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Theoretical study of order parameter at different temperatures by known data of optical anisotropy of new nematic liquid crystal $4'$-cyano-(4-chlor-benzyloxy)-azobenzene

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Abstract. The importance of liquid crystals lies in their extensive use in display devises, as well as many other scientific applications. However the use of liquid crystals in different devises depends upon various properties owned by them like order parameter, dielectric constant, dielectric anisotropy, birefringent behaviour, optical transmittance, elastic constants etc. The nematic liquid crystalline state can be described through its positional, orientational order. The orientational order is measure of how the rings and functional groups within a molecule are oriented. In view of applications in the liquid crystal display, it is usually the orientation order parameter S which is most important. Optical anisotropy data used to determine order parameter new nematic liquid crystal $4'$-cyano-(4-chlor-benzyloxy)-azobenzene by Vuks approach and also its variation with temperature has been discussed.

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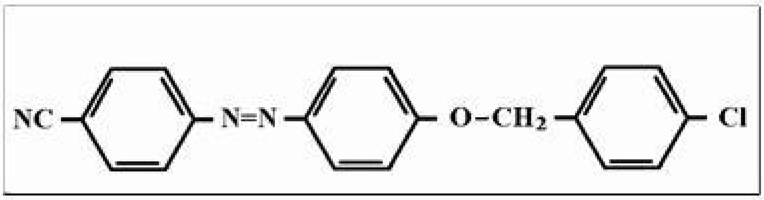
1 Introduction

Nematic liquid crystal 4′-cyano-(4-chlor-benzyloxy)-azobenzene (4CN) are very complex condensed system



The molecules of 4CN liquid crystals are long and lath shaped. The 4CN liquid crystals are optically uniaxial positive and strongly birefringent. The birefringence in the nematic phase decreases with increase of temperature and at the nematic-isotropic transition temperature the birefringence drops abruptly to zero. The nematic phase is characterized by the long range orientational order, but the translational order does not occur. The long axes of molecules in this phase are statistically oriented about the preferred direction referred to as the nematic director. The degree of orientation or orientational order parameters S is defined as [1, 10],

$$\frac{\langle(3\cos^2\theta - 1)\rangle}{2} \tag{1.1}$$

where θ is the angle made by long axis of the molecules with the nematic director. The value of S in the nematic phase lies between 0 and 1. The effect of orientational or molecular ordering is connected with the anisotropy of physical properties, for example, molecular shape, polarizability, refractive index, dielectric constant and diamagnetic susceptibility [3].

2 Theory

The orientational order parameter S may also be expressed in terms of effective polarizabilities associated with the molecules in the nematic phase and the principal polarizabilities of the individual molecules. We shall assume that for the sake of simplicity,the polarizability ellipsoid of the molecules in question is spheroid. Let $\alpha_{||}$ and $\alpha_{\perp}$ be the principal polarizabiliesof the molecules when the electric vector is respectably parallel and perpendicular to the long axis. Choosing $\mathbf{i}, \mathbf{j}$ and $\mathbf{k}$ as the three orthogonal unit vectors along $\mathbf{x}, \mathbf{y}$ and $\mathbf{z}$-directions in the nematic medium and assuming that the director is along $\mathbf{k}$ it is shown [5] that

$$\alpha_e = \alpha_{||} - \alpha_{\perp} \langle (\mathbf{a_m} \cdot \mathbf{k})^2 \rangle + \alpha_{\perp} \quad \text{and} \tag{2.1}$$

$$\alpha_o = \alpha_{||} - \alpha_{\perp} \langle (\mathbf{a_m} \cdot \mathbf{j})^2 \rangle + \alpha_{\perp} \tag{2.2}$$

In the above equations $\mathbf{a_m}$ is an unit vector parallel to the long axis of the n^{th} molecule and α_e and α_o are the effective polarizabilities of molecules corresponding to the electric vector being parallel and perpendicular to the optics axis respectively.since the molecules are oriented statically around the direction $\mathbf{k}$, it follows that,

$$\langle (\mathbf{a_m} \cdot \mathbf{i})^2 \rangle = \langle (\mathbf{a_m} \cdot \mathbf{j})^2 \rangle \tag{2.3}$$

Further from the fact

$$\langle (\mathbf{a_m} \cdot \mathbf{j})^2 \rangle = \langle (\cos^2 \theta_m) \rangle \tag{2.4}$$

$$\text{and} \qquad \langle (\mathbf{a_m} \cdot \mathbf{i})^2 \rangle + \langle (\mathbf{a_m} \cdot \mathbf{j})^2 + \langle (\mathbf{a_m} \cdot \mathbf{k})^2 \rangle = 1. \tag{2.5}$$

We have

$$\alpha_e = (\alpha_{||} - \alpha_{\perp}) \langle (\cos^2 \theta_m) \rangle + \alpha_{\perp} \tag{2.6}$$

and

$$\alpha_o = 1/2(\alpha_{||} - \alpha_{\perp})(1 - \langle (\cos^2 \theta_m) \rangle) + \alpha_{\perp} \tag{2.7}$$

Combining equation 1.1, 2.6, & 2.7

$$\alpha_e = 1/3[(\alpha_{||} - \alpha_{\perp})(2S + 1)] + \alpha_{\perp} \tag{2.8}$$

and

$$\alpha_o = 1/3[(\alpha_{||} - \alpha_{\perp})(1 - S)] + \alpha_{\perp} \tag{2.9}$$

so the orientational order parameters may be expressed as

$$S = (\alpha_e - \alpha_o)/(\alpha_{||} - \alpha_{\perp}) \tag{2.10}$$

The Classical Clausius–Mosotti relation correlates the dielectric constant of an isotropic media with molecular polarizabilities and molecular packing density

$$\frac{\in -1}{\in +2} = \frac{4\pi\alpha_m}{3v_m} \tag{2.11}$$

here, v_m is the volume per formula unit, and α_m is the sum of the polarizabilities of the ions which compose a formula unit.

In the optical frequencies,we substitute $\in = n^2$, and obtain Lorentz–Lorentz equation [4],

$$\frac{n^2-1}{n^2+2} = \frac{4\pi N\alpha_m}{3} \tag{2.12}$$

For anisotropic liquid crystal,there two principal refractive indices, n_e (extra ordinary rays) and n_o (ordinary rays). Each refractive index determined by its corresponding molecular polarizabilities α_e and α_o.

Vuks [9] postulated that the local field is isotropic even in an anisotropic crystal and is assumed to be given by

$$\mathbf{E}_{\text{loc}} = [(\langle n^2\rangle + 2)/3]\mathbf{E} \tag{2.13}$$

where $\langle n^2\rangle$ is the mean square of the principal refractive indices of the medium

$$\langle n^2\rangle = (n_e^2 + 2n_o^2)/3 \tag{2.14}$$

$$\frac{n_e^2-1}{\langle n^2\rangle+2} = \frac{4\pi N_{lc}\alpha_e}{3} \tag{2.15}$$

and

$$\frac{n_o^2-1}{\langle n^2\rangle+2} = \frac{4\pi N_{lc}\alpha_o}{3} \tag{2.16}$$

Finally, Vuks model can be modified as,

$$S\Delta\alpha = (3/4\pi N_{lc})\left(\frac{n_{11}^2 - n_{\perp}^2}{\langle n^2\rangle+2}\right) \tag{2.17}$$

3 Results and discussion

The continuous demand on faster electro-optic response time is the driving force for developing novel nematic liquid crystal (LC) mixtures. Almost all LC-related devices,

Table 1: Variation of order parameter with temperature.

Temperature (Celsius)	Ordinary refractive index [7] n_o	Extra refractive index [7] n_e	Order parameter S (Present study)
160	0.39690	0.46878	0.65
165	0.39812	0.46791	0.64
170	0.40776	0.46498	0.52
175	0.41250	0.45479	0.39
180	0.42131	0.44030	0.17

such as liquid crystal display (LCD) panels, LCD TVs, spatial light modulators, and optical phased arrays (OPAs) for laser communications require faster response times. In order to achieve a fast response time, low rotational viscosity ($c1$) LC mixtures are preferred [6]. Most of the physical properties of the liquid crystal emerge from the order that exist in the sample and thus followed by the order parameter (S) [1], which makes order parameter so important while studying liquid crystals.

Various methods have been adopted by different workers to calculate the order parameter, like Neugebaar's anisotropic field model, Vuks isotropic internal field model and Saupe and Maier anisotropic model etc. The properties described above depend upon the molecular arrangement in liquid crystal sample, which changes according to temperature. In the present paper we report studies on a newly synthesized nematic liquid crystal 4′-cyano-(4-chlor-benzyloxy)-azobenzene (4CN), a thermotropic liquid crystal for its electrical and optical properties. The refractive indices and birefringence data have been used to calculate order-parameter (S), here Vuks direct extrapolation method has been used to calculate the microscopic order parameter.

Cyano (CN) and isothiocyanato (NCS) are two commonly employed polar groups for elongating the molecular conjugation. The CN group has a larger dipole moment than NCS because of its linear structure. However, due to the very strong polarization of the carbon–nitrogen triple bond, the Huckel charges of carbon and nitrogen are high and well localized . Without the knowledge of $\Delta\alpha$, the order parameter cannot be extracted. The polarizability anisotropy $\Delta\alpha$ is calculated from the bond polarizability data. We draw a figure of molecule assuming standard values for bond lengths and an-

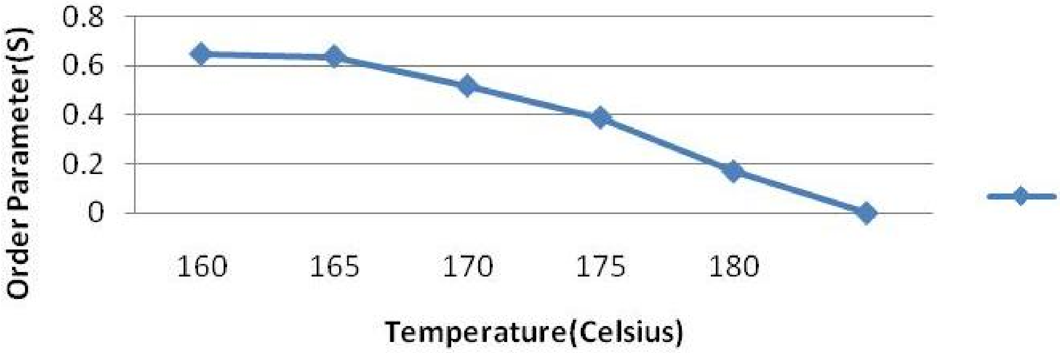


Figure 1: Transition from liquid crystal phase to isotropic crystal phase.

gles. The molecular axis is taken to along the line joining the outer para carbon atoms of three benzene rings and assumes the molecule to be rigid. Because the polarizability anisotropy of the C–H bond is small, the contributions of the benzene rings are taken to be equal to their average polarizabilities. Consequently the sum of the polarizability contribution of all the various bonds and groups parallel to the molecular axis gives $\alpha_{||}$ for the molecule. Also the sum of all contributions normal to the molecular axis gives $\alpha_{\perp}$. The density of the liquid crystal material is determined as functions of temperature with a digital density meter. The refractive indices of a new nematic liquid crystal 4′-cyano-(4-chlor-benzyloxy)-azobenzene have been determined by using an interference method for the plane-parallel nematic cell [7]. Vuks equations correlate the microscopic molecular polarizabilities to the macroscopic refractive indices of anisotropic crystalline materials [2, 8].

4 Conclusion

The order parameter of new nematic liquid crystal 4′-cyano-(4-chlor-benzyloxy)-azobenzene have been determined by using optical anisotropy data in the temperature range of 160 °C to 180 °C. The variation of microscopic order parameter with temperature is shown in the Figure 1 and shows that it has good agreement. It is maximum in liquid crystalline phase and as we increase the temperature the order parameter (S) decreases.

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