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Refractive Indices, Densities, Polarizabilities and Molecular Order in Nematic *p*-Ethoxy Benzylidene-*p*-*n*-Butylaniline

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Refractive index measurements of EBBA (*p*-Ethoxy-Benzylidine, *p*-*n*-Butylaniline) have been made in the crystalline, liquid crystalline and liquid phases using prism technique. The principal refractive indices of the crystalline phase have been obtained by making measurements on two different specimens of crystals grown in the prisms with small angles, with molecular axis parallel and perpendicular to the prism axis respectively. Orientational order parameters have been evaluated making use of the density data of liquid crystalline phase extrapolated from the density value at one temperature in the liquid crystalline phase and the thermal expansion coefficient and the densities of the crystal and liquid measured by floatation and specific gravity bottle techniques respectively. The estimated values of the *S*-factors are in very good agreement with those obtained by wide line NMR studies on deuterated EBBA molecule.

1 INTRODUCTION

We have reported the 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 in a previous investigation.[1] We used the Neugebauer's relations[2–4] along with Lorenz–Lorentz relation for the isotropic phase, for calculating the orientational order parameters, in that investigation. Later, one of us has estimated[5] the orientational order parameter for another nematic liquid crystalline compound *p*-ethoxy benzylidine-*p*-*n*-butylaniline (EBBA) by studying the wide line NMR absorption spectra of the compound. We also found that we could grow the crystals of this compound in prisms with small angles, with molecular axis parallel and perpendicular to the prism axis respectively.

With a view to investigate the generality of Neugebauer's approach we have extended the method used for the case of 4,4′Bis(pentyloxy)azoxy benzene, for this compound also and determined the refractive indices and densities in the three phases and have calculated the orientational order parameters from Neugebauer's relations and compared the values with those obtained from NMR data.

2 EXPERIMENTAL

EBBA (supplied by Vari-light Corporation, U.S.A.) was purified by successive recrystallization and the nematic–isotropic temperature for the purified sample was determined by the microscope hot stage to be 81°C.

Oriented specimens were prepared inside special hollow glass prisms, with small angles, precalibrated by measuring the refractive indices of distilled water, benzene and methyl iodide. Homogeneous nematic specimen with the molecular axis parallel and perpendicular to the prism axis were produced by techniques of, rubbing and placing the prism in a strong external magnetic field with its refracting edge parallel and perpendicular to the field respectively.

Goniometer spectrometer reading to 2″ of arc is used for measuring angles. These and other necessary experimental details are described in our earlier paper.[1]

For the measurement of n_x and n_y the crystal indices for horizontal polarization and n_z that for vertical polarization, a procedure different from the one used earlier was employed.

Measurements were carried out for two specimens of crystals grown in prisms with small angles with molecular axis parallel and perpendicular to the prism axis respectively. The first measurement enabled us to determine n_z and n_y directly whereas the second measurement, n_x and n_z directly. The refractive indices in the case of λ5780 and λ5461 are estimated to be accurate to ± 0.001. But, that in the case of λ4358, in particular, the extraordinary indices, the accuracy is estimated to be ± 0.002, owing to the comparatively larger spread of the lines and weaker intensity. The values are presented in Tables I and II.

Measurements of densities in the crystalline and liquid phases are done as described previously.[1] Densities at various temperatures in liquid crystalline phase are calculated from the density at 40°C and coefficient of expansion which are given as 1.02 gms/cc and 0.957×10^{-3}/°C respectively. The density data is given in Table III.

TABLE I

Refractive indices of crystal at room temperature

λÅ	n_x	n_y	n_z
4358	1.436	1.562	2.105
5461	1.430	1.554	1.971
5780	1.426	1.547	1.931

TABLE II

Refractive index in nematic and isotropic phases

	λ5780		λ5461		λ4358	
Temp °C	n_e	n_0	n_e	n_0	n_e	n_0
41.6	1.765	1.524	1.785	1.535	1.886	1.555
43.5	1.763	1.524	1.782	1.535	1.884	1.556
47.5	1.761	1.524	1.781	1.535	1.881	1.556
49.1	1.758	1.524	1.778	1.535	1.877	1.556
53.0	1.752	1.524	1.772	1.535	1.869	1.557
57.6	1.743	1.525	1.764	1.536	1.859	1.559
60.0	1.734	1.526	1.754	1.537	1.847	1.561
63.4	1.724	1.527	1.743	1.538	1.835	1.562
65.9	1.718	1.529	1.736	1.540	1.825	1.564
69.5	1.707	1.532	1.726	1.543	1.812	1.567
73.0	1.693	1.538	1.710	1.550	—	—
81.0 (Liquid)	1.592		1.606		1.654	

TABLE III

Densities in solid, liquid crystalline and liquid phases

	Crystal	Liquid Crystal							Liquid
Temp °C		40	45	50	55	60	65	70	
Density (gm/cc)	1.06	1.02	1.015	1.010	1.006	1.001	0.996	0.992	0.9815

3 RESULTS AND DISCUSSIONS

Polarizabilities in the crystalline, liquid and at different temperatures in the liquid crystalline, phases have been evaluated using measured values of refractive indices and densities, from the Neugebauer's relations which are given in detail in our earlier paper.[1] Orientational order parameter S has been calculated from these polarizabilities. S values and polarizabilities are tabulated in Table IV.

TABLE IV

Polarizabilities and orientational order parameters

	λ5780			λ5461			λ4358		
T°C	α_e	α_0	S	α_e	α_0	S	α_e	α_0	S
41.6	50.868	32.241	0.630	52.009	32.769	0.627	57.432	33.752	0.636
43.5	50.710	32.320	0.622	51.785	32.880	0.616	57.231	33.852	0.627
47.5	50.396	32.477	0.606	51.521	33.013	0.603	56.805	34.065	0.610
49.1	50.239	32.555	0.598	51.358	33.094	0.595	56.630	34.153	0.603
53.0	50.023	32.663	0.587	51.114	33.216	0.583	56.279	34.328	0.589
57.6	49.492	32.929	0.560	50.626	33.460	0.559	55.677	34.629	0.564
60.0	49.276	33.037	0.549	50.423	33.561	0.549	55.477	34.729	0.557
63.4	49.099	33.125	0.540	50.138	33.704	0.536	55.176	34.879	0.545
65.9	48.667	33.341	0.518	49.732	33.907	0.516	54.625	35.155	0.523
69.5	48.018	33.665	0.485	49.061	34.242	0.483	53.773	35.581	0.488
73.0	47.016	34.166	0.434	47.963	34.791	0.429	—	—	—

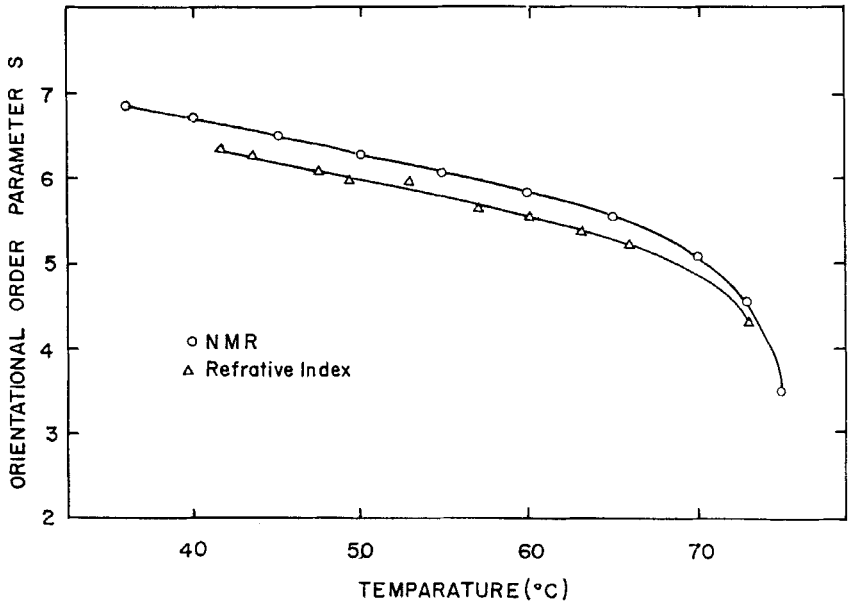

FIGURE 1 Orientational order versus temperature.

S values at same temperature in majority of cases show a close agreement for $\lambda 5780$ and $\lambda 5461$. But that for $\lambda 4358$ shows slight deviation in majority of the cases which may be ascribed to comparatively higher degree of inaccuracy in the measurement of indices in this case. Figure 1 gives a plot or orientational order parameter versus temperature. We have also given a curve of variation of S with temperature for the same compound as determined by the wide line NMR absorption spectra data,[5] for comparison. There is a broad agreement between the two sets of values. But the values of S obtained by birefringence data are somewhat less than those obtained from NMR data. This is also true in case of PAA, and PAP.[4,6] The qualitative explanation for this discrepancy has already been provided.[6]

The isotropic polarizability for EBBA as calculated from bond polarizability data[6] for $\lambda 5893$ is 38.1×10^{-24}. This is in good agreement with the value 38.4×10^{-24} for $\lambda 5790$ as calculated from our present investigation. We also notice a similar agreement in the case of longitudinal polarizability in the crystalline phase. The two values are 54.0 and 58.1 respectively, though not as good as the other.

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