Orientational Order in MBBA From Optical Anisotropy Measurements

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Orientational Order in MBBA From Optical Anisotropy Measurements†

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The orientational order parameters of MBBA from two sources (clearing temperatures 317.5°
and 318.9°K) as functions of temperature were obtained from optical anisotropy (birefringence)
measurements of orientated thin films by a variable wave-length method. The formula proposed
by Vuks for the polarization field associated with strongly anisotropic organic molecules was
used as the basis for the development of new expressions used in our evaluation of the order
parameter. The order parameters versus temperature reported in this paper are in very good
agreement with recent NMR and Raman scattering measurements reported in the literature.

I INTRODUCTION

The use of nematic liquid crystals for alphanumeric display devices has been
widespread. The single most important characteristic of a nematic mesophase
is the orientational order parameter. A precise determination of the orienta-
tional order parameter in nematic liquid crystals from optical anisotropy
data requires a knowledge of the polarization field in the medium. The exact
relationship between optical anisotropy and orientational order parameter
is complicated, since the effective electric field seen by one molecule is a
superposition of the field due to external sources plus that due to all other
molecules.

Approximate treatments of the relationship between the two have been
reported in literature. The first estimates of the orientational order in nematic
liquid crystals from optical measurements were made by Chatelain,[1,2]
who pointed out the necessity to take into account the effect of the anisotropic
polarization field in evaluating the polarizabilities and who used an expres-
sion similar to that proposed originally in the theory of Kerr effect in
liquids.[3,4] Saupe and Maier[5] used the more elaborate form of the polarization

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field suggested by Neugebauer.[6] Vuks[7] later proposed a new but simpler formula for the polarization field associated with strongly anisotropic organic molecules to interpret successfully the light scattering and Kerr effect measurements on a number of liquids. The Vuks formula was applied by Chandrasekhar et al.[8,9] to evaluate the orientational order parameter S in three nematic liquid crystals (p-azoxyanisole, p-azoxyphenetole and anisaldazine). From the internal consistency of the calculations these authors concluded that the anisotropic polarization field in nematic liquid crystals is represented accurately by the Vuks equation. The conclusion was subsequently confirmed by the theoretical treatment of Subramhanyam and Krishnamurti[10] on the polarization field and molecular order in nematic liquid crystals.

It is the purpose of this paper to verify further the above discussed relationship between the orientational order parameter and optical anisotropy of nematic liquid crystals. A technique to measure quantatitively the optical anisotropy of nematic liquid crystal films at different temperatures previously discussed by the author[11] is used. We are particularly interested in the pretransition (nematic to isotropic) region where the fluctuation in the orientational order is large. These studies are important from both the fundamental and applied points of view.[12,13]

II EXPERIMENTAL

When a uniaxial film normal to the Z-axis of a Cartesian coordinate system is placed between a polarizer and analyzer such that the extraordinary refractive index n_e corresponds to the Y-direction and ordinary refractive index n_0 corresponds to the X-direction, the transmitted intensities and phase shifts will depend on the orientations of the polarizer and analyzer with respect to the film. We consider the special case of normal incidence where the polarizer and analyzer are parallel to each other and at an angle of $\pi/4$ to the X- and Y-directions.[11] The maximum transmission corresponds to $I_{max} = I_0$, where I_0 is the intensity of the incident beam. The minimum transmission corresponds to $I = I_0 (1 - \sin^2 \delta_t/2) = 0$, where the phase shift $\delta_t = 2\pi(n_e - n_0)d/\lambda$ (d being the film thickness and λ the wave length) and $\sin^2 \delta_{t/2} = 1$ for $\delta_t = \pi, 3\pi, 5\pi. \ldots$

The liquid crystal film was sandwiched between two glass plates (about 2.5 cm × 1 cm × 0.1 cm) with Mylar spacers of appropriate thickness. Unidirectional horizontal alignment of the liquid crystal was accomplished by rubbing the glass surfaces with diamond dust. The two ends of the glass plates were tightly held by means of metal clamps. The thickness of the cell was measured by a travelling microscope and averaged over the long dimen-

sion of the cell. The cell containing the liquid crystal film was placed vertically inside a double-jacketed water-cooled glass vessel (having four nearly optically flat walls parallel to the liquid crystal film) in the sample compartment of a Cary-14 spectrophotometer between a pair of Glan–Thompson prisms as polarizer and analyzer. The beam at normal incidence was carefully collimated by means of narrow entrance and exit slits in order to monitor the intensity of the transmitted light only. In actual experiments, the maximum transmitted intensity is not that of the incident beam (I_0) but that of I_0 minus absorption through the glass plates, the liquid crystal film, the four walls of the double-jacketed glass vessel, and the flowing water through the later; the minimum transmitted intensity is not zero but includes light leakage and multiple scattering through the liquid crystal cell. Since the modulating part of the transmitted light corresponding to $I_0(1 - \sin^2 \delta_t/2)$ is not changed by the additional perturbations, the direct output of the Cary-14 was used in our calculation without any further correction.

MBBA from two sources (MBBA-I, clearing temperature 317.5°K; MBBA-II, clearing temperature 318.9°K) was used. Films with thicknesses varying between 10 to 60 microns sandwiched between glass slides were used. The cell temperature was controlled to $\pm 0.05°$ with thermostated circulating water. The temperature difference between the film (measured with a copper-constantan thermocouple) and the water bath was less than 0.1° in the temperature range (290° to 320°K) studied.

III RESULTS AND DISCUSSION

The Vuks[7] formula for the polarization field associated with strongly anisotropic organic molecules applied to uniaxial nematic liquid crystals is

$$\frac{n_e^2 - 1}{\overline{n}^2 + 2} = \frac{4\pi}{3} \frac{N\rho}{M} \alpha_e \tag{1a}$$

$$\frac{n_0^2 - 1}{\overline{n}^2 + 2} = \frac{4\pi}{3} \frac{N\rho}{M} \alpha_0 \tag{1b}$$

where α_e, α_0 are the principal polarizabilities (parallel and perpendicular, respectively to the liquid crystal directors) of the medium; n_e, n_0 the respective refractive indices; $\overline{n}^2$ equals $(\frac{1}{3}n_e^2 + \frac{2}{3}n_0^2)$; N is Avogadro's number; M the molecular weight; ρ the density of the medium. Subtracting equation (1b) from equation (1a) and replacing $(n_e - n_0)$ by Δn, the birefringence, we have

$$\Delta n = \frac{4\pi}{3} \frac{N\rho}{M} (\alpha_e - \alpha_0) \frac{\overline{n}^2 + 2}{n_e + n_0} \tag{2}$$

The degree of orientational order S is defined as

$$S = \tfrac{1}{2}\overline{(3\cos^2\theta - 1)} \tag{3}$$

where θ is the angle between the long axis of the molecule and the optic axis of the medium (the directors). The relationships between S and α_e, α_0 are given by[1,2]

$$\alpha_e = \bar{\gamma} + \tfrac{2}{3}(\gamma_{\parallel} - \gamma_{\perp})S \tag{4a}$$

$$\alpha_0 = \bar{\gamma} - \tfrac{1}{3}(\gamma_{\parallel} - \gamma_{\perp})S \tag{4b}$$

$$S = \frac{(\alpha_e - \alpha_0)}{(\gamma_{\parallel} - \gamma_{\perp})} \tag{4c}$$

where $\gamma_{\parallel}$, $\gamma_{\perp}$ are the principal polarizabilities of the liquid crystal molecule and $\bar{\gamma}$ equals $(\tfrac{1}{3}\gamma_{\parallel} + \tfrac{2}{3}\gamma_{\perp})$. Combining equations (2) and (4c), we obtain

$$\Delta n = \frac{4\pi}{3}\frac{N\rho}{M}(\gamma_{\parallel} - \gamma_{\perp})\frac{\overline{n^2} + 2}{n_e + n_0}S \tag{5}$$

Equation (5) implies, according to the Vuks polarization field approximation, that Δn is directly proportional to the order parameter S. The order parameter S can thus be calculated from the experimentally measured Δn values provided that the molecular polarizabilities $(\gamma_{\parallel} - \gamma_{\perp})$, the refractive indices $(\overline{n^2} + 2)$, $(n_e + n_0)$, and the density ρ of the medium are known as functions of the temperature of measurement.

Three experimental techniques have been reported in the literature for Δn measurements: the Chatlelain prism method,[14] the variable temperature method,[15] and the variable film thickness method.[16] Single wave-length monochromatic light sources were used in these methods. We present here a fourth variable wave-length method the details of which have been previously reported by us.[11] The method is accurate and provides additional information on the wave-length dependence (or dispersion) of the refractive indices. A typical Cary-14 spectrophotometer trace (MBBA, 60 micron-film, measured at $311.2°K$) employing the variable wave-length method described in reference (11) is shown in Figure 1. The phase difference $\delta_{i,j}$ between each successive pair of peaks (or valleys) in the absorption-wavelength trace of Figure 1 is 2π. We thus write the following sequence of m equations

$$\delta_{1,2} = 2\pi = 2\pi d\left(\frac{\Delta n_{\lambda_1}}{\lambda_1} - \frac{\Delta n_{\lambda_2}}{\lambda_2}\right) \tag{6-1}$$

$$\delta_{2,3} = 2\pi = 2\pi d\left(\frac{\Delta n_{\lambda_2}}{\lambda_2} - \frac{\Delta n_{\lambda_3}}{\lambda_3}\right) \tag{6-2}$$
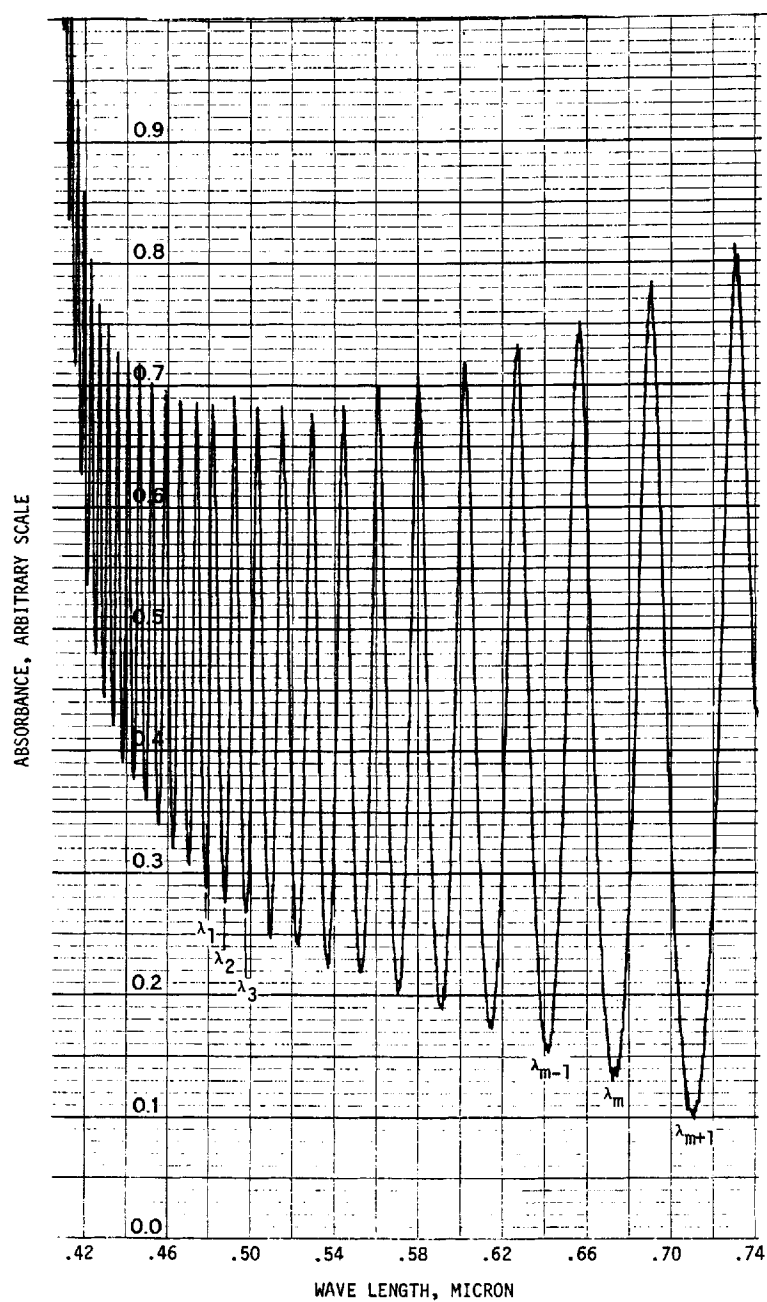
FIGURE 1   Cary-14 Trace, MBBA, film thickness 60 microns, measuring temperature 311.2°K.

$$\delta_{m, m+1} = 2\pi = 2\pi d \left(\frac{\Delta n_{\lambda_m}}{\lambda_m} - \frac{\Delta n_{\lambda_{m+1}}}{\lambda_{m+1}} \right) \qquad (6\text{-m})$$

where d is the film thickness and Δn_{λ_i} is the birefringence at wave-length λ_i. Summing up the m equations, we have

$$m = d \left(\frac{\Delta n_{\lambda_1}}{\lambda_1} - \frac{\Delta n_{\lambda_{m+1}}}{\lambda_{m+1}} \right) \qquad (7)$$

The accuracy of measurement of m increases with increasing wave-length range $\lambda_1 - \lambda_{m+1}$, i.e., with increasing m. Combining equations (5) and (7), we have

$$m = \frac{4\pi}{3} \frac{N}{M} \left\{ \left[\frac{\overline{(n^2 + 2)}(\gamma_\| - \gamma_\perp)}{\lambda(n_e + n_0)} \right]_{\lambda_1} - \left[\frac{\overline{(n^2 + 2)}(\gamma_\| - \gamma_\perp)}{\lambda(n_e + n_0)} \right]_{\lambda_{m+1}} \right\} \rho.d.S \qquad (8a)$$

or

$$m = K_1 \cdot K_2(\lambda, T) \cdot d \cdot S \qquad (8b)$$

where

$$K_1 = \frac{4\pi}{3} \frac{N}{M} \qquad (8c)$$

$$K_2 = \left\{ \left[\frac{\overline{(n^2 + 2)}(\gamma_\| - \gamma_\perp)}{\lambda(n_e + n_0)} \right]_{\lambda_1} - \left[\frac{\overline{(n^2 + 2)}(\gamma_\| - \gamma_\perp)}{\lambda(n_e + n_0)} \right]_{\lambda_{m+1}} \right\} \rho. \qquad (8d)$$

In equation (8d) K_2 is strongly wave-length dependent but weakly temperature dependent, while the order parameter S is strongly temperature dependent. The wave-length dependence (dispersion) of the molecular polarizabilities and refractive indices depends on the molecular structure of the liquid crystal. Suffice it to say that for a given liquid crystal material this dependence is characteristic and is invariant for any given pair of chosen λ_1 and λ_{m+1} values. The temperature dependence of K_2 is very weak. We have calculated K_2 at various temperatures for anisaldazine at $\lambda_{m+1} = 5893\,\text{Å}$ and $\lambda_1 = 5461\,\text{Å}$ from the best available information in literature.[9] The results are summarized in Table I. The temperature variation of the order parameter S is orders of magnitude larger. We express the temperature dependence of K_2 and S by the following empirical equations

$$K_2 = K_2^0(-\varepsilon)^\alpha \qquad (9)$$

$$S = S^0(-\varepsilon)^\beta \qquad (10)$$

where

$$\varepsilon = \frac{T - T_c}{T_c} \qquad (11)$$

TABLE I

Calculation of the temperature dependence of K_2 for anisaldazine

$T_c - T$, degree	$\lambda = 5893$ Å		$\lambda 5461$ Å		ρ, gm/cm^3	K_2 (see equation 8d)
	n_e	n_0	n_e	n_0		
1.0	1.784	1.559	1.807	1.569	1.042	0.382×10^{-23} gm
2.5	1.798	1.555	1.820	1.564	1.044	0.381×10^{-23} gm
3.8	1.806	1.552	1.830	1.561	1.045	0.382×10^{-23} gm
4.8	1.810	1.550	1.835	1.559	1.047	0.382×10^{-23} gm
5.4	1.815	1.549	1.840	1.558	1.048	0.382×10^{-23} gm
6.6	1.819	1.547	1.845	1.556	1.049	0.383×10^{-23} gm
8.0	1.828	1.546	1.853	1.555	1.050	0.384×10^{-23} gm
9.2	1.833	1.545	1.858	1.544	1.052	0.384×10^{-23} gm
11.8	1.842	1.543	1.867	1.552	1.054	0.385×10^{-23} gm
13.8	1.848	1.542	1.875	1.550	1.056	0.384×10^{-23} gm
15.5	1.853	1.541	1.880	1.550	1.058	0.386×10^{-23} gm
17.4	1.858	1.540	1.885	1.548	1.060	0.385×10^{-23} gm
18.9	1.862	1.540	1.890	1.548	1.061	0.386×10^{-23} gm
20.6	1.867	1.539	1.894	1.547	1.063	0.387×10^{-23} gm
26.7	1.878	1.533	1.906	1.542	1.067	0.389×10^{-23} gm

is the reduced temperature, T being the temperature of measurement and T_c a virtual critical temperature slightly above the nematic-isotropic transition temperature. Substituting equations (9), (10) and (11) into equation (8b), we have

$$m = K_1 \cdot K_2^0 \cdot S^0 \cdot d \cdot (-\varepsilon)^{\alpha+\beta} \qquad (12a)$$

or

$$m = m^0 \cdot d \cdot (-\varepsilon)^{\alpha+\beta} \qquad (12b)$$

where $m^0 = K_1 K_2^0 S^0$ is a material constant dependent on the chosen wavelength range $\lambda_1 - \lambda_{m+1}$ within which m is counted. In practice m can be measured accurately from the recording chart (see Figure 1) with a precision of ± 0.2. The usual ranges of m, depending on the film thickness and wavelength range $\lambda_1 - \lambda_{m+1}$ used, are 5 to 40, giving a measurement error of ± 4 to ± 0.5 percent.

The exponent α determining the temperature dependence of K_2 was calculated according to data shown in Table I for anisaldazine and is 0.005. A similar calculation for MBBA from available experimental information[16,17] (results not shown in this paper for the sake of space) yields $\alpha = 0.004$. For all practical purposes, we can indeed neglect the temperature dependence of K_2 and rewrite equation (12b) as

$$m = m^0 \cdot d \cdot (-\varepsilon)^{\beta} \qquad (12c)$$

where m^0 is a material constant (dependent on choice of wave-length range $\lambda_1 - \lambda_{m+1}$), d is the film thickness, ε is the normalized temperature defined by equation (11), and β is a critical exponent[12] measuring the temperature dependence of the orientational order parameter S according to equation (10).

The best estimated value, consistent with our birefringence data and with values reported in the literature,[16] of the molecular polarizability anisotropy of MBBA at $\lambda = 0.65$ micron is $\gamma_\| - \gamma_\perp = 34 \times 10^{-24}$ cm^3. From an experimentally measured value of $\Delta n = 0.30$ at $\lambda = 0.65$ micron, and $T = 293°K$ the order parameter calculated according to equation (5) is $S = 0.62$. Our measurements show that for a given nematic liquid crystal the experimentally measured m values are directly proportional to the film thickness at a given temperature and the temperature dependence of m for a given film thickness is independent of the wave-length limits $\lambda_1 - \lambda_{m+1}$. These observations are in direct support of the validity of our theoretical formulations given above.

Since the temperature dependence of K_2 is negligibly small, equation (8b) says that for a given film thickness d and a given choice of the wavelength
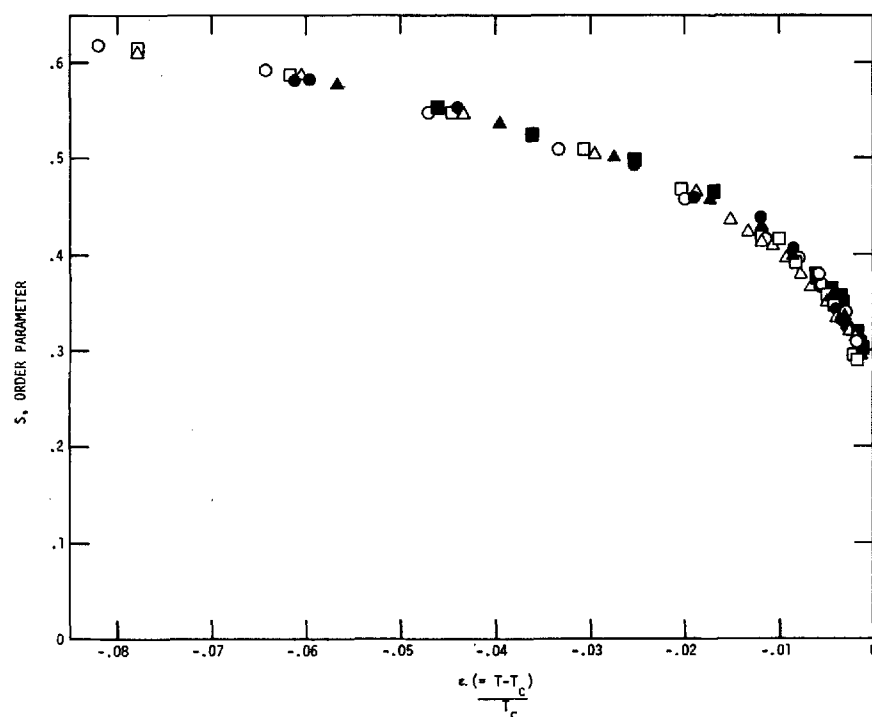

FIGURE 2   Order parameters versus reduced temperature for MBBA from six independent runs.

TABLE II

Experimental m values and calculated order parameter S versus temperature for six individual experiments ($\lambda_{m+1} = 0.72$ micron, $\lambda_1 = 0.42$ micron)

MBBA-Ia $(d = 60$ microns$)$ $(T_c = 317.7°K)$			MBBA-Ib $(d = 40$ microns$)$ $(T_c = 317.2°K)$			MBBA-Ic $(d = 27$ microns$)$ $(T_c = 317.7°K)$		
$-\varepsilon$	m	S	$-\varepsilon$	m	S	$-\varepsilon$	m	S
0.0779	29.6	0.618	0.0778	19.5	0.609	0.0567	12.7	0.578
0.0617	28.1	0.586	0.0605	18.8	0.587	0.0396	11.8	0.535
0.0448	26.2	0.547	0.0433	17.5	0.546	0.0275	11.0	0.501
0.0309	24.4	0.509	0.0293	16.1	0.503	0.0173	10.1	0.457
0.0205	22.4	0.467	0.0188	14.9	0.465	0.0119	9.5	0.432
0.0118	20.1	0.420	0.0152	13.9	0.434	0.0084	8.9	0.403
0.0080	18.7	0.391	0.0133	13.5	0.422	0.0060	8.2	0.373
0.0050	17.1	0.357	0.0117	13.2	0.412	0.0043	7.8	0.355
0.0044	16.6	0.347	0.0107	13.0	0.406	0.0032	7.4	0.337
0.0021	14.1	0.295	0.0093	12.7	0.397	0.0023	7.0	0.318
0.0016	13.9	0.290	0.0077	12.1	0.378	0.0018	6.6	0.300
			0.0066	11.7	0.365	0.0013	6.5	0.296
			0.0050	11.2	0.350			
			0.0038	10.6	0.331			
			0.0024	10.2	0.318			
			0.0018	10.0	0.312			

MBBA-Id $(d = 16$ microns$)$ $(T_c = 317.7°K)$			MBBA-IIa $(d = 32$ microns$)$ $(T_c = 319.1°K)$			MBBA-IIb $(d = 12$ microns$)$ $(T_c = 319.1°K)$		
$-\varepsilon$	m	S	$-\varepsilon$	m	S	$-\varepsilon$	m	S
0.0597	7.4	0.584	0.0821	15.5	0.618	0.0852	5.9	0.611
0.0463	7.0	0.552	0.0644	14.7	0.586	0.0612	5.6	0.580
0.0362	6.7	0.525	0.0472	13.7	0.546	0.0440	5.3	0.554
0.0254	6.3	0.497	0.0334	12.7	0.506	0.0254	4.7	0.491
0.0169	5.9	0.466	0.0200	11.4	0.454	0.0190	4.4	0.460
0.0099	5.3	0.418	0.0115	10.4	0.415	0.0120	4.2	0.439
0.0062	4.8	0.379	0.0080	9.9	0.393	0.0084	3.9	0.408
0.0045	4.6	0.363	0.0062	9.5	0.379	0.0051	3.5	0.366
0.0035	4.5	0.355	0.0054	9.3	0.369	0.0040	3.3	0.340
0.0031	4.4	0.347	0.0042	9.0	0.359	0.0031	3.2	0.334
0.0026	4.2	0.331	0.0030	8.5	0.337	0.0027	3.1	0.324
0.0023	4.1	0.324	0.0023	8.1	0.323	0.0020	3.0	0.314
0.0019	4.0	0.316	0.0017	8.0	0.319	0.0015	2.9	0.303
0.0016	3.9	0.308				0.0013	2.85	0.298
0.0013	3.85	0.304						
0.0007	3.8	0.300						

region $\lambda_1 - \lambda_{m+1}$ within which m is measured, the order parameter is directly proportional to m. The experimentally observed m values and the calculated order parameters as functions of temperature for six runs are summarized in Table II. The order parameters are plotted versus the reduced temperature ε in Figure 2.

IV SUMMARY CONCLUSION

The order parameters shown in Table II and Figure 2 are in good agreement with recent nuclear magnetic resonance (partially deutrated MBBA) results of Lee et al,[18] Raman scattering measurements of Jen and coworkers[19] and Carbon-13-proton double resonance data of Pines and Chang.[20] It is noted in reference 19 that refractive index measurements and the Vuks equation were also used to obtain the order parameter in MBBA. These, plus the observed facts that at a given temperature the measured m values are directly proportional to the film thickness and that for a given film thickness the temperature dependence of m is independent of the wave-length limits $\lambda_1 - \lambda_{m+1}$ used, lead us to conclude that the variable wavelength method is a useful one to study the anisotropic optical properties and order parameter of nematic liquid crystals.

Acknowledgements

References

1. P. Chatelain, *Bull. Soc. franc. Miner. Crist.*, **50**, 280 (1937).
2. P. Chatelain, *Bull. Soc. franc. Miner. Crist.*, **78**, 262 (1955).
3. C. V. Raman and K. S. Krishnan, *Phil. Mag.* **5**, 498 (1928).
4. J. W. Beams, *Rev. Mod. Phys.*, **4**, 133 (1932).
5. A. Saupe and W. Maier, *Z. Naturforschg.*, **16a**, 816 (1961).
6. H. E. J. Neugebauer, *Can. J. Phys.*, **18**, 292 (1950).
7. M. F. Vuks, *Optics and Spectroscopy*, **20**, 361 (1966).
8. S. Chandrasekhar and N. V. Madhusudana, *Jour. de Physique*, C4, (Supplement No. 11–12), 24 (1969).
9. N. V. Madhusudana, R. Shashidhar and S. Chandrasekhar, *Molec. Cryst., Liquid Cryst.*, **13**, 61 (1971).
10. H. S. Subramhanyam and D. Krishnamurti, paper presented at the 4th International Liquid Crystal Conference at Kent, Ohio, 1972 (to be published).
11. R. Chang, *Materials Research Bulletin*, **7**, 267 (1972).
12. R. Chang, *Solid State Comm.*, **14**, 403 (1974).

13. R. Chang and J. C. Gysbers, 5th International Liquid Crystal Conference, Stockholm, Sweden, 1974 (to be published in Jour. de Physique).
14. O. Pellet and P. Chatelain, *Bull. Soc. franc. Miner. Crist.*, **73**, 154 (1950); M. Brunet-Germain, *Compt. Rend.*, **271B**, 1075 (1970).
15. D. A. Balzarini, *Phys. Rev. Letters*, **25**, 914 (1970).
16. I. Haller, H. A. Huggins, and M. J. Freiser, *Molec. Cryst., Liquid Cryst.*, **16**, 53 (1972).
17. M. J. Press and A. S. Arrott, *Phys. Rev.*, **A8**, 1459 (1973).
18. Y. S. Lee, U. Y. Hsu, and D. Dolphin, *Liquid Crystals and Ordered Fluids*, J. F. Johnson and R. S. Porter, editors, Plenum Press. Vol. 2, p. 357, 1973.
19. S. Jen, N. A. Clark, and P. S. Pershan, *Phys. Rev. Letters*, **31**, 1552 (1973).
20. A. Pines and J. J. Chang, *Phys. Rev.*, **A10**, 946 (1974).