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Order Parameter and Molecular Polarizabilities in 60.4, 60.2 and 70.1

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In some N(p-n-alkoxy benzylidene) p-n-alkylanilines the refractive indices n_e, n_o and the order parameter are measured as a function of temperature. From the experimental data the molecular polarizabilities and its anisotropies at different wavelengths were calculated using different internal field models. The merits of each model were discussed.

INTRODUCTION

The molecular polarizabilities and their anisotropy are considered to be important characteristic inherent molecular properties[1] of liquid crystalline substances because the intermolecular interaction energies, according to several theoretical models, are dependent on them. In the last decade and a half different theoretical models[2–7] are proposed to define the internal field which partly lead to significantly different molecular polarizability values. Since molecular polarizabilities cannot be measured directly in the liquid crystalline state, the different proposed internal models to calculate them are described briefly along with the results of refractive indices, densities and order parameter obtained from electron spin resonance experiment. The compounds studied are N(p-n-hexyloxy benzylidene) p-n-butyl ani-

line 60.4, N(p-n-hexyloxy benzylidene) p-ethyl aniline 60.2 and N(p-n-heptyloxy benzylidene) p-toluidine 70.1.

THEORY

In uniaxial liquid crystals the extraordinary polarizability, α_e, and ordinary polarizability, α_o, corresponding to the electric vector parallel and perpendicular to the optical axis respectively are given by

$$\alpha_e = \bar{\alpha} + 2(\alpha_\parallel - \alpha_\perp)\, S/3$$

$$\alpha_o = \bar{\alpha} - (\alpha_\parallel - \alpha_\perp)\, S/3 \qquad (1)$$

Where S is the order parameter and $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities of a molecule parallel and perpendicular to the long molecular axis. The average polarizability $\bar{\alpha}$ may be expressed by

$$\bar{\alpha} = (\alpha_e + 2\alpha_o)/3 = (\alpha_\parallel + 2\alpha_\perp)/3 \qquad (2)$$

Combining equations 1 and 2, we obtain

$$S = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp) \qquad (3)$$

In the following the different internal field models are presented.
Vuks model: In the Vuks model[8] first applied to nematic liquid crystals by Chandrasekhar and Madhusudana[2] it is assumed that the internal field is isotropic even in anisotropic crystal. This assumption leads to the following equations

$$\alpha_{e,o} = (3/4\pi N)\, (n_{e,o}^2 - 1)/(\bar{n}^2 + 2) \qquad (4)$$

Where N is the number of molecules per unit volume, n_e is the extraordinary and n_o is the ordinary refractive indices.

$$\bar{n}^2 = (n_e^2 + 2n_o^2)/3 \qquad N = N_A\rho/M$$

N_A is the Avogadro's number, ρ is the density and M is the molecular weight.
Neugebauer model: Saupe and Maier[9] and later on Subrmhanyam and Krishna Murti[3] applied the anisotropy of the internal field in a crystal, put forward by Neugebauer,[10] to liquid crystals. The mole-

cules are assumed as point polarizabilities distributed anisotropically in space. The molecular polarizabilities following Subramhanyam and Krishna Murti are given by

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

$$\alpha_o = \frac{AB + 3 \pm \sqrt{(AB+3)^2 - 16AB}}{4A} \qquad (5)$$

Where

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

$$B = (\alpha_{\parallel} + 2\alpha_{\perp}) = (\alpha_e + 2\alpha_o) = 3\bar{\alpha} = 9(n^2-1)/(4\pi N_i)\,(n^2+2)$$

N is the number of molecules per unit volume in the nematic phase and N_i is the number of molecules per unit volume in isotropic phase. The polarizabilities obtained from Maier and Saupe equations are in good agreement to significant figures with those calculations obtained from Subramhanyam and Krishna Murti equations (5). Hence Maier and Saupe equations are not given here. Our conclusion is in agreement with Van Hecke et al.[11] results. However the reported variance of α_e and α_o values by Sen et al.,[12] obtained from Maier-Saupe and Neugebauer equations are due to some calculation errors.

de Jeu-Bordewijk model: de Jeu and Bordewijk[4] following Kuznetsov model[13] replaced the molecular point polarizability of Neugebauer model by an approximation, that the molecule is represented by an anisotropic homogeneously polarizable prolate spheroid. Moreover the molecule and its surroundings are represented on a continuum basis i.e., the anisotropic homogeneously polarizable spheroid is filling up the cavity in the anisotropic homogeneously polarized continuum. The internal field of axially symmetric molecules is taken as independent of the anisotropy of the surroundings of a molecule. The molecular polarizabilities are given by

$$\alpha_e = (1/4\pi N)[K_e + \{(\epsilon_{\perp} - 1) + (1/3)(\epsilon_{\parallel} - \epsilon_{\perp})(1 + 2/S)\}^{-1}]^{-1}$$

$$\alpha_o = (1/4\pi N)[K_o + \{(\epsilon_{\perp} - 1) + (1/3)(\epsilon_{\parallel} - \epsilon_{\perp})(1 - 1/S)\}^{-1}]^{-1} \qquad (6)$$

where K_e and K_o are the shape factors given by

$$K_e = 1 - W^2 + (W/2)\,(W^2-1)\,\ln((W+1)/(W-1))$$

$$K_o = (1 - K_e)/2$$

$$W^2 = a^2/(a^2 - b^2)$$

a and b are the long and short axes of the prolate spheroid. a is the length of the all-stretched molecule and b is derived from the molar volume at the transition temperature, $\epsilon = n^2$ and S is the order parameter.

When S = 0 in the isotropic liquid the isotropic refractive index can be estimated from the following equation 7.

$$\epsilon_{iso} = n^2 = 1 + 4\pi N\,\{(\alpha_e/(1-4\pi N\alpha_e K_e)) + (2\alpha_o/(1-4\pi N\alpha_o K_o))\} \quad (7)$$

Ibrahim and Haase model: Ibrahim and Haase[5] have also extended the model of Kuznetsov et al.[13] to the case of a spheroidal cavity. The corresponding equations are

$$\alpha_e = [\gamma_e + 8\pi N S g_e\,(\Delta\epsilon + S\,(\epsilon_\parallel + \epsilon_\perp - 2))^{-1}]^{-1}$$

$$\alpha_o = [\gamma_o - 16\,N S g_o\,(\Delta\epsilon - 2S(\epsilon_\parallel + \epsilon_\perp - 2))^{-1}]^{-1} \quad (8)$$

Where γ and g are the diagonal tensors in the reaction and cavity fields respectively in the (x, y, z) system whose principal axes coincide with principal axes of ϵ. They are given by

$$\gamma_e = \gamma_\parallel - (2/3)\,(1-S)\Delta\gamma$$

$$\gamma_o = \gamma_\perp + (1/3)\,(1-S)\Delta\gamma$$

$$\Delta\gamma = \gamma_\parallel - \gamma_\perp$$

$$\gamma_\parallel = 4\pi N\,K_\parallel\,(1 - K_\parallel)\,(\epsilon_\parallel - 1)/(\epsilon_\parallel - K_\parallel\,(\epsilon_\parallel - 1))$$

$$\gamma_\perp = 4\pi N\,K_\perp\,(1 - K_\perp)\,(\epsilon_\perp - 1)/(\epsilon_\perp - K_\perp\,(\epsilon_\perp - 1))$$

$K_\parallel$ and $K_\perp$ are the depolarizing factors of a prolate spheroid with eccentricity, $e = (1 - (b^2\epsilon_\parallel/a^2\epsilon_\perp))^{1/2}$, $(a/\sqrt{\epsilon_\parallel})$ and $(b/\sqrt{\epsilon_\perp})$ are the semi axes of the prolate spheroid, with the dielectric constant components $\epsilon_\parallel^{-1}$ and $\epsilon_\perp^{-1}$ located in vaccum. $\epsilon = n^2$ at optical frequency and $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$.

$$g_e = g_\parallel - (2/3)\,(1-S)\Delta g$$

$$g_o = g_\perp + (1/3)\,(1-S)\Delta g$$

$$\Delta g = g_\parallel - g_\perp$$

$$g_\parallel = (1 - K_\parallel\,(1 - 1/\epsilon_\parallel))^{-1}$$

$$g_\perp = (1 - K_\perp\,(1 - 1/\epsilon_\perp))^{-1}$$

The refractive index in the isotropic phase can be estimated, from the molecular polarizabilities in the nematic phase calculated from equation (8), is given by

$$n_i^2 = 1 + (4\pi N/3)\,((\bar{g}\alpha_e/1 - \bar{\gamma}\alpha_e) + (2\,\bar{g}\alpha_o/1-\bar{\gamma}\alpha_o)) \qquad (9)$$

where

$$\bar{g} = (g_\parallel + 2g_\perp/3)$$

and

$$\bar{\gamma} = (\gamma_\parallel + 2\gamma_\perp/3)$$

The ratio of b/a is estimated following deJeu-Bordewijk procedure. *Derzhanski-Petrov model:* Derzhanski and Petrov[14,15] derived a generalised theory following the Scholte's model[16] to interpret the microwave permittivities of p-azoxyanisole. Hauser et al.[6] applied the above theory to calculate the molecular polarizabilities of liquid crystals. Unlike in the de Jeu-Bordewijk and Ibrahim-Haase models the molecular shape i.e., the ratio of the short and long axes of a prolate spheroid $q = (b/a)$ is determined from the optical birefringence rather than geometrical one. The molecular polarizabilities are calculated from

$$\alpha_i = (V/4\pi)\,(\epsilon_i^m - 1)/(1 + D_i\,(\epsilon_i^m - 1)) \qquad (10)$$

where

$$i = 1, 3 \qquad \alpha_i = \alpha_1 = \alpha_2 = \alpha_o$$

and

$$\alpha_i = \alpha_3 = \alpha_e$$

V = volume of the spheroid.
$D_i = D_1 = D_2 = D_o$, and $D_i = D_3 = D_e$ are the depolarizing factors and are determined from the following expressions

$$D_e = \frac{1 - e^2}{2e^3}((\ln (1 + e)/(1 - e)) - 2e); \; D_o = (1 - D_e)/2$$

where

$$e = (1 - q^2)^{1/2}$$

The spheroidal parameters V, q, ϵ_1^m and ϵ_3^m are determined as follows. The isotropic permittivity at any given temperature above T_{NI} or its extrapolated value below T_{NI} is expressed by

$$((n_i^2 - 1)/4\pi) = (N_i/3)\,(2g_o^{is}\,F_o^{is}\,\alpha_o^{is} + g_e^{is}\,F_e^{is}\,\alpha_e^{is}) \qquad (11)$$

g and F are cavity and reaction field factors respectively. Further they assumed that i) the mean micropermittivity of the material in the spheroid is equal to the isotropic permittivity and ii) the value q = b/a is chosen such that the calculated macroscopic dielectric anisotropy from the reaction and cavity field factors is equal to the experimentally measured anisotropy.

Palffy-Muhoray-Balzarini model: Palffy-Muhoray and Balzarini[7,17] have modified the Clausius-Mosotti relation, in the point dipole approximation neglecting fluctuations for anisotropic fluids in terms of the molecular pair correlation function, which can be applied to the analysis of refractive index measurements of nematic liquid crystals. However in the evaluation of molecular polarizabilities the estimation of longitudinal and transverse molecular polarizabilities in solid state is required. Since the additive bond polarizability data cannot give correct values of polarizability anisotropy in conjugated systems, which is true in the compounds studied in the present work, the calculations of Palffy-Muhoray-Balzarini method are not carried out.

EXPERIMENTAL

The refractive indices of the liquid crystals were measured with a wedge shaped glass cell, similar to the one used to obtain birefringence by Haller et al.[18] and modified spectrometer.[19] A wedge shaped glass cell was formed with two optically flat rectangular (75 mm × 25 mm) glass plates sandwiched with a glass plate (≈0.5 mm) which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge, i.e., parallel to the wedge glass plate, to get the alignment of nematic molecules. The cell is filled with liquid crystal material aligned parallel to the edge of the wedge. The liquid crystal in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block was ± 0.1°C. The accuracy in the measured refracive indices was ± 0.0005. The transition temperatures and formulae of the compounds studied are presented in Table I.

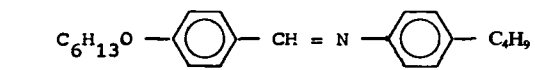
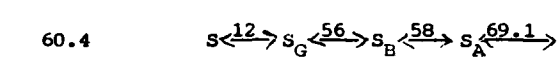
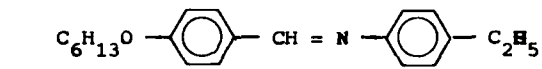
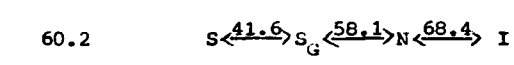
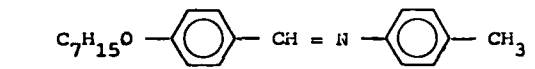
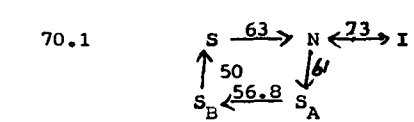
The ESR spectra were recorded with a varian E-4-X band spectrometer after the liquid crystalline samples were dissolved with a nitroxide probe (10^{-3}M concentration) in a quartz tube. The order parameter is determined following the procedure described earlier.[20] The molar volumes are calculated from the densities reported earlier.[21-23]

DISCUSSION

The refractive indices (n_e, n_o) variation with temperature in different compounds is shown in Figures 1–3. The molar volume V and the order parameter S, at different temperatures, of the substances investigated are presented in Table 2. It is interesting to compare the order parameter variation with temperature, which is illustrated in Figure 4, in the nematic phase of different compounds. The order parameter shows a strong temperature dependence. All the compounds possess more or less same temperature coefficient of order parameter. The molecular polarizabilities α_e, α_o, the polarizability anisotropies and the average polarizability $\bar{\alpha}$ calculated from the experimental data by use of different internal field models are presented in Tables III–V. It is evident from Tables III–V that the average molecular polarizability $\bar{\alpha}$ is temperature independent for all internal field models in 60.4, 60.2 and 70.1. The $\bar{\alpha}$ values obtained from the three spheroidal models (de Jeu-Bordewijk, Ibrahim-Haase and Derzhanski-Petrov) are higher, whereas the Vuks and Neugebauer models give lower values. Moreover in the nematic range these $\bar{\alpha}$ values are

TABLE I

Molecular structural formulae and transition temperatures of compounds

Substance molecular formula	abbreviated name	Transition temps. in °C
 N(p-n-hexyloxy benzylidene) p-n-butyl aniline	60.4	
 N(p-n-hexyloxy benzylidene) p-ethylaniline	60.2	
 N(p-n-heptyloxy benzylidene) p-toluidine	70.1	

S = Solid; S_G = Smectic G; S_B = Smectic B; S_A = Smectic A; N = Nematic; I = Isotropic.

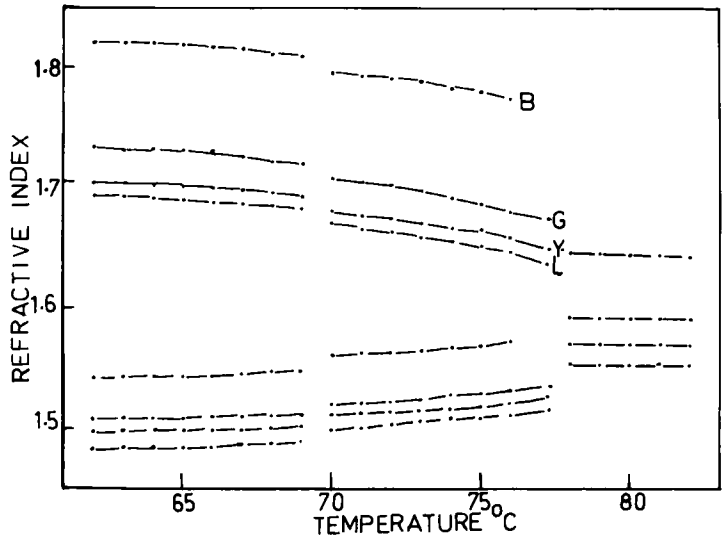


FIGURE 1 Refractive indices variation with temperature at different wavelengths of 60.4.

constant within the experimental errors at each wavelength. Subramhanyam et al.[24] criticized that in a medium with anisotropic molecular distribution the local field would not be isotropic as assumed in Vuks formulae. deJeu-Bordewijk have shown that the Vuks relations gave anomalous dispersion of α_o and also incorrect signs of polarizability anisotropy. Further in Neugebauer's relations the point polarizability of a molecule is taken into consideration, rather than the anisotropic distribution of molecular polarizability in space, which leads to plausible results.[11] Thus the three spheroidal models are realistic with the assumptions made but they also give different molecular polarizability anisotropies. α_e and $\alpha_e - \alpha_o$ show pronounced changes in deJeu-Bordewijk or Petrov model while they are almost constant in Ibrahim-Haase model. The equation 3, in which the order parameter is defined as the ratio of the molecular polarizability anisotropy in the liquid crystalline state to that in solid state, can be explained as follows. If the molecular conformation is taken into account, in most cases, motions of parts of the molecule viz., the free rotation about the single bonds like CH_3 group at the ends of a molecule, the hindered rotation like the presence of bulk groups or double bonds and acoplanarity of two benzene rings reducing the conjugation effects, are always possible in the liquid crystalline phase. The fractional number of molecules in which such motions take place and the amplitudes of

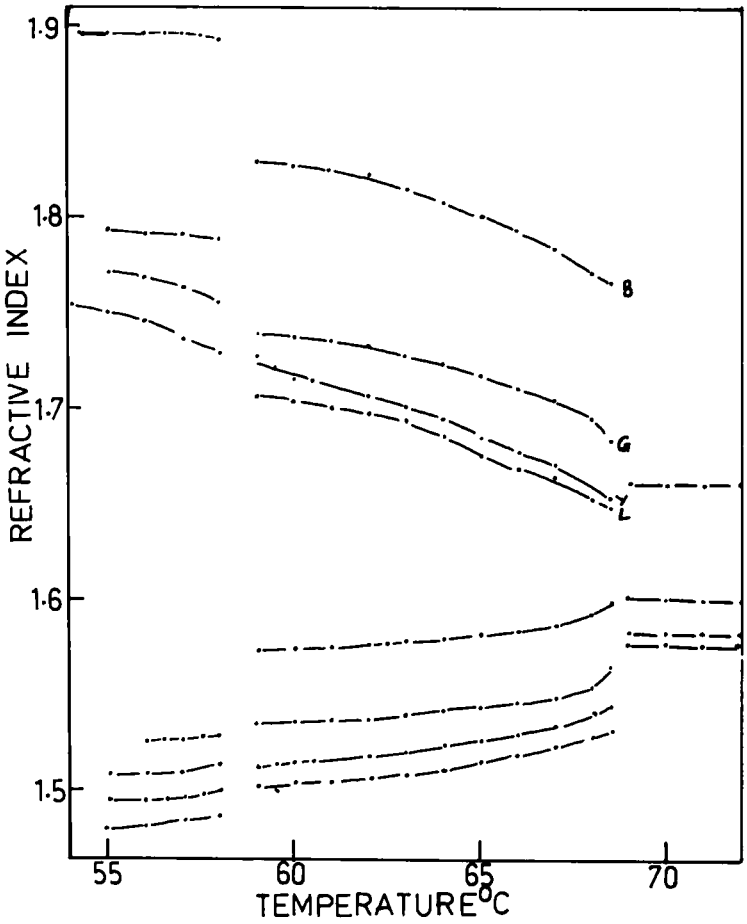


FIGURE 2 Refractive indices variation with temperature at different wavelengths of 60.2.

such motions increase with increasing temperature. Hence either a small or systematic decrease in optical anisotropy with increasing temperature is expected. However the two spheroidal models viz., deJeu-Bordewijk and Derzhanski-Petrov give increasing optical anisotropy with increasing temperature which is anomalous. On the otherhand the calculated refractive indices (Table VI) in the isotropic state from the molecular polarizabilities α_e and α_o in nematic phase give reasonable values which are in agreement with the observed isotropic refractive index or its extrapolated line in the nematic region. The Ibrahim-Haase model shows its superiority in optical anisotropy decrease with increasing temperature but fails in regard of

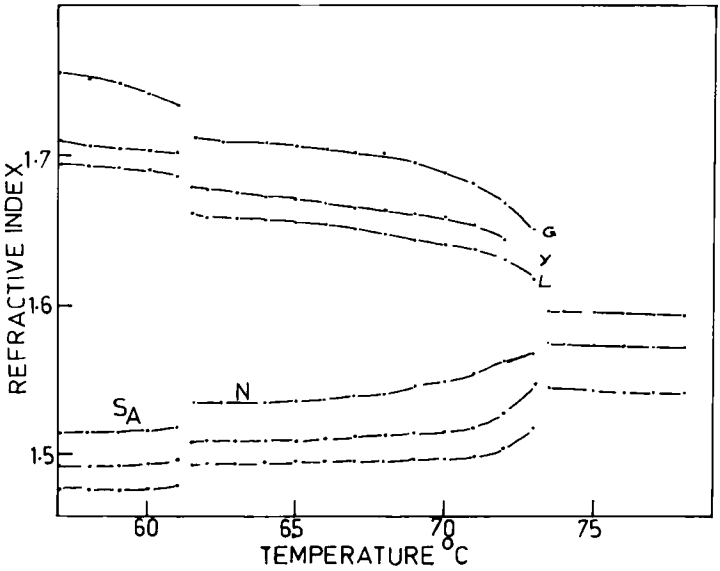


FIGURE 3 Refractive indices variation with temperature at different wavelengths of 70.1.

calculated isotropic refractive index to the observed experimental value.

With the exception of Vuks and Neugebauer the molecular polarizability anisotropies obtained are quite large. Further it is to be noted that Hauser et al.[6] reported lower α_e values than the real values due to oversight in the substitution of D_i values in equation 10 in their programming, the computed values of α_e in all the tables by Hauser et al. are less than the true values. This leads to different conclusions from that they made regarding molecular polarizability anisotropy.

The $\bar{\alpha}$ values obtained for the two molecules 60.2 and 70.1 from the three models are almost constant within the experimental errors. The exchange of one methylene unit from one end of the molecule to the other end cause little variation in $\bar{\alpha}$ value as is observed. The increment in methylene unit from the $\bar{\alpha}$ (at λ = 5893Å) values of 60.2 and 60.4 is found to be 1.9, 2.9 and 1.8 $\times$ 10^{-24} cm^3 from the deJeu-Bordewijk, Ibrahim-Haase and Derzhanski-Petrov models respectively.

In conclusion it may be mentioned that the superiority of any single model, out of the three spheroidal models, to prove is difficult. However all the three methods are realistic in approach. A reasonable test of such from these equations can be made only when the data is available in gaseous state of these liquid crystal molecules.

TABLE II

Molar volume and order parameter at different temperatures of the compounds 60.4, 60.2 and 70.1

60.4			60.2			70.1		
T°C	S	M_V	T°C	S	M_V	T°C	S	M_V
76.0	0.47	352.4	68.4	0.40	318.7	72.0	0.42	317.8
75.5	0.49	352.2	68.0	0.41	318.4	71.5	0.44	317.7
75.0	0.51	351.9	67.0	0.47	317.8	71.0	0.46	317.6
73.5	0.54	351.2	66.0	0.49	317.4	70.5	0.49	317.4
73.0	0.55	350.9	64.0	0.54	316.7	69.5	0.51	317.1
72.0	0.59	350.5	62.0	0.59	316.0	68.5	0.53	316.8
71.0	0.65	349.9	59.0	0.64	314.9	67.5	0.57	316.4
70.0	0.69	349.5				66.5	0.59	316.1
						65.5	0.62	315.7
						64.5	0.63	315.3
						63.5	0.63	315.0

TABLE III

Molecular Polarizabilities at different temperatures of 60.4

T°C	α_e					α_o					$\alpha_e-\alpha_o$					$\bar{\alpha}$				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
										BLUE										
75.0	64.5	64.3	101.7	81.6	85.9	43.3	44.1	36.4	43.1	36.5	21.2	20.2	65.3	38.5	49.4	50.3	50.8	58.1	55.9	52.9
73.5	64.8	64.7	100.7	81.7	84.1	43.1	43.9	36.7	43.3	37.1	21.7	20.8	64.0	38.4	47.0	50.3	50.8	58.0	56.1	52.7
73.0	65.1	65.1	100.3	82.0	83.6	42.9	43.7	36.7	43.3	37.3	22.2	21.5	63.6	38.7	46.3	50.3	50.8	57.9	56.2	52.7
72.0	65.4	65.6	99.4	82.2	82.1	42.7	43.4	36.9	43.5	36.9	22.7	22.2	62.5	38.7	45.3	50.2	50.8	57.7	56.4	51.9
71.0	65.4	65.8	96.8	82.1	78.4	42.6	43.3	37.6	43.9	39.2	22.8	22.5	59.2	38.2	39.2	50.2	50.8	57.3	56.6	52.2
70.0	65.7	66.4	95.6	82.5	76.6	42.3	43.1	37.9	44.0	39.8	23.3	23.3	57.7	38.5	36.8	50.1	50.8	57.1	56.8	52.0
										GREEN										
76.0	56.5	59.6	86.9	70.6	73.0	41.6	41.2	35.2	40.5	36.4	14.9	18.4	51.7	30.1	36.6	46.6	47.3	52.4	50.5	48.6
75.5	56.9	59.7	86.6	70.9	72.4	41.5	41.2	35.3	40.6	36.6	15.4	18.5	51.3	30.3	33.8	46.6	47.3	52.4	50.7	48.5
75.0	57.2	59.6	86.6	71.3	72.3	41.4	41.2	35.4	40.7	36.7	15.7	18.4	51.2	30.6	35.6	46.6	47.3	52.4	50.9	48.5
73.5	57.9	60.6	86.9	72.2	72.6	40.9	40.7	35.2	40.6	36.5	17.0	19.9	51.7	31.6	36.1	46.5	47.3	52.4	51.1	48.5
73.0	58.1	61.0	86.7	72.5	72.3	40.7	40.5	35.2	40.6	36.7	17.5	20.5	51.5	31.9	35.6	46.5	47.3	52.3	51.2	48.5
72.0	58.6	61.4	86.4	73.0	71.7	40.4	40.3	35.2	40.7	36.9	18.2	21.1	51.2	32.3	34.8	46.4	47.3	52.2	51.4	48.5
71.0	58.7	61.6	84.3	72.9	68.9	40.3	40.2	35.8	41.0	37.9	18.3	21.4	47.5	31.9	31.0	46.4	47.3	51.9	51.6	48.2
70.0	58.9	62.1	83.5	73.3	67.7	40.1	39.9	35.9	41.1	38.4	18.9	22.1	47.6	32.2	31.3	46.3	47.3	51.7	51.8	48.1

contd....

TABLE III (continued)

T°C	α_e					α_o					$\alpha_e - \alpha_o$					α				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
										YELLOW										
76.0	54.9	54.8	83.5	68.2	69.4	41.2	41.6	34.9	40.0	35.8	13.7	13.2	48.6	28.2	34.6	45.7	46.0	51.1	49.4	47.0
75.5	55.3	55.5	83.4	68.7	69.3	40.9	41.2	34.9	40.0	35.8	14.4	14.3	48.5	28.7	34.5	45.7	46.0	51.0	49.5	46.9
75.0	55.4	55.8	83.2	68.9	69.1	40.9	41.0	34.9	39.9	35.9	14.7	14.7	48.3	29.0	34.2	45.7	46.0	51.0	49.5	46.9
73.5	55.7	56.5	82.6	69.1	68.3	40.5	40.7	35.0	40.0	36.2	15.2	15.8	47.6	29.1	32.1	45.5	46.0	50.8	49.7	46.9
73.0	55.9	56.7	82.3	69.3	68.	40.4	40.5	35.0	40.1	36.4	15.5	16.2	47.3	29.2	32.5	45.5	46.0	50.7	49.8	47.2
72.0	56.2	56.7	81.7	69.6	66.9	40.2	40.6	35.3	40.2	36.8	15.9	16.2	46.4	29.4	30.1	45.5	46.0	50.7	50.0	46.8
71.0	56.5	57.3	80.4	69.9	65.2	40.0	40.3	35.5	40.4	37.4	16.5	17.0	44.9	29.5	27.8	45.5	46.0	50.4	50.2	46.6
70.0	56.7	57.7	79.6	70.3	64.1	39.9	40.0	35.7	40.5	37.9	16.8	17.6	43.9	30.8	26.2	45.5	46.0	50.3	50.4	46.6
										RED										
76.0	54.1	50.8	81.9	67.2	68.0	40.5	41.9	34.5	39.4	34.8	13.5	8.9	47.4	27.8	33.2	45.0	44.8	50.3	48.6	45.8
75.5	54.2	51.3	81.3	67.3	67.3	40.4	41.7	34.6	39.5	35.1	13.8	9.6	46.7	27.8	32.2	45.0	44.8	50.1	48.7	45.8
75.0	54.5	51.2	81.3	67.5	67.1	40.4	41.7	34.7	39.6	35.2	14.1	9.4	46.6	27.9	31.9	45.1	44.8	50.2	48.9	45.8
73.5	54.8	52.0	80.9	67.9	66.6	40.1	41.3	34.7	39.6	35.4	14.8	10.8	46.2	28.3	31.2	45.0	44.8	50.1	49.0	45.8
73.0	55.0	52.4	80.6	68.1	66.2	39.9	41.1	34.7	39.6	35.6	15.0	11.3	45.9	28.5	30.6	44.9	44.8	50.0	49.1	45.8
72.0	55.6	53.1	80.7	68.9	66.1	39.6	40.7	34.7	39.6	35.6	16.0	12.4	46.0	29.3	30.5	44.9	44.8	50.0	49.3	45.7
71.0	55.9	54.4	79.5	69.3	64.6	39.2	40.1	34.8	39.7	36.2	16.8	14.2	44.7	29.6	28.4	44.7	44.8	49.7	49.5	45.6
70.0	56.2	55.3	78.7	69.6	63.6	38.9	39.7	34.9	39.7	35.6	17.3	15.6	44.8	28.9	28.0	44.6	44.8	49.5	49.6	44.9

TABLE IV

Molecular Polarizabilities at different temperatures of 60.2

T°C	α_e					α_o					$\alpha_e - \alpha_o$					$\bar{\alpha}$				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
BLUE																				
68.4	56.2	57.1	91.1	70.8	78.4	41.4	41.6	33.9	39.5	33.8	14.8	15.5	57.2	31.3	44.6	46.3	46.8	52.9	49.9	48.6
68.0	57.4	58.5	93.3	72.7	82.0	40.9	40.9	33.1	39.0	32.6	16.7	17.5	60.2	33.7	49.4	46.4	46.8	53.1	50.2	49.0
67.0	57.9	59.2	91.3	72.7	78.6	40.3	40.6	33.6	39.5	33.8	17.6	18.6	57.7	33.2	44.8	46.2	46.8	52.8	50.5	48.7
66.0	58.7	59.4	91.7	73.6	78.9	40.0	40.4	33.6	39.5	33.7	18.7	19.0	58.1	34.1	45.2	46.2	46.8	52.9	50.8	48.7
64.0	59.8	59.9	91.5	74.7	77.9	39.5	40.2	33.7	39.8	34.0	20.3	19.6	57.8	34.9	43.9	46.3	46.8	52.9	51.4	48.6
62.0	61.0	60.2	91.4	75.9	77.0	39.0	40.0	33.9	40.1	34.3	21.9	20.2	57.5	35.8	42.7	46.3	36.8	53.0	52.0	48.5
59.0	61.4	61.3	90.0	76.3	74.9	38.6	39.5	34.1	40.3	35.1	22.9	21.8	55.9	36.0	39.8	46.2	46.8	52.7	52.3	48.3
GREEN																				
68.4	50.5	49.1	78.1	62.3	65.1	39.8	40.5	33.4	38.0	34.0	10.7	8.6	44.7	24.3	31.1	43.3	43.3	48.3	46.1	44.3
68.0	52.1	51.5	81.8	65.2	70.4	38.7	39.3	32.1	37.1	32.0	13.3	12.3	49.7	28.1	38.4	43.1	43.3	48.6	46.4	44.8
67.0	52.4	52.2	79.9	65.1	67.7	38.5	38.9	32.6	37.5	33.0	14.0	13.3	47.3	27.6	34.7	43.1	43.3	48.3	46.7	44.5
66.0	53.0	52.6	80.2	65.8	68.0	38.2	38.7	32.5	37.5	32.9	14.8	13.9	47.7	28.0	35.1	43.1	43.3	48.4	46.9	44.6
64.0	54.0	53.2	80.2	66.9	67.5	37.7	38.4	32.5	37.6	33.1	16.2	14.8	47.7	29.3	34.4	43.1	43.3	48.4	47.3	44.5
62.0	54.7	53.8	79.8	67.6	66.6	37.3	38.1	32.6	37.8	33.4	17.4	15.7	47.2	29.8	33.3	43.1	43.3	48.3	47.7	44.4
59.0	55.2	55.0	78.9	68.1	65.4	36.9	37.5	32.7	37.9	33.9	18.3	17.4	46.2	30.2	31.5	43.0	43.3	48.1	47.9	44.4

contd....

TABLE IV (continued)

T°C	α_e					α_o					$\alpha_e - \alpha_o$					$\bar{\alpha}$				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
										YELLOW										
68.4	48.5	49.0	74.0	59.6	61.8	38.8	38.9	32.8	37.0	33.7	9.7	10.1	41.2	22.6	28.1	42.0	42.2	46.5	44.5	43.0
68.0	48.9	50.1	74.5	60.2	62.7	38.5	38.3	32.5	36.8	33.4	10.4	11.7	42.0	23.4	29.3	41.9	42.2	46.5	44.6	43.1
67.0	50.3	51.2	75.7	62.2	64.0	37.7	37.7	32.1	36.6	32.8	12.7	13.5	43.6	25.6	31.2	41.9	42.2	46.6	45.1	43.2
66.0	51.0	52.2	76.3	63.1	64.8	37.2	37.3	31.8	36.5	32.5	13.7	14.9	44.5	26.6	32.3	41.8	42.2	46.6	45.3	43.2
64.0	52.4	52.5	77.4	64.9	65.7	36.6	37.1	31.6	36.6	32.2	15.8	15.5	45.8	28.3	33.5	41.8	42.2	46.8	46.0	43.3
62.0	53.2	53.4	77.1	65.7	65.1	36.1	36.6	31.6	36.7	32.4	17.1	16.8	45.5	29.0	32.7	41.8	42.2	46.7	46.3	43.3
										RED										
68.4	48.5	50.3	74.5	60.0	63.4	37.9	37.6	31.8	36.2	32.6	10.6	12.7	42.7	23.8	30.8	41.4	41.8	46.0	44.1	42.8
68.0	48.9	50.9	74.8	60.5	64.0	37.7	37.4	31.6	36.1	32.4	11.2	13.5	43.2	24.4	31.8	41.4	41.8	46.0	44.2	42.9
67.0	49.9	51.8	74.9	61.6	63.8	37.1	36.9	31.5	36.1	32.4	12.8	14.9	43.4	25.5	31.4	41.3	41.8	45.9	44.6	42.8
66.0	50.3	52.7	75.0	62.2	63.1	36.7	36.4	31.4	36.0	32.3	13.6	16.3	43.6	26.2	31.8	41.2	41.8	45.9	44.7	42.9
64.0	51.7	53.8	76.1	64.0	65.3	35.9	35.9	31.0	35.9	31.9	15.8	17.9	45.1	28.1	33.4	41.1	41.8	46.0	45.2	43.0
62.0	52.6	54.4	76.0	64.9	64.8	35.4	35.6	31.0	36.0	32.0	17.2	18.8	45.0	28.9	32.8	41.1	41.8	46.0	45.6	42.9
59.9	53.1	55.2	75.1	65.3	63.5	35.1	35.2	31.1	36.2	32.5	18.1	20.1	44.0	29.1	31.0	41.1	41.8	45.7	45.9	42.8

TABLE V

Molecular Polarizabilities at different temperatures of 70.1

T°C	α_e					α_o					$\alpha_e - \alpha_o$					$\bar{\alpha}$				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
										GREEN										
72.0	48.2	48.5	71.8	58.3	58.3	40.1	40.1	34.4	38.3	36.2	8.1	8.4	37.4	20.0	22.1	42.8	42.9	46.8	44.9	43.5
71.5	48.6	49.5	72.1	59.0	58.8	39.7	39.6	34.2	38.2	36.0	8.9	10.0	37.9	20.8	22.8	42.6	42.9	46.8	45.1	43.6
71.0	49.5	49.9	73.7	60.5	60.4	39.3	39.4	33.8	38.0	35.3	10.2	10.5	39.9	22.5	25.1	42.7	42.9	47.1	45.5	43.6
70.5	49.9	49.8	74.0	61.0	60.7	39.2	39.5	33.8	38.0	35.3	10.8	10.3	40.2	23.0	25.4	42.7	42.9	47.2	45.6	43.7
69.5	50.7	50.1	74.6	62.1	61.2	38.8	39.3	33.7	37.9	35.0	11.9	10.8	40.9	24.2	26.2	42.7	42.9	47.3	45.9	43.7
68.5	51.4	50.8	75.6	63.2	62.3	38.4	38.9	33.4	37.8	34.6	13.0	11.9	42.2	25.4	27.7	42.7	42.9	47.4	46.2	43.8
67.5	51.9	51.4	75.4	63.9	61.9	38.1	38.7	33.4	37.8	34.8	13.8	12.7	42.0	26.1	27.1	42.7	42.9	47.4	46.5	43.8
66.5	52.1	52.0	75.1	64.1	61.0	37.9	38.3	33.4	37.8	35.1	14.2	13.7	41.7	26.3	25.9	42.6	42.9	47.3	46.5	43.7
65.5	52.3	52.9	74.7	64.3	61.2	37.7	37.9	33.3	37.8	35.1	14.6	15.0	41.4	26.5	26.1	42.5	42.9	47.1	46.6	43.8
64.5	52.4	53.5	74.6	64.5	61.1	37.4	37.6	33.2	37.7	35.1	15.0	15.9	41.4	26.8	26.0	42.4	42.9	47.0	46.6	43.7
63.5	52.6	53.7	74.8	64.7	61.4	37.3	37.5	33.1	37.6	34.9	15.2	16.3	41.7	27.1	26.5	42.4	42.9	47.0	46.6	43.7
										YELLOW										
72.0	48.3	51.3	73.2	59.5	62.4	37.6	36.9	31.7	36.0	32.9	10.7	14.3	41.5	23.5	29.5	41.1	41.7	45.5	43.8	42.7
71.5	48.6	51.8	73.0	59.8	62.1	37.3	36.7	31.7	36.0	33.0	11.3	15.1	41.3	23.8	29.1	41.0	41.7	45.4	43.9	42.7
71.0	48.9	52.3	73.0	60.2	62.2	37.1	36.4	31.6	36.0	33.0	11.8	15.8	41.4	24.2	29.2	41.0	41.7	45.4	44.0	42.7
70.5	49.2	52.3	73.0	60.5	62.1	36.9	36.4	31.6	36.0	33.1	12.2	15.9	41.4	24.5	29.0	41.0	41.7	45.4	44.1	42.7
69.5	49.6	52.6	72.8	60.9	61.6	36.7	36.3	31.7	36.1	33.2	12.8	16.3	41.1	24.8	28.4	41.0	41.7	45.4	44.3	42.6

TABLE V (continued)

T°C	α_e					α_o					$\alpha_e - \alpha_o$					$\bar{\alpha}$				
	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P	V	N	D	I	P
YELLOW continued																				
68.5	49.8	53.0	72.6	61.2	61.4	36.6	36.1	31.7	36.1	33.3	13.2	16.8	40.9	25.1	28.1	41.0	41.7	45.3	44.4	42.6
67.5	50.0	53.2	71.8	61.2	60.2	36.4	36.0	31.9	36.2	33.8	13.5	17.3	39.9	25.0	26.4	40.9	41.7	45.2	44.5	42.6
66.5	50.1	53.4	71.4	61.4	59.7	36.3	35.9	32.0	36.3	34.0	13.8	17.5	39.4	25.1	25.7	40.9	41.7	45.1	44.6	42.5
65.5	50.2	53.5	71.0	61.5	59.1	36.2	35.8	32.1	36.4	34.2	14.0	17.7	38.9	25.1	24.9	40.8	41.7	45.0	44.7	42.5
64.5	50.3	53.8	70.8	61.7	58.9	36.1	35.7	32.1	36.4	34.3	14.2	18.2	38.7	25.3	24.6	40.8	41.7	45.0	44.8	42.5
63.5	50.4	54.1	71.0	61.8	59.2	36.0	35.5	32.0	36.3	34.2	14.4	18.5	39.0	25.5	25.0	40.8	41.7	45.0	44.8	42.5
RED																				
72.0	47.6	45.3	72.5	59.1	62.3	36.2	37.2	30.4	34.7	30.4	11.9	8.9	42.1	24.4	31.9	40.0	39.9	44.4	42.8	41.0
71.5	47.9	45.8	72.0	59.2	61.7	36.0	36.9	30.4	34.8	30.7	11.9	8.9	41.6	24.4	31.0	39.9	39.9	44.2	42.9	41.0
71.0	48.1	46.4	71.8	59.5	61.5	35.8	36.6	30.4	34.8	30.7	12.3	9.7	41.4	24.7	30.8	39.9	39.9	44.2	43.0	40.9
70.5	48.2	46.7	71.4	59.5	60.9	35.7	36.5	30.5	34.9	31.0	12.5	10.2	40.9	24.6	29.9	39.8	39.9	44.1	43.1	40.9
69.5	48.5	48.7	70.8	59.6	60.0	35.6	36.4	30.7	35.1	31.3	12.9	10.5	40.1	24.5	28.7	39.9	39.9	44.0	43.2	40.8
68.5	48.7	46.9	70.7	59.8	59.7	35.5	36.4	30.8	35.1	31.4	13.2	10.5	39.9	24.7	28.3	39.9	39.9	44.1	43.3	40.8
67.5	49.0	47.0	70.1	60.0	58.6	35.4	36.3	31.0	35.3	31.8	13.6	10.6	39.1	24.7	26.8	39.9	39.9	44.0	43.5	40.7
66.5	49.2	47.1	69.8	60.3	58.2	35.3	36.3	31.1	35.4	32.0	13.9	10.8	38.7	24.9	26.2	39.9	39.9	44.0	43.7	40.7
65.5	49.3	47.2	69.2	60.2	57.3	35.3	36.2	31.3	35.5	32.4	14.0	11.0	37.9	24.7	24.9	39.9	39.9	43.9	43.7	40.7
64.5	49.4	47.7	69.1	60.4	57.2	35.1	36.0	31.3	35.5	32.4	14.2	11.7	37.8	24.9	21.7	39.8	39.9	43.8	43.8	40.6
63.5	49.6	47.8	69.5	60.7	57.7	35.1	36.0	31.2	35.5	32.2	14.6	11.8	38.3	25.2	25.5	39.9	39.9	43.9	43.9	40.7

TABLE VI

Experimental and Calculated isotropic refractive index from de Jeu-Bordewijk (equation 7), Ibrahim-Haase (equation 9) and Derzhanski-Petrov (equation 11) models [60.4, yellow].

T°C	N_{iso} (Experimental)	N_{iso} (calculated) D	I	P
80.0	1.57	-	-	-
76.0	-	1.569	1.611	1.570
75.5	-	1.568	1.613	1.570
75.0	-	1.568	1.614	1.570
73.5	-	1.568	1.616	1.571
73.0	-	1.568	1.618	1.571
72.0	-	1.570	1.621	1.572
71.0	-	1.570	1.624	1.572
70.0	-	1.570	1.627	1.573

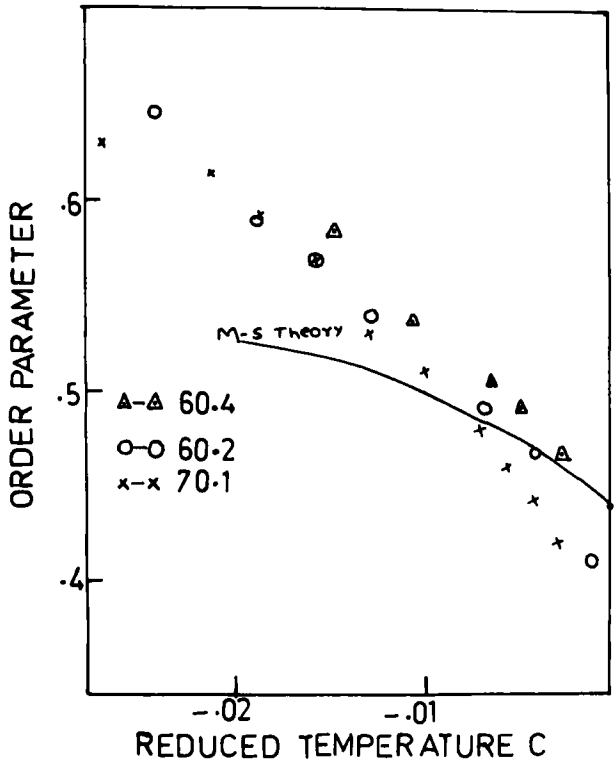


FIGURE 4 Variation of order parameter 'S' obtained from ESR with temperature. Solid line = Maier-Saupe theoretical graph.

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