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Refractive Indices and Molecular order in 4,4′Bis(Pentyloxy)azoxy Benzene in the Nematic State

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The refractive indices and densities of 4,4′Bis(pentyloxy)azoxy benzene

$$[CH_3(CH_2)_4OC_6H_4N{:}N(:O)C_6H_4O(CH_2)_4CH_3]$$

have been measured in the crystalline, nematic and isotropic phases. The orientational order parameters and polarizabilities in the mesophase have been evaluated by Neugebauer's approach for several temperatures and wavelengths. The order parameter at the same temperature for different wavelengths turns out to be same. The universal curve of the order parameter is given.

1 INTRODUCTION

A precise determination of the orientational order parameters and polarizabilities in nematic liquid crystals from optical anisotropy requires a knowledge of the polarization field in the medium. The generality of Neugebauer's approach[1,2] and the limitations of Vuks formula[3] have been established in detail.[4–6] In the light of this, we report in this paper measurements of refractive indices and densities of the nematic liquid crystalline compound 4,4′Bis(pentyloxy)azoxy benzene in the crystalline, nematic and isotropic phases and the application of the Neugebauer's relations for calculating the order parameters in the nematic phase.

2 EXPERIMENTAL

The commercially available yellow compound of 4,4′Bis(pentyloxy)azoxy benzene (supplied by Eastman Organic Chemicals, USA) was purified by successive recrystallization from its solution in toluene to obtain fine transparent flakes; the solid-nematic and nematic-isotropic temperatures of

the purified crystal were determined by the microscope hot stage to be 78°C and 122°C. The oriented specimens of the sample were prepared inside special hollow glass prisms with very small refracting angle. The glass plates which were used for the hollow prisms were optically flat and the two surfaces of the plates were perfectly parallel. This eliminated the error in the angle of minimum deviation which would have crept in due to the refracting effect of the glass plates themselves if their surfaces formed a wedge. The prism was precalibrated by measuring the refractive indices of distilled water, acetone, benzene and methylene iodide. The inside surfaces of the prism were rubbed vertically along the refracting edge and the liquid crystal sample was allowed to flow along the edge by melting a few crystals placed at the top. The sample was magnetically aligned in a strong field by placing the refracting edge of the prism parallel to the field. The combination of rubbing and flow together with the magnetic field produced a homogeneous nematic specimen with the optic axis vertical.

The prism was put inside an electrically controlled aluminum block. The temperature was measured by using thermocouples which were precalibrated against the melting points of pure benzoic acid and salicylic acid. Two thermocouples were embedded with junctions at two different points in the copper foil suitably wrapped around the prism to ensure good thermal contact. The relative temperatures were obtained to an accuracy of ± 0.01°C and could be maintained constant to within the same limits during different sets of observations. The nearly same thermo emf recorded in the two different thermocouples assured uniformity of temperature throughout the specimen. The aperture of the optical system was so chosen that a very small area was used for the experiment. The choice of small area assured the uniform orientation in this limited area. The angles of minimum deviation and the angle of the prism were measured with a precision Goniometer Spectrometer reading to 2″ of arc. The homogeneity and orientation of the nematic and crystalline phases were tested by the clarity of the image of the slit of the spectrometer for both horizontal and vertical polarizations and the constancy at a given temperature of the refractive index for vertical polarization irrespective of the angle of incidence.

n_x and n_y, the principal refractive indices of the crystal for horizontal polarization were derived from the observed values of n at different angles of incidence by constructing the principal section of the index ellipsoid according to the equation

$$\frac{1}{n^2} = \frac{\sin^2 \theta}{n_x^2} + \frac{\cos^2 \theta}{n_y^2} \tag{1}$$

where θ is the inclination of the direction of the ray in the crystal with respect to its X-axis. Such a procedure was necessary as the setup did not allow

TABLE I

Refractive indices of the crystal at room temperature

λÅ	n_x	n_y	n_z
6563	1.503	1.571	2.025
5893	1.505	1.573	2.079
5461	1.511	1.581	2.120

the entire 90° range of θ to be investigated. One of the principal refractive indices was determined directly, whilst the others had to be derived from (1).

The measurements were carried out for two specimens taken in two different prisms, in the crystalline, nematic and isotropic phases, and the two gave consistent values. The refractive indices are estimated to be accurate to ± 0.001. The values are presented in Tables I and II.

The density of the crystal was obtained by flotation technique in a mixture of bromoform and hexane. A rough estimation of the densities of the liquid crystalline phase for few temperatures and the isotropic phase was made by the help of a suitably constructed density bottle which could take in only small quantities of the sample. From the experimental values the values of the

TABLE II

Refractive indices in the nematic and isotropic phases. Solid nematic transition temperature is 78°C; nematic isotropic transition temperature is 122°C

Temp. °C	λ6563		λ5893		λ5461	
	n_e	n_o	n_e	n_o	n_e	n_o
79.2	1.837	1.507	1.872	1.513	1.908	1.522
83.4	1.825	1.507	1.861	1.513	1.896	1.522
84.5	1.822	1.508	1.858	1.514	1.892	1.523
87.7	1.816	1.509	1.851	1.515	1.885	1.524
90.5	1.811	1.509	1.844	1.516	1.878	1.525
95.7	1.799	1.510	1.831	1.517	1.863	1.526
99.0	1.792	1.510	1.826	1.517	1.858	1.526
103.3	1.781	1.511	1.812	1.518	1.845	1.527
108.6	1.768	1.511	1.797	1.519	1.830	1.528
113.1	1.758	1.513	1.786	1.522	1.818	1.532
117.9	—	1.516	1.769	1.524	1.803	1.532
120.4	—	1.521	1.758	1.526	1.794	1.534
123.0 (liquid)	1.584		1.599		1.614	

densities at the required temperatures were extrapolated from the best straight line that could be drawn over the experimental points. The density data is given in Table III.

TABLE III

Densities in solid, liquid crystalline and liquid phases

	Crystal	Liquid crystal					Liquid
Temp. °C	26	80	90	100	110	120	123
Density gm/cc	1.27	1.114	1.104	1.092	1.083	1.072	1.063

3 NEUGEBAUER'S RELATIONS

The Neugebauer's relation for the crystalline phase is obtained from the equations of the form

$$n_i^2 - 1 = 4\pi N_c \alpha_i (1 - N_c \alpha_i \gamma_i)^{-1}$$

and

$$\gamma_1 + \gamma_2 + \gamma_3 = 4\pi$$

where the n_i's (n_1, n_2, n_3) are the principal refractive indices, the γ_i's $(\gamma_1, \gamma_2, \gamma_3)$ are the corresponding internal field constants, the α_i's $(\alpha_1, \alpha_2, \alpha_3)$ are the principal polarizabilities of the molecules and N_c the number of molecules per unit volume in the crystalline phase. If $\alpha_{\|}$ and $\alpha_{\perp}$ are respectively the polarizabilities along the long axis and the average value perpendicular thereto, the above relations reduce to

$$\frac{1}{\alpha_{\|}} + \frac{2}{\alpha_{\perp}} = \frac{4\pi N_c}{3}\left[\frac{n_1^2 + 2}{n_1^2 - 1} + \frac{n_2^2 + 2}{n_2^2 - 1} + \frac{n_3^2 + 2}{n_3^2 - 1}\right].$$

For the liquid phase, the Lorenz–Lorentz relation given below is valid.

$$(\alpha_{\|} + 2\alpha_{\perp}) = \frac{9}{4\pi N_1}\left(\frac{n^2 - 1}{n^2 + 2}\right).$$

Here N_1 is the number of molecules per unit volume of the liquid and n is the refractive index of the liquid. From the above equations $\alpha_{\|}$ and $\alpha_{\perp}$ can be calculated.

In the nematic phase, the effective polarizabilities of the molecules α_e and α_0, corresponding to the electric vector being parallel and perpendicular to the optic axis respectively, are given by

$$\alpha_e = \frac{1}{3}(\alpha_{\|} - \alpha_{\perp})(2S + 1) + \alpha_{\perp}$$

and

$$\alpha_0 = \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})(1 - S) + \alpha_{\perp},$$

so that the order parameter S may be expressed as

$$S = (\alpha_e - \alpha_0)/(\alpha_{\parallel} - \alpha_{\perp}).$$

The expressions for the extraordinary and ordinary indices of the nematic phase, are

$$n_e^2 - 1 = 4\pi N\alpha_e(1 - N\alpha_e\gamma_e)^{-1}$$
$$n_0^2 - 1 = 4\pi N\alpha_0(1 - N\alpha_0\gamma_0)^{-1}.$$

Here N is the number of molecules per unit volume of the nematic phase and γ_e and γ_0 are the corresponding internal field constants similar to the case of the crystal, and they satisfy the relation $\gamma_e + 2\gamma_0 = 4\pi$. The Neugebauer relation for the nematic phase is hence given by

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_0} = \frac{4\pi N}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_0^2 + 2)}{n_0^2 - 1}\right].$$

For the liquid, the Lorenz-Lorentz relation may be written as

$$\alpha_e + 2\alpha_0 = \frac{9}{4\pi N_1}\left(\frac{n^2 - 1}{n^2 + 2}\right).$$

TABLE IV

Polarizabilities and orientational order parameters

T°C	λ6563			λ5893			λ5461		
	α_e x10²⁴	α_o x10²⁴	S	α_e x10²⁴	α_o x10²⁴	S	α_e x10²⁴	α_o x10²⁴	S
79.2	61.774	38.470	0.660	64.021	38.791	0.663	65.629	39.415	0.660
83.4	61.581	38.566	0.652	63.772	38.915	0.653	65.384	39.538	0.650
84.5	61.319	38.700	0.641	63.617	39.048	0.645	65.146	39.657	0.642
87.7	60.831	38.941	0.620	63.060	39.271	0.625	64.681	39.889	0.624
90.5	60.575	39.069	0.609	62.652	39.476	0.609	64.268	40.095	0.608
95.7	59.975	39.369	0.584	62.083	39.760	0.586	63.746	40.356	0.589
99.0	59.678	39.517	0.571	61.702	39.950	0.571	63.343	40.558	0.573
103.3	59.200	39.756	0.551	61.328	40.137	0.556	62.679	60.881	0.557
108.6	58.838	39.937	0.535	60.802	40.401	0.536	62.330	41.065	0.535
113.1	57.986	40.363	0.499	59.766	40.918	0.495	61.325	41.567	0.497
117.9	—	—	—	59.186	41.208	0.472	60.841	41.809	0.479
120.4	—	—	—	58.790	41.407	0.456	60.289	42.085	0.458

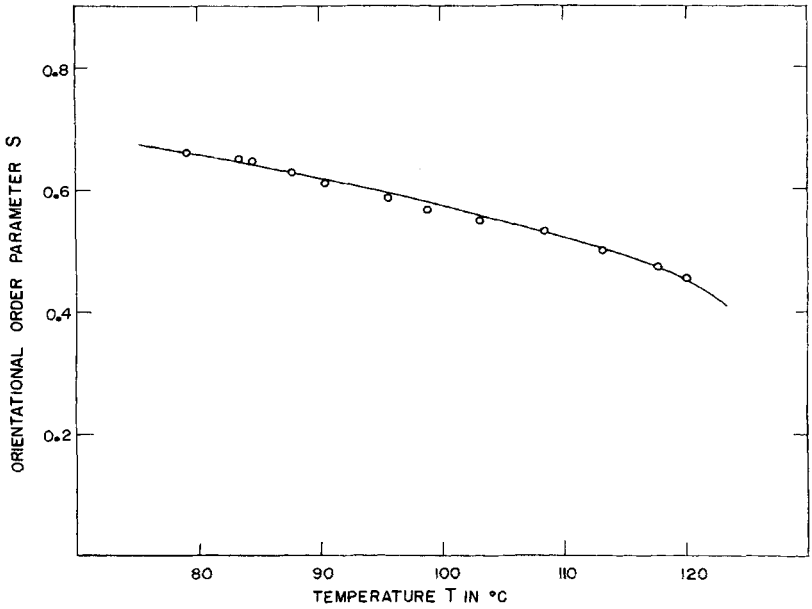

FIGURE 1 Orientational order parameter versus temperature.

From the above equations α_e and α_0 can be evaluated. We have evaluated the polarizabilities for different temperatures and wavelengths using the measured values of refractive indices and densities from the above relations. The orientational order parameter has been calculated from the molecular polarizabilities. We have tabulated the polarizabilities and orientational order parameters "S" in Table IV. We can observe that the orientational order parameter at the same temperature for different wavelengths is essentially a constant. Figure 1 gives a plot of the orientational order parameter versus temperature.

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