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N. V. Madusudana [a], R. Shashidhar [a] & S. Chandrasekhar [a]
[a] Department of Physics, University of Mysore, Mysore, India
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Orientational Order in Anisaldazine in the Nematic Phase†

N. V. MADHUSUDANA, R. SHASHIDHAR and
S. CHANDRASEKHAR

Department of Physics
University of Mysore
Mysore, India

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Abstract—The refractive indices of anisaldazine,

$$CH_3OC_6H_4CH:NN:CHC_6H_4OCH_3,$$

have been measured in the crystalline, nematic and isotropic phases and the orientational order parameter in the mesophase has been evaluated by the application of the Vuks formula. The curve for the order parameter versus the relative temperature $(T_c - T)$ is nearly parallel with those for *p*-azoxyanisole and *p*-azoxyphenetole and lies approximately midway between them.

1. Introduction

A precise determination of the orientational order parameter in nematic liquid crystals from optical anisotropy requires a knowledge of the polarization field in the medium. Recently, it was shown[1] that a new and simple formula proposed by Vuks[2] for the highly anisotropic polarization field in certain organic molecular crystals gives accurate and internally consistent values of the order parameter in *p*-azoxyanisole and *p*-azoxyphenetole. We report in this paper measurements of the refractive indices of anisaldazine,

$$CH_3OC_6H_4CH:NN:CHC_6H_4OCH_3,$$

in the crystalline, nematic and isotropic phases and the application of the Vuks formula for calculating the order parameter in the nematic phase.

2. Experimental

The commercial sample of anisaldazine (supplied by Eastman

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Organic Chemicals) was purified by double recrystallization from its solution in toluene. Oriented specimens were prepared in a small-angled hollow glass prism. The inside surfaces of the prism were rubbed vertically, i.e., parallel to the refracting edge, and the liquid crystal was allowed to flow along the edge by melting a few crystals placed at the top. The combined effect of rubbing and flow produced a homogeneous nematic specimen with the optic axis vertical. The single crystal was grown by slow cooling of the mesophase.

The prism was mounted in a copper block whose temperature could be controlled electrically. The temperature was measured by means of a thermocouple calibrated previously against the melting points of pure benzoic acid and salicylic acid. The thermocouple junction was imbedded in a thin copper foil suitably wrapped round the prism to ensure good thermal contact. The relative temperatures $(T_c - T)$ could be determined to an accuracy of $\pm 0.1\,^{\circ}C$ and could be maintained constant to within the same limits during any set of observations.

The aperture of the optical system was so arranged that an area of only about $2 \times 2\ mm^2$ of the specimen was used for the experiments. The refractive index measurements were carried out on a precision spectrometer reading to 2″ of arc. The homogeneity and orientation of the nematic and crystalline phases were tested by (i) the clarity of the image of the slit of the spectrometer for both horizontal and vertical polarizations and, (ii) the constancy at a given temperature of the refractive index for vertical polarization irrespective of the angle of incidence.

The principal refractive indices n_x and n_y of the crystal for horizontal polarization were derived from the observed values of n at various 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 geometry of the set up did not allow the entire 90° range of θ to be investigated. One of the principal refractive indices was determined directly, whilst the other had to be derived from (1).

Measurements on two specimens in the crystalline and nematic phases gave consistent results. The refractive indices are reckoned to be accurate to ± 0.001. The data are presented in Tables 1 and 2.

TABLE 1 Refractive indices of the crystal at room temperature

λ(Å)	n_x	n_y	n_z
5893	1.519	1.602	2.201
5461	1.522	1.613	2.251

TABLE 2 Refractive indices in the nematic and isotropic phases ($T_c = 454\,°K$)

$T_c - T$	λ5893 Å		λ5461 Å		λ4358 Å	
	n_e	n_o	n_e	n_o	n_e	n_o
0.5	1.781	1.560				
1.0	1.784	1.559	1.807	1.569	1.950	1.626
2.5	1.798	1.555	1.820	1.564	1.968	1.619
3.8	1.806	1.552	1.830	1.561	1.980	1.615
4.8	1.810	1.550	1.835	1.559	1.988	1.612
5.4	1.815	1.549	1.840	1.558	1.993	1.611
6.6	1.819	1.547	1.845	1.556	2.001	1.608
8.0	1.828	1.546	1.853	1.555	2.012	1.606
9.2	1.833	1.545	1.858	1.554	2.019	1.605
11.8	1.842	1.543	1.867	1.552	2.030	1.601
13.8	1.848	1.542	1.875	1.550	2.042	1.599
15.5	1.853	1.541	1.880	1.550	2.049	1.597
17.4	1.858	1.540	1.885	1.548	2.056	1.595
18.9	1.862	1.540	1.890	1.548	2.062	1.595
20.6	1.867	1.539	1.894	1.547	2.068	1.593
24.7					2.077	1.588
26.7	1.878	1.533	1.906	1.542	2.085	1.587
$T_c + 0.5$	$n = 1.628$		1.643		1.729	

3. Calculation of the Order Parameter in the Nematic Phase

The Vuks formula is

$$\frac{n_i^2 - 1}{\overline{n^2} + 2} = \frac{4\pi\nu}{3}\alpha_i \quad , \qquad i = x, y, z, \tag{2}$$

where $\overline{n^2} = \frac{1}{3}\sum_i n_i^2$,

ν the number of molecules/cc and α_i the principal polarizabilities of the medium. To test the applicability of (2) we consider Born's relation[3] between the refractive indices and densities of the crystalline, nematic and liquid phases which takes the form

$$\left(\frac{1}{\rho}\frac{\overline{n^2}-1}{\overline{n^2}+2}\right)_{\text{cryst}} = \left(\frac{1}{\rho}\frac{\overline{n^2}-1}{\overline{n^2}+2}\right)_{\text{nem}} = \left(\frac{1}{\rho}\frac{n^2-1}{n^2+2}\right)_{\text{liq}} = \frac{4\pi}{3}\frac{N}{M}\bar{\gamma}, \qquad (3)$$

where ρ is the density, $\bar{\gamma}$ the average molecular polarizability, N the Avogadro number and M the molecular weight. The only available density data in the nematic and liquid phases are the early measurements of Conrat[4] recalibrated by Porter and Johnson.[5] Since some interpolation and extrapolation of the values in the nematic phase were required for the calculations, it was found convenient to fit the data with the following empirical relation

$$\rho_{\text{nem}} = 1.04\,[1 + 1.895 \times 10^{-3}(T_c - T)^{0.8}].$$

The density of the crystal was calculated to be 1.23 from X-ray measurements of the lattice constants.[6] Substituting for ρ and n in (3), $\bar{\gamma}$ has been evaluated and shown in Table 3. The average molecular polarizability is indeed very nearly the same in all three phases.

TABLE 3 Average molecular polarizability $\bar{\gamma} \times 10^{24}$ cc

		λ5893 Å	λ5461 Å	λ4358 Å
Crystal,	Room Temp.	36.9	37.8	
Nematic,	$T_c - T = 0.5$	36.6		
	1.0	36.6	37.3	41.2
	2.5	36.7	37.3	41.2
	3.5	36.7	37.3	41.2
	4.8	36.7	37.3	41.3
	5.4	36.7	37.3	41.3
	6.6	36.7	37.3	41.3
	8.0	36.7	37.3	41.3
	9.2	36.7	37.4	41.3
	11.8	36.7	37.4	41.3
	13.8	36.7	37.4	41.4
	15.5	36.7	37.4	41.4
	17.4	36.7	37.4	41.4
	18.9	36.7	37.4	41.4
	20.6	36.7	37.4	41.3
	24.7			41.3
	26.7	36.6	37.3	41.3
Liquid,	$T_c + 0.5$	36.5	37.2	41.0

The principal molecular polarizabilities deduced from the crystal structure[6] and the three principal refractive indices are:

	λ5893 Å	λ5461 Å
$\gamma_{\parallel}(=\gamma_z)$	63.4	66.0×10^{-24}
$\gamma_{\perp}\left(=\frac{\gamma_x+\gamma_y}{2}\right)$	23.7	23.7×10^{-24}

The orientational order parameter was calculated from the molecular polarizabilities by making use of the relation

$$s = \frac{\alpha_e - \alpha_0}{\gamma_{\parallel} - \gamma_{\perp}},$$

where α_e, α_0 are the principal polarizabilities of the nematic medium obtained by substituting n_e and n_0 in Vuks formula. The values are tabulated below (Table 4). As the crystal refractive indices were not

TABLE 4 Orientational order parameter in nematic phase $T_c = 454°K$

$T_c - T$	λ5893 Å	λ5461 Å	λ4358 Å	Average s
0.5	0.406			0.406
1.0	0.413	0.410	0.411	0.411
2.5	0.445	0.440	0.441	0.442
3.8	0.466	0.463	0.462	0.464
4.8	0.477	0.476	0.476	0.476
5.4	0.486	0.484	0.484	0.485
6.6	0.496	0.496	0.496	0.496
8.0	0.516	0.511	0.513	0.513
9.2	0.525	0.522	0.523	0.523
11.8	0.547	0.540	0.540	0.542
13.8	0.556	0.554	0.557	0.556
15.5	0.567	0.563	0.567	0.566
17.4	0.578	0.574	0.577	0.576
18.9	0.585	0.581	0.585	0.584
20.6	0.594	0.590	0.593	0.592
24.7			0.610	0.610
26.7	0.622	0.616	0.621	0.620

measured for λ4358 Å, s for this wavelength was brought to the same scale as for the other wavelengths by equating the values at one temperature ($T_c - T = 6.6$). We have also verified that s evaluated from n_e and n_0 separately (see Ref. 1) agree with those in Table 4

generally to 3–4%. This discrepancy is slightly greater than for *p*-azoxyanisole and *p*-azoxyphenetole[1] possibly because the absolute densities of the liquid crystal are not known as accurately for anisaldazine as for the other two compounds,

Pellet and Chatelain[7] have measured the refractive indices of the liquid crystal for λ5893 Å at a few temperatures, but not those of the crystal. We have evaluated the order parameters from their data using our $\gamma_{\parallel}$ and $\gamma_{\perp}$. The results are in approximate agreement with our values, the maximum discrepancy being about 4%.

The excellent agreement between the *s* values for the different wavelengths in Table 4 indicates that this method of determining the order parameter is a reliable one. Figure 1 shows the mean *s*

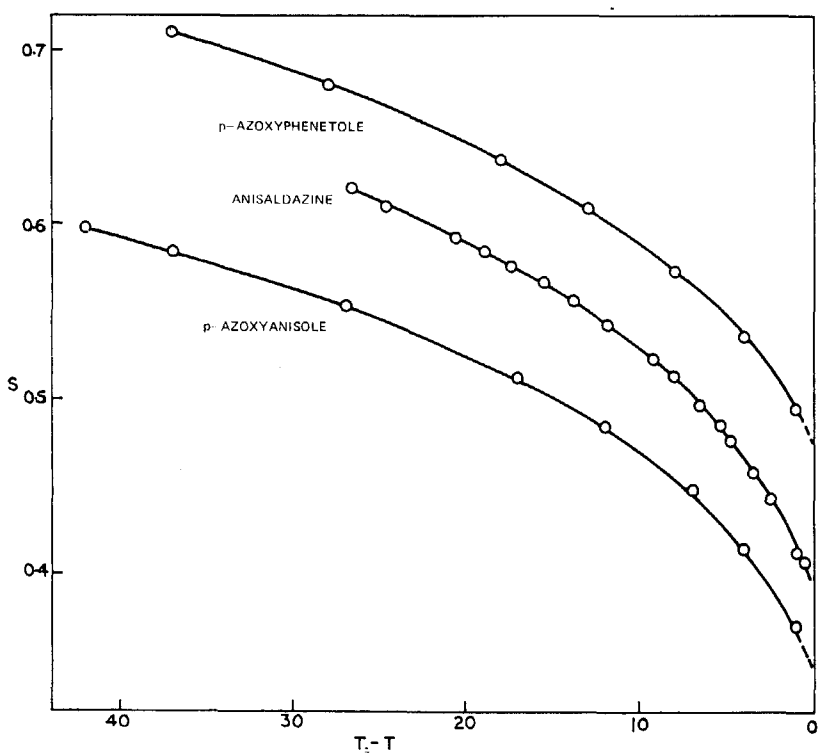

Figure 1. Orientational order parameter in *p*-azoxyphenetole, anisaldazine and *p*-azoxyanisole.

plotted against $T_c - T$ together with the curves for *p*-azoxyanisole and *p*-azoxyphenetole also derived from optical data.[1]

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