSTRACT

Temperature and low frequency dependence of conductivity and dielectric permittivity are studied for the two nematic 4-n pentylphenyl 4'-cyano-thiobenzoate& 4-cyanophenyl 4'-n-pentyl-thiobenzoate isomers. The changes in conductivities and dielectric permittivities under the influence of applied magnetic field are also reported. The dielectric and conductivity anisotropies observed are discussed on the light of the results obtained previously from x-ray, thermal analysis as well as infrared studies.

INTRODUCTION

The nematic liquid crystals are characterized by a temperature dependent orientational ordering. The anisotropic rod-like molecules are, on the average, aligned with their long axes parallel to a preferred direction. The orientational order is given by the order parameter.

$$S = < 1/2 \ (3 \cos^2\theta \ -1) >$$

Where θ is the angle between the long axis of a molecule and the preferred direction (1). Such asymmetrical of molecules is expected to produce anisotropic dielectric and conductivity behaviour (1 - 4).

The growing interest in the nematic liquid crystals exhibiting dielectric and conductivity anisotropies is due to the various electro-optical effects produced upon the application of a suitable electric or magnetic field (5). The results obtained upon the application of an electric or magnetic field depend upon the sign of dielectric and conductivity anisotropies of the material and upon the initial boundary conditions prior to the application of the field (4).

Several workers (4-6) have discussed the relation between the constitution of liquid crystal molecules and the sign of their dielectric anisotropy. However no general accepted theory has been developed yet to accurately correlate the structure of liquid crystal and their expected physical

properties.

4,'4-disubstituted phenyl thiobenzoates were first reported by Krause et al (7). The diamagnetic properties, densities and optical properties of the two isomeric compounds 4-n penytyl phenyl 4-cyano - thiobenzoate (NCS5) and 4-cyano phenyl 4-n - pentyl - thiobenzoate (5SCN) were also reported (8,9). On the other hand, the crystal and molecular structure of these two isomers were also studied (10) using X-ray diffraction method. The results indicated that the two compounds possess different molecular packing.

In this work, the dielectric and conductivity anisotropies of these two isomeric compounds were studied around the nematic range of temperatures and in the frequency range of 100 Hz to 10 KHz.

MATERIALS AND METHODS

The two isomeric compounds (NCS5 and 5SCN) were kindly presented by E. Merck Co., Darmstadt, F.R. Germany. The purity of the materials was checked by applying a differential scanning calorimeter test throughout the temperature range 300-400 K. A Heraus differential scanning calorimeter DSC 500, fitted with a pt-100 thermocouple, was used. The heating rate applied was 2 K min^{-1}. Sharp endothermic bands appeared at 340.5 K and 375 K for NCS5 were assigned to solid-nematic (K-N) transition and nematic-isotropic (N-I) transition respectively, while those

appeared at 350 and 373 K for 5SCN were assigned similarly. This suggested that the materials could be used without further purification.

Electrical permittivity and conductivity measurements were carried out in a special cell containing two glass electrodes coated with either silver or tin oxide. Sample thickness was controlled using a spacer about 90 to 100 μm thick between the two electrodes. Parallel and perpendicular orientation of samples were achieved by applying a 3 KG magnetic field.

Capacitance and conductivity values were measured using a Wayne-Kerr B-331 auto-balance precission bridge at a fixed frequency of 1592 Hz. For other frequencies, in the audio range, the same bridge was used in combination with an additional external generator and detector.

RESULTS AND DISCUSSION

a) Dielectric anisotropy studies

The results obtained for the variation of dielectric constant as a function of temperature for the two 5SCN and NCS5 isomers are shown in figures 1 and 2 respectively. It is clear that the two compounds possess positive dielectric anisotropy i.e $\Delta\varepsilon = \varepsilon_{11} - \varepsilon_{\perp} > 0$. It is also to be noted that that both the value of ε_{11} and $\varepsilon_{\perp}$ are larger in the case of sample I as compared to sample II. On the other hand the variation of the mean value of permittivity $\bar{\varepsilon}$ as a

function of temperature for the two compounds are also shown, where $\bar{\varepsilon} = (\varepsilon_{11} + 2\varepsilon_{\perp})/3$.

The dielectric behaviour of nematic liquid crystals may be understood by application of Maier and Meier's extension (11) of Onsager's theory applied for isotropic liquids. This leads to the following expressions for ε_{11} and $\varepsilon_{\perp}$ or alternatively for $\bar{\varepsilon}$ & $\Delta\varepsilon$.

$$\frac{\bar{\varepsilon}-1}{4\pi} = NhF\left\{\bar{\alpha} + F\frac{\mu^2}{3KT}\right\}$$

$$\frac{\Delta\varepsilon}{4\pi} = NhF\left\{\Delta\alpha - F\frac{\mu^2}{2KT}(1-3\cos^2\beta)\right\} S$$

$N = N_A\rho/M$ is the particle density, where ρ is the density, N_A is Avogadro's No. and M is the molecular weight, $\bar{\alpha}$ and $\Delta\alpha$ are the spherical mean and anisotropy of the molecular polarization, h is the cavity field factor for the empty cavity and F is the reaction field factor, both calculated using an isotropic continuum (5).

The sign of $\Delta\varepsilon$ is determined by the magnitude of the total dipole moment and its angle β with the long molecular axis. Approximately μ and β can be obtained by addition of the group moments of the various polar groups in a molecule. The positive sign of dielectric anisotrpy is consistant with the results obtained previously using diamagnetic (8) and optical (9) measurements on the same compounds as well as on compounds of similar structures (12,13). The strong polar nature of the cyano group seems to have a dominant effect on such behaviour of the isomers. The higher values of the

The temperature dependence of conductivity and conductivity anisotropies of the two compounds are shown in figures 6,7 and 8 respectively. The two isomers also possess positive conductivity anisotropy. On the other hand, the values of conductivity for 5SCN is about two order of magnitude higher as compared to its isomer. The differences in the conductivity values of these two isomers may be accounted for by the differences in the mode of molecular packing. X-ray data obtained for the two siomers showed that there are two different packing modes, both exhibiting a semi-bilayer configuration (10). However the partial electronic overlap of molecules in 5SCN nematic phase is relatively larger than in the case of NCS5 as previously shown in ref. (10). This clearly explains the higher conductivity of 5SCN as compared to that of NCS5.
Finally it is to be noted that although the two samples possess positive conductivity anistropies, the change of $\Delta\sigma$ with temperature is higher in the case of 5SCN compound as shown in figure 8.

CONCLUSIONS

The results obtained from measurements on both dielectric and conductivity anisotropy seem to agree with previous X-ray studies on the mode of packing of molecules in these two isomers. There is also an agreement between these results and infrared studies presented earlier (14).

We hope that the correlation between observed anisotropy and

the structure of the two isomers may help to understand and hence to control the role played by this class of nematic liquid crystals.

REFERENCES

(1) W.H. de. Jou and Th. W. Lathouwer;
Philips, Res. Repts. 905-911(1974).

(2) W.H. de Jou and Th. Lathouwers;
Philips, Res. Repts. 30a, 79-82 (1974).

(3) Hp. Schad, G. Baur and G. Meier;
J. Chem. Phys. 71 (8), 3174-3181(1979).

(4) V.V. Titov, E.I. Kovshev, A. I. Pavluchenko,
V.T. Lazareva and M.F. Griebenkin;
J. Phys. (Paris) C1-(1975).

(5) M.G. Glark;
Mol. Cryst. Liq. Cryst. 127, 1-41 (1985).

(6) R.T. Klingbiel, D.J. Genova and H.K. Bucher;
Mol. Cryst. Liq. Cryst. 27, 1-21 (1973)

(7) J. Kranse and L. Phol;
Proceedings of the 6th international liquid crystal conference, Kent 23-27 August (1976).

(8) I.H. Ibrahim and W. Haase,
J. Phys. (Paris), 40, C3-164 (1979).

(9) I.H. Ibrahim and W. Haase;
J. Phys. (Paris), 40, 191(1979).

(10) W. Haase, H. Paulus and I.H. Ibrahim;
Mol. Cryst. Liq. Cryst. 107, 377-389 (1984).

(11) W. Maier And G. Meier;

Z. Naturforsch. 16a, 262(1961).

(12) G.J. Brownsey and A.J. Leadbetter;
Phys. Rev. Lett. 44, 1608 (1980).

(13) A.T. Leadbetter, R. M. Richardson and C.N. Colling;
J. Phys. (Paris) 36, 37 (1975).

(14) S.H. Kandil, I. H. Ibrahim, M.A. El-Gamal and N.G. Gomma. , Bull. Fac. Eng. Alex. Univ. 25-26, 437(1986-1987).