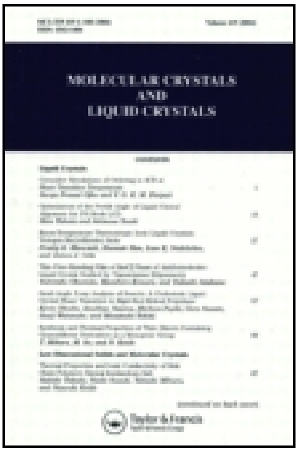

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Density, Optical and Static Dielectric Studies of a Nematogenic Tolan Compound

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We report here temperature variation of refractive indices, dielectric permittivities and densities of a nematogenic tolan compound (4-n-butyl-4′-ethoxytolan). The sample exhibits high birefringence. The refractive indices and density values have been analyzed to obtain the orientational order parameters. Experimental order parameters are compared with theoretical Maier-Saupe values. The variation of dielectric permittivities with temperature has been determined for the sample at frequency 1 kHz. The sample shows very low dielectric anisotropy. The molecular dipole moment and the angle of inclination β of the molecular dipole moment with the director are also calculated.

Keywords Angle of inclination; density; dielectric permittivity; dipole moment; refractive index

1. Introduction

The importance of liquid crystalline materials lies in their extensive applications in diverse fields. Physical parameters of liquid crystalline materials govern their use in different devices. A particular application demands the physical parameters in a particular range. To meet the requirements, chemists are designing and synthesizing new liquid crystalline materials whose characterization are very much important. However, ultimate tailoring of different physical parameters for applications are generally realized by multicomponent mixtures.

High birefringence materials are required for many applications. There are many ways to influence Δn. A very effective means to increase $n_{||}$ and thereby Δn is to employ triple (tolan) bond in the rigid core [1]. Considerable number of works have been reported by different workers on tolan-based compounds and their mixtures [2,3].

Here we report refractive indices, dielectric permittivities and densities of a nematogenic tolan compound. The orientational order parameters are calculated at different temperatures for the compound. The variation of molecular dipole moment and the angle of inclination β of the molecular dipole moment with the director as a function of temperature are also calculated.

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2. Experimental

The compound was kindly donated to us by Prof. K. Czuprynski, Military University of Technology, Poland and was used without further purification.

The structural formula and chemical name are as shown in Figure 1.

2.1. *Texture Studies*

Prior to undertaking the refractive index, density and dielectric studies, routine texture studies were carried out to confirm the nature of the mesophases and the phase–transition temperatures. The texture studies were conducted by using a Leica Make DMLP polarizing microscope equipped with a Linkam hot stage LTSE-350 with TMS 94 temperature programmer. The samples were heated at a rate of 1°C/min. Representative texture photographs for the compound were taken and phase-transition-temperatures were noted.

2.2. *Density Studies*

The temperature variation of the densities of the compound were measured by putting weighed samples inside a dilatometer of the capillary type which was placed in a water bath heated electrically and controlled manually. The length of the sample column was measured by a travelling microscope. The densities were calculated by correcting for the expansion of the glass capillary. Experimental uncertainty in density measurements is 0.1%.

2.3. *Refractive Index Studies*

The ordinary and extra-ordinary refractive indices (n_o,n_e) for wavelength $\lambda = 546$ nm of the compound were measured within ±0.001 by the thin prism method (refracting angle $<2°$) [4]. The prism was made by cutting a microscopic slide and treating it with 1% poly vinyl alcohol on one side and then rubbed for surface alignment. The treated surface was kept inside and rubbing direction was kept parallel to the refracting edge of the prism. The sample was placed at the top of the prism and heated to isotropic state, thereby allowing it to flow in the prism. The combination of surface treatment by PVA and rubbing produced a homogeneous nematic specimen with the optic axis parallel to the refracting edge of the prism. The prism was placed inside an electrically heated brass thermostat which is controlled manually to ±0.5°C. The refractive indices (n_o, n_e) of the sample were measured with a precision spectrometer.

2.4. *Dielectric Studies*

The dielectric permittivities ($\varepsilon_{\|}$ and $\varepsilon_{\perp}$) were measured by a digital LCR bridge (HIOKI 3522-50 LCR HiTESTER) at frequency 1 kHz. The liquid crystal samples were filled in glass cells in isotropic state by capillary action and then sealed. The cell consists of two plane parallel ITO-coated glass plates which have inside polymer-coating for homogeneous alignment of the sample. The homogeneous alignment of the sample gave the dielectric component $\varepsilon_{\perp}$. The homeotropic alignment of the sample was obtained by applying electric field above threshold voltage

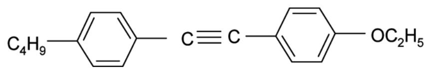

Figure 1. 4-n-butyl-4′-ethoxytolan (PTP4O2).

(V_{th}) of the sample which gave the other component $\varepsilon_{\|}$. All the data were recorded during cooling of the sample. The thickness of the sample was ~5 μm. To obtain the temperature variation of dielectric permittivities the cell was put in a thermostated block fabricated by us whose temperature was controlled to ±0.5°C. The bridge voltage across the sample was maintained sufficiently low (~0.3 V) to prevent electric field induced instabilities. For the standardization of the apparatus several standard liquids were used.

3. Results and Discussion

3.1. *Texture Studies*

The transition temperatures for PTP4O2 as observed from texture studies are as follows:

$$\text{Solid} \underset{36.3^{\circ}\text{C}}{\overset{53.1^{\circ}\text{C}}{\rightleftharpoons}} \text{Nemaic} \overset{81.1^{\circ}\text{C}}{\longleftrightarrow} \text{Isotropic}$$

Typical nematic textures are obtained under polarizing microscope. Representative nematic texture of the sample is shown below in Figure 2.

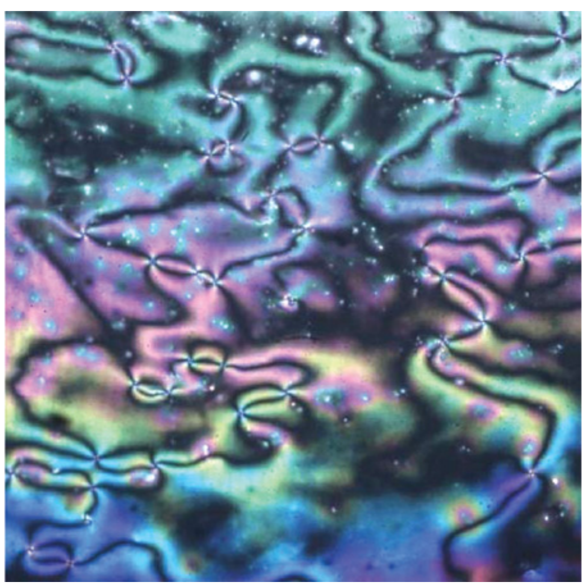

Figure 2. Nematic schlieren texture at 80.5°C during heating. (Figure appears in color online.)

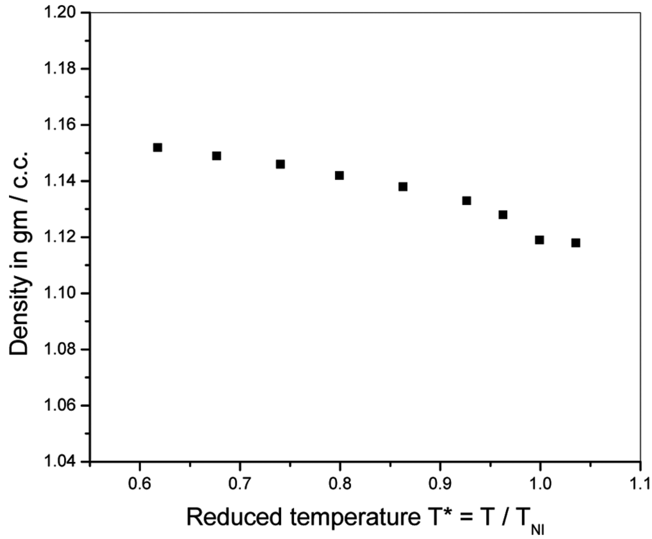

Figure 3. Dependence of density of PTP4O2 on reduced temperature.

3.2. *Density Studies*

The variation of density of PTP4O2 with reduced temperature $T^* = T/T_{NI}$ is shown in Figure 3. The temperature variation of the density of the sample show normal behavior i.e., density decreases with increasing temperature. There is a small jump in density value near T_{NI},suggesting a weakly first order N-I transition.

3.3. *Refractive Index Studies*

The temperature dependence of the refractive indices n_o and n_e of the compound PTP4O2 at wavelength $\lambda = 546\,nm$ is shown in Figure 4.

The high value of birefringence arises due to the triple bond in the rigid core and also due to the oxygen atom in the alkoxy chain which elongate the π-electron conjugation. The refractive index and density data have been analyzed to determine the orientational order parameter $\langle P_2 \rangle$. The order parameter is given by the relation

$$\langle P_2 \rangle = (\alpha_e - \alpha_o)/\Delta\alpha \tag{1}$$

where α_e and α_o are the effective polarizabilities for extraordinary and ordinary rays which were calculated from the measured values of refractive indices using Vuks' formulae [5].

$$(n_o^2 - 1)/(n^2 + 2) = 4\pi N\alpha_o/3 \tag{2a}$$

and

$$(n_e^2 - 1)/(n^2 + 2) = 4\pi N\alpha_e/3 \tag{2b}$$

Here $n^2 = (2n_o^2 + n_e^2)/3$, n is the mean refractive index and N is the number of molecules per c.c. $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities parallel and

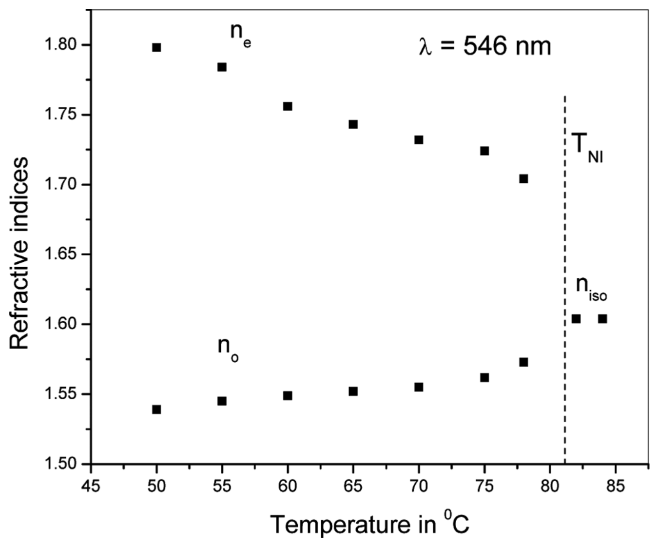

Figure 4. Temperature variation of refractive indices (n_o and n_e) for PTP4O2.

perpendicular to the long axis of the molecule in the solid state. The polarizability anisotropy in the perfectly ordered state ($\Delta\alpha$) has been estimated by applying the well-known Haller's extrapolation procedure [6].

The temperature variation of order parameter for the compound PTP4O2 is shown in Figure 5.

In case of PTP4O2, at lower temperature experimental $\langle P_2 \rangle$ values more or less agree with Maier-Saupe values, but at higher temperature experimental values fall quicker than predicted by Maier-Saupe. This lowering of experimental order parameter may be due to the thermal fluctuation of the chain part at higher temperatures which was not considered in theoretical calculations.

3.4. *Dielectric Studies*

The variation of dielectric permittivities of PTP4O2 with temperature is shown in Figure 6.

The effective dipole moment μ and the angle of inclination β between the molecular dipole moment and the molecular axis is obtained by applying the following expressions [7]:

$$\varepsilon_{avg} = 1 + 4\pi NhF(\alpha_{avg} + F\mu^2/3KT) \tag{3a}$$

$$\Delta\varepsilon = 4\pi NhF\{\Delta\alpha - F\mu^2(1 - 3\cos^2\beta)/2KT\}\langle P_2 \rangle \tag{3b}$$

where $\varepsilon_{avg} = (\varepsilon_{\|} + 2\varepsilon_{\perp})/3$, $\alpha_{avg} = (\alpha_{e} + 2\alpha_{o})/3$, $f = 4\pi N(2\varepsilon_{avg} - 2)/3(2\varepsilon_{avg} + 1)$ $h = 3\varepsilon_{avg}/(2\varepsilon_{avg} + 1)$, $F = 1/(1 - \alpha_{avg} f)$ and $N = N_A d/M$ where N_A is the Avogadro number, d is the density and M is the molecular weight.

Figures 7 and 8 depict the variation of dipole moment μ and angle of inclination β of PTP4O2 with temperature. The dipole moment μ increases with temperature

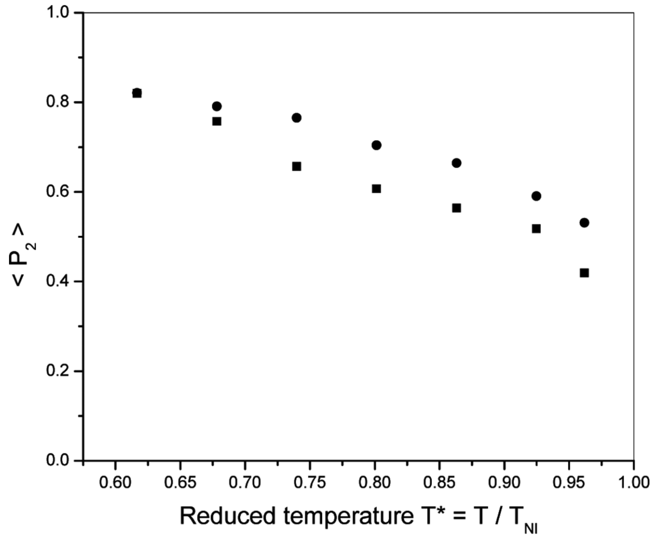

Figure 5. Variation of order parameter <P_2> with reduced temperature for PTP4O2 ■ indicates experimental order parameter from refractive index data ● indicates theoretical Maier-Saupe values.

initially but as the nematic-isotropic transition temperature is approached, μ becomes almost constant.

However β decreases continuously as temperature is increased. This decrease of angle of inclination β with temperature is responsible for the observed decrease of $\varepsilon_{\perp}$ with temperature.

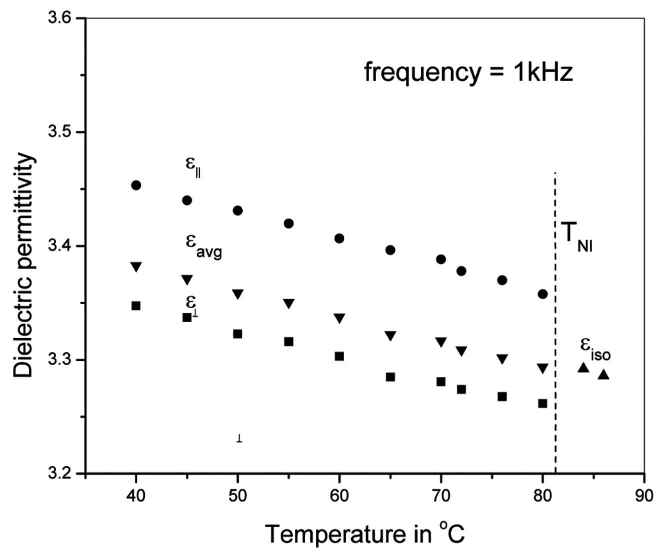

Figure 6. Variation of dielectric permittivities of PTP4O2 with temperature.

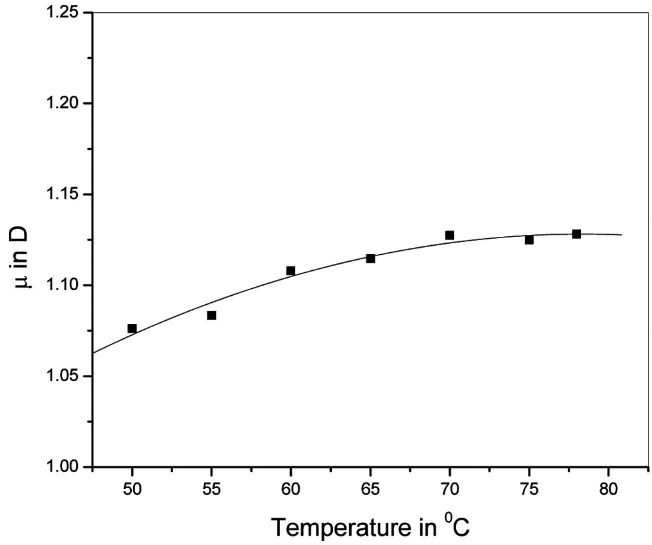

Figure 7. Variation of dipole moment of PTP4O2 with temperature.

In the present work we have also calculated dielectric anisotropy by using two components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ and variation of dielectric anisotropy ($\Delta\varepsilon$) with the temperature is shown in Figure 9.

The decrease of dielectric anisotropy with the temperature is prominent near nematic-isotropic transition temperature (T_{NI}), however as we go away from T_{NI}, dielectric anisotropy is almost constant. This behavior can be explained on the basis of the expression (3b). The dependence of the parameters h, F and μ on temperature

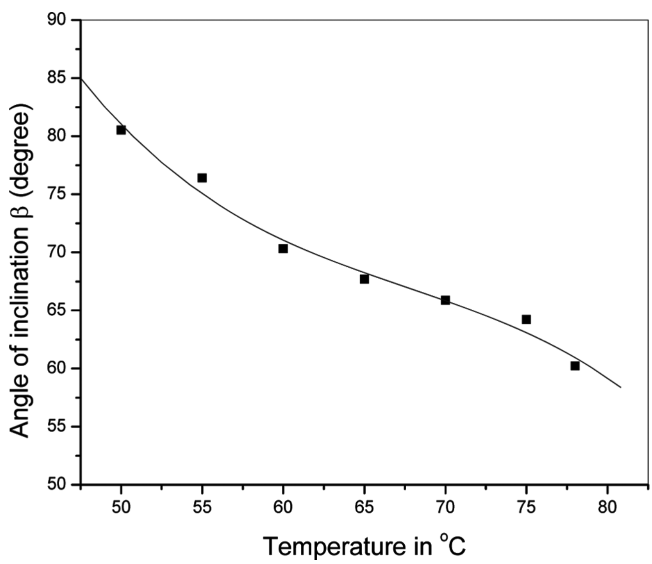

Figure 8. Variation of angle of inclination β of PTP4O2 with temperature.

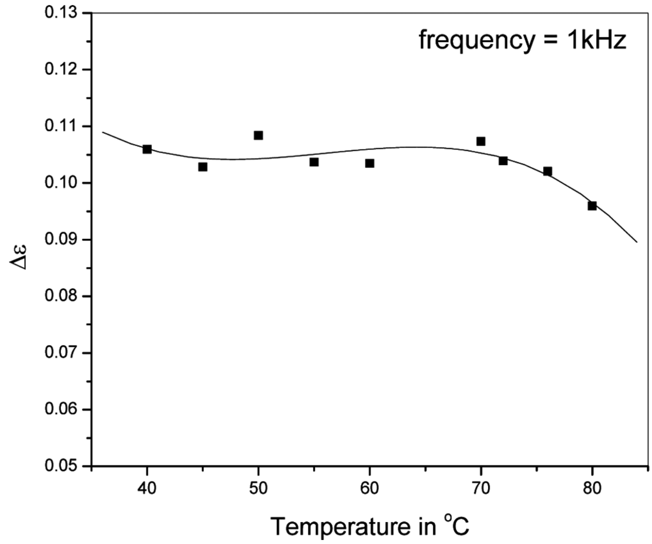

Figure 9. Variation of dielectric anisotropy ($\Delta\varepsilon$) of PTP4O2 with temperature.

is very weak. Here as the angle of inclination β is decreasing with temperature as shown in Figure 8 and β is greater than critical angle 54.7° for the entire temperature range of the liquid crystal PTP4O2, the term within second bracket is increasing with temperature while $<P_2>$ is decreasing with temperature. Naturally, $<P_2>$ decreases sharply with temperature near T_{NI} and thereby showing a prominent decrease of $\Delta\varepsilon$ with temperature near T_{NI}. At temperature away from T_{NI}, the term within second bracket increases with temperature slowly while $<P_2>$ show slow decrease with temperature, thereby making $\Delta\varepsilon$ almost independent of temperature at temperature far away from T_{NI}, which is in qualitative agreement with our experimental observation.

4. Conclusion

In conclusion, it may be said that the tolan compound studied here exhibits a moderate nematic range (53.1°C–81.1°C) with large supercooling (supercooling temperature 36.3°C). The compound exhibits high birefringence ($\Delta n = 0.259$ at 50°C) and very low dielectric anisotropy ($\Delta\varepsilon = 0.108$ at 50°C). The dipole moment of the compound is small enough ($\mu = 1.076$ at at 50°C). The steep decrease of angle of inclination β with temperature is responsible for the observed anomalous temperature variation of perpendicular component of dielectric permittivity $\varepsilon_{\perp}$.

Acknowledgment

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