An Optical Study to Estimate Orientational Order Parameter on Some Benzylideneaminophenylbenzoate Liquid Crystals

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The birefringence technique has been used for the evaluation of order parameter in the nematic phase along with the density measurements, which are needed for the calculation of molecular polarizabilities of the compounds. Birefringence and density studies have been carried out on the three liquid crystalline compounds viz.

(1) (*E*)-4-((4-hexyloxy)benzylidene)amino)phenyl 4-butoxybenzoate

(2) (*E*)-4-((4-hexyloxy)benzylidene)amino)phenyl 4-(decyloxy)benzoate and

(3) (*E*)-4-((4-hexyloxy)benzylidene)amino)phenyl 4-(tridecyloxy)benzoate.

Using birefringence and density data the molecular polarizabilities are evaluated by two different internal field models due to Vuks and Neugebauer. The mean molecular polarizability of the compounds is also evaluated by employing modified Lippincott δ -function model. The results reveal that both the theoretical and experimental values obtained are very near to each other.

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1. Introduction

Liquid crystalline material research has been contributed both to the development of liquid crystal display technology and also to the better understanding of phase behavior for soft condensed matter system. Thus the knowledge of physical properties is necessary. The attempts are continuously being made to study the material properties of compounds for better insight into the basic understanding of liquid crystalline behavior, so that a newer and more acceptable class of materials suitable for display devices is to emerge.

The orientational order parameter is considered to be one of the most important material parameter of the nematic phase, which determines all of its anisotropic properties and the relations between macroscopic and microscopic properties [1, 2].

In the present work, the birefringence and dilatometry techniques [3, 4] are employed for the determination of refractive indices and densities at various temperatures. By using the refractive indices and density data, molecular polarizabilities and order parameters were estimated for the compounds viz.,
comp. 1: (*E*)-4-((4-(hexyloxy)benzylidene)amino)phenyl 4-butoxy benzoate

melting temperature 110 °C, clearing temperature 244.9 °C

comp. 2: (*E*)-4-((4-(hexyloxy)benzylidene)amino)phenyl 4-(decyloxy)benzoate

melting temperature 106 °C, clearing temperature 210.5 °C

comp. 3: (*E*)-4-((4-(hexyloxy)benzylidene)amino)phenyl 4-(tridecyloxy)benzoate

melting temperature 94.9 °C, clearing temperature 199.6 °C.

2. Experimental

A polarizing microscope (SD-Techs)/1510 with hot stage is used to measure the transition temperatures. The substance is sandwiched between a glass plate and cover slip which is placed in heating block along with thermometer. The temperature of the hot stage is controlled by varying the voltage of the variac. The temperature is measured by thermocouple sensor which is placed in the heating block.

The refractive indices of the liquid crystalline compounds were measured with wedge shaped glass cell and modified spectrometer [5, 6]. A wedge shaped glass cell was prepared with two optical flat rectangular glass

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Fig. 1. Temperature variation of refractive index.

plates (50 mm × 25 mm) sandwiched with glass slide of 0.05 mm thick which acts as a wedge spacer. The cell is filled with the liquid crystal material. The liquid crystal material in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The accuracy in the measured refractive indices was ± 0.0005 .

The U-shaped bi-capillary pyknometer in conjunction with cathetometer was used for the density measurements at various temperatures. The absolute error of the measurement of the densities is $\pm 10^{-4}$ g/cm³. The cooling rate during the measurement was 0.5 K/h.

For the estimation of the molecular polarizabilities of liquid crystalline compounds, the authors have considered the Vuks and Neugebauer models. The relevant equations of the two models are given below.

2.1. Vuks method

Recently Pardhasaradhi et al. [7] applied this method to estimate molecular polarizabilities of liquid crystalline molecules and the equations are as follows:

$$\alpha_e = \left[\frac{3}{4\pi N} \right] \frac{n_e^2 - 1}{\bar{n}^2 - 1}, \quad (1)$$

$$\alpha_o = \left[\frac{3}{4\pi N} \right] \frac{n_o^2 - 1}{\bar{n}^2 - 1}, \quad (2)$$

where N is the number of molecules per unit volume, n_e and n_o are the extraordinary and ordinary refractive indices of the LC molecule, $\bar{n}^2 = \frac{n_e^2 + 2n_o^2}{3}$ and $N = N_A \rho / M$, where N_A is the Avogadro number, ρ is the density and M is the molecular weight.

2.2. Neugebauer method

Subramanyam et al. [8] applied this method to liquid crystal molecules and recently Lalitha Kumari et al. [9] also used this method. According to this method the molecular polarizabilities are

$$\alpha_e = AB - 3 \pm \sqrt{(AB - 3)^2 - 4AB}/2A, \quad (3)$$

$$\alpha_o = AB + 3 \pm \sqrt{(AB + 3)^2 - 16AB}/4A, \quad (4)$$

where

$$A = \left[\frac{4\pi N}{3} \right] \left[\frac{n_e^2 + 2}{n_e^2 - 1} \right] + \left[\frac{2(n_o^2 + 2)}{n_o^2 - 1} \right]$$

and

$$B = 9(\bar{n}^2 - 1) / [(4\pi N_i)(\bar{n}^2 + 2)].$$

N_i is the number of molecules per unit volume in the isotropic phase.

Using the above two models the molecular polarizabilities and the polarizability anisotropy ($\alpha_e - \alpha_o$) of the above liquid crystalline compounds were calculated and illustrated in Tables I, II and III.

TABLE I

Ordinary and extraordinary polarizabilities of comp. 1 in liquid crystalline state [10^{-24} cm³].

T [°C]	Vuks			Neugebauer		
	α_e	α_o	$\alpha_e - \alpha_o$	α_e	α_o	$\alpha_e - \alpha_o$
245	63.063	44.045	19.018	60.970	45.020	15.950
244	64.355	43.375	20.980	62.101	44.430	17.671
243	64.800	43.120	21.680	62.489	44.203	18.286
242	65.494	42.813	22.681	63.097	43.939	19.158
241	66.148	42.610	23.538	63.673	43.775	19.898
240	66.423	42.508	23.915	63.915	43.690	20.225
239	66.747	42.450	24.297	64.202	43.650	20.552
238	66.828	42.367	24.461	64.271	43.573	20.698
237	66.961	42.305	24.656	64.387	43.519	20.868
236	67.039	42.231	24.808	64.454	43.451	21.003
235	67.188	42.115	25.073	64.582	43.346	21.236
234	67.236	42.096	25.140	64.624	43.329	21.295
233	67.385	42.034	25.351	64.755	43.277	21.478
232	67.497	41.998	25.499	64.853	43.248	21.605
231	67.506	41.965	25.541	64.860	43.216	21.644
230	67.618	41.876	25.742	64.956	43.135	21.821
229	67.709	41.869	25.840	65.037	43.133	21.904
228	67.814	41.860	25.954	65.130	43.130	22.000
227	67.814	41.860	25.954	65.130	43.130	22.000
226	67.814	41.860	25.954	65.130	43.130	22.000

2.3. Estimation of mean polarizability from modified Lippincott δ -function method

The modified Lippincott δ -function model is found to be effective [10, 11] for different types of liquid crystals. In the present study the modified Lippincott δ -function model has been used to estimate the mean polarizability in terms of parallel bond component ($\sum \alpha_{\parallel p}$) the perpendicular bond component ($\sum 2\alpha_{\perp}$) and the non-bond region electron contribution ($\sum \alpha_{\parallel n}$). The expression for the mean polarizability is given as

$$\alpha_M = \frac{1}{3} \left(\sum \alpha_{\parallel p} + \sum \alpha_{\parallel n} + \sum 2\alpha_{\perp} \right), \quad (5)$$

where the parallel bond component is given as

TABLE II

Ordinary and extraordinary polarizabilities of comp. 2 in liquid crystalline state [10^{-24} cm³].

T [°C]	Vuks			Neugebauer		
	α_e	α_o	$\alpha_e - \alpha_o$	α_e	α_o	$\alpha_e - \alpha_o$
210	73.287	64.750	8.537	72.233	66.634	5.599
209	73.969	64.265	9.704	72.933	66.110	6.823
208	74.537	63.775	10.762	73.441	65.567	7.874
207	75.227	63.384	11.843	74.043	65.139	8.904
206	75.911	62.918	12.993	74.678	64.695	9.983
205	76.752	62.495	14.257	75.448	64.307	11.141
204	77.245	62.152	15.093	75.890	63.989	11.901
203	78.104	61.713	16.391	76.659	63.594	13.065
202	79.053	61.187	17.866	77.518	63.139	14.379
201	79.623	60.551	19.072	78.000	62.543	15.457
200	80.695	59.874	20.821	78.930	61.934	16.996
199	81.308	59.350	21.958	79.452	61.453	17.999
198	82.089	58.763	23.326	80.119	60.921	19.198
197	83.035	58.242	24.793	80.936	60.463	20.473
196	83.888	57.843	26.045	81.674	60.122	21.552
195	84.805	57.525	27.280	82.413	59.816	22.597
194	85.733	57.188	28.545	83.219	59.541	23.678
193	86.501	56.988	29.513	83.890	59.391	24.499
192	86.865	56.927	29.938	84.147	59.306	24.841
191	87.173	56.881	30.292	84.417	59.280	25.137
190	87.459	56.811	30.648	84.644	59.213	25.431
189	87.750	56.733	31.017	84.917	59.171	25.746
188	87.761	56.642	31.119	84.921	59.083	25.838
187	87.719	56.629	31.090	84.881	59.068	25.813
186	87.934	56.592	31.342	85.069	59.045	26.024
185	88.026	56.563	31.463	85.148	59.022	26.126
184	87.869	56.561	31.308	85.007	59.011	25.996

$$\sum \alpha_{\parallel p} = \frac{4nA}{a_0} \exp\left(\frac{(T - T_c)}{T_c}\right) \left(\frac{R^2}{4} + \frac{1}{2C_R^2}\right) \times \exp\left(-\frac{(x_A - x_B)^2}{4}\right). \quad (6)$$

Here n is the bond order, A — the δ -function strength, T is the temperature in the liquid crystalline phase, T_c is the clearing temperature, R is the bond length, X_A and X_B are the Pauling electronegativities of atoms A and B in the bond AB, a_0 is the radius of the first Bohr orbit of the atomic hydrogen, and C_R is the geometric mean molecular δ -function strength. For the second term on the right hand side of Eq. (5) we have

$$\sum \alpha_{\parallel n} = \sum_j f_j \alpha_j. \quad (7)$$

Here f_j is the fraction of the non-bonded electrons of the j -th atom and α_j is its atomic polarizability.

For the third term in Eq. (5):

$$\sum 2\alpha_{\perp} = n_{df} \frac{\sum x_j^2 \alpha_j}{\sum x_j^2}. \quad (8)$$

Here n_{df} is the number of degrees of freedom given by

TABLE III

Ordinary and extraordinary polarizabilities of comp. 3 in liquid crystalline state [10^{-24} cm³].

T [°C]	Vuks			Neugebauer		
	α_e	α_o	$\alpha_e - \alpha_o$	α_e	α_o	$\alpha_e - \alpha_o$
199	83.306	62.530	20.776	80.706	63.830	16.876
198	84.804	61.302	23.502	81.982	62.713	19.269
197	86.152	60.430	25.722	83.137	61.937	21.200
196	88.129	59.402	28.727	84.839	61.047	23.792
195	89.079	58.334	30.745	85.624	60.061	25.563
194	89.970	58.035	31.935	86.398	59.821	26.577
193	90.877	57.346	33.531	87.164	59.202	27.962
192	91.699	56.886	34.813	87.868	58.801	29.067
191	92.344	56.222	36.122	88.405	58.191	30.214
190	92.545	55.917	36.628	88.567	57.906	30.661
189	93.243	55.351	37.892	89.156	57.395	31.761
188	93.614	55.016	38.598	89.468	57.089	32.379
187	93.811	54.663	39.148	89.625	56.756	32.869
186	93.991	54.699	39.292	89.785	56.802	32.983
185	94.009	54.478	39.531	89.790	56.587	33.203
184	94.483	54.000	40.483	90.188	56.148	34.040
183	94.566	53.759	40.807	90.250	55.917	34.333
182	94.579	53.488	41.091	90.249	55.653	34.596
181	94.451	53.146	41.305	90.121	55.311	34.810
180	94.773	52.917	41.856	90.395	55.106	35.289
179	94.681	52.860	41.821	90.311	55.045	35.266
178	94.625	52.882	41.743	90.261	55.064	35.197
177	94.739	52.873	41.866	90.360	55.062	35.298
176	94.522	52.844	41.678	90.163	55.023	35.140
175	94.497	52.830	41.667	90.140	55.009	35.131
174	94.473	52.816	41.657	90.117	54.994	35.123

the equation

$$n_{df} = 3N - 2n_b$$

where N is the number of atoms and n_b is the number of bonds in the molecule.

2.4. Estimation of orientational order parameter in the nematic phase

In the Vuks method the order parameter is given by [7, 12]:

$$S = \left(\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right) \frac{n_e^2 - n_o^2}{\bar{n}^2 - 1}, \quad (9)$$

where

$$\bar{n}^2 = \left(\frac{n_e^2 + 2n_o^2}{3}\right).$$

The order parameter in case of the Neugebauer method [13]:

$$S = \left(\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right) f(B), \quad (10)$$

where

$$f(B) = \frac{9}{4AB} \left[\left(B^2 - \frac{10}{3}B + 1 \right)^{1/2} + \left(\frac{B}{3} \right) - 1 \right]$$

and

$$B = \frac{n^2 - 1}{n^2 + 1} \left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1} \right].$$

3. Results and discussion

In the present investigation the refractive indices of the benzylidene amino phenyl benzoate liquid crystalline compounds with alkoxy chain length $n = 4, 10, 12$ and $m = 6$ are measured using modified spectrometer with small angled prism which houses the crystalline compound. The small angled prism is placed in a heating block for measurement of refractive indices with temperature and a monochromatic source of wavelength 589.3 nm is used. During isotropic-nematic phase transformation the incident light splits into two one higher and the other lower than the isotropic value called extraordinary n_e and ordinary n_o refractive indices. In the nematic region the value of n_e increases where as the value of n_o decreases with temperature and both attains saturation deep in nematic region. The variation of refractive indices with temperature in isotropic and nematic region is illustrated in Fig. 1.

The temperature variation of density is measured by dilatometer attached with U-shape bicapillary pycnometer and represented in Fig. 2. It is found that with rise in temperature density decreases and at phase transformations there are density jumps.

Fig. 2. Temperature variation of density.

The molecular polarizabilities are estimated by Vuks and Neugebauer internal field models and their molecular anisotropies are presented in Tables I, II and III. Further the mean molecular polarizability is evaluated by modified Lippincott δ -function model and the values are compared with Vuks and Neugebauer models and the results are shown in Table IV. The order parameter is evaluated for both Vuks and Neugebauer model and shown in Fig. 3.

Fig. 3. Variation of order parameter with temperature.

TABLE IV

Mean molecular polarizabilities obtained in the liquid crystalline compounds by different methods [10^{-24}cm^3]

meth.	Lippincott δ -function			Vuks	Neugebauer
comp.	$\alpha_{\parallel}$	$\alpha_{\perp}$	$2\alpha_{\perp}$	α_M	
1	94.79	1.87	52.34	49.67	50.46
2	123.94	1.87	64.24	63.35	67.02
3	129.33	1.87	70.95	67.38	67.79

4. Conclusions

1. The birefringence observed in the compounds is around 0.15 to 0.23;
2. The ordinary and extraordinary refractive indices attain saturation deep in the nematic phase;
3. The mean molecular polarizabilities obtained from birefringence data using the internal field models due to Vuks and Neugebauer are in reasonably good agreement with modified Lippincott δ -function model;
4. The orientational order parameter evaluated using both the models shows decrease with increase of temperature;
5. The orientational order parameter estimated by the Vuks and Neugebauer method is in between 0.3 to 0.7 which is in accordance with literature data available;
6. The orientational order parameter value evaluated using the Neugebauer method is always low when compared to other methods. The same results are obtained in our investigations.

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