PHYSICAL STUDIES OF
n-ALKYL-p-(4-ETHOXYBENZYLIDENE AMINO)-
α-METHYL CINNAMATES

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The applicability of modified Lippincott δ-function model (MlδP) method is tested in the case of liquid crystalline compounds exhibiting smectic A and nematic phases. Using the MlδP method the mean polarizabilities, polarizability anisotropies, mean diamagnetic susceptibilities and order parameters of n-alkyl-p-(4-ethoxybenzylidene amino)-α-methyl cinnamates are evaluated and compared with the reported data. A close agreement between the values estimated from the present method and the reported data confirms the applicability of MLδP method to the liquid crystals exhibiting smectic A and nematic phases.

I. INTRODUCTION

The studies on liquid crystals got enormous considerations not only because of their peculiar nature, but also because of their tremendous technological applications to which they are being used, chiefly among them being electro- optical digital displays and thermal sensors. 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 models [2-6] are dependent on them. Since molecular polarizabilities cannot be measured directly in the liquid crystalline state, different models are proposed to calculate them. Among these methods the modified Lippincott δ-function potential model (MLδP) method is found to be effective [7-10] for different types of liquid crystals and their mixtures. In the present investigation the applicability of this method is tested in the case of compounds exhibiting smectic A and nematic phases.

The homologous compounds selected for this study are n-alkyl-p-(4-ethoxyben-zylidene amino)-α-methyl cinnamates. These compounds have the chemical formula

$$C_2H_5O(C_6H_4)CH : N(C_6H_4)CH : C(CH_3)(COOR)$$

where R is the alkyl group $CH_3(CH_2)_n$ with n = 1 to 8. The transition temperatures of these compounds are given below.

1. Ethyl ester   (n = 1) T_{SN} = 94.0°C, T_{NI} = 123.0°C
2. Propyl ester   (n = 2) T_{SN} = 90.9°C, T_{NI} = 121.8°C
3. Butyl ester   (n = 3) T_{SN} = 86.0°C, T_{NI} = 100.6°C
4. Amyl ester   (n = 4) T_{SN} = 84.2°C, T_{NI} = 100.5°C
5. Hexyl ester   (n = 5) T_{SN} = 83.0°C, T_{NI} = 91.2°C
6. Heptyl ester   (n = 6) T_{SN} = 82.3°C, T_{NI} = 90.2°C
7. Octyl ester   (n = 7) T_{SN} = 81.8°C, T_{NI} = 85.3°C
8. Nonyl ester   (n = 8) T_{SN} = 82.4°C, T_{NI} = 85.0°C

II. METHOD

1. ESTIMATION OF MEAN POLARIZABILITY

The MLδP method has been used to estimate the mean polarizability in terms of the parallel bond component ($\sum \bar{\alpha}_{\|p}$), the perpendicular bond component ($\sum \bar{\alpha}_\perp$) and the non-bond region electron contribution ($\sum \bar{\alpha}_{\|n}$). The expression for the mean polarizability is given as

$$\alpha_1 = \frac{1}{3}\left(\sum \bar{\alpha}_{\|p} + \sum \bar{\alpha}_{\|n} + 2\sum \bar{\alpha}_\perp\right)$$ (1)

where the parallel bond component is given as

$$\sum \bar{\alpha}_{\|p} = \frac{4nA[exp(T-T_c)/T_c]}{a_o}\left[\frac{R^2}{4}+\frac{1}{2C_R^2}\right]^2 exp\left\{-\left(\frac{X_A-X_B}{4}\right)^2\right\}.$$ (2)

Here n is the bond order, A the δ - function strength, R the bond length, X_A, X_B are Pauling's electronegativities for the atoms A and B in the bond A − B, a_o is the radius of the first Bohr orbit of the atomic hydrogen, and C_R is the geometric mean molecular δ-function strength. The expression for the non-bond region electron contribution is given as

$$\sum \bar{\alpha}_{\|n} = \sum f_j \alpha_j.$$ (3)

Here f_j is the fraction of the non-bonded electrons of the jth atom and α_j is its atomic polarizability. The perpendicular bond component is given by the expres-

$$\sum 2\bar{\alpha}_\perp = n_{df}\frac{\sum x_j^2 \alpha_j}{\sum x_j^2}.$$ (4)

Here n_{df} is the number of degrees of freedom given by $n_{df} = 3N - 2n_b$; N is the number of atoms and n_b is the number of the bonds in the liquid crystals. The mean polarizability in liquid crystalline phase can be expressed as

$$\alpha = \alpha_1[1-\frac{m}{\rho_1}(T-T_c)].$$ (5)

Here m is the slope of the ρ versus T curve. T_c is the transition temperature, ρ_1 is the density in liquid phase and α is the mean polarizability in liquid crystalline phase. Details of derivation of eqn. (5) are discussed in the author's previous paper [7].

The necessary data on bond lengths are taken from reference [11]. The density data and transition temperatures for the system are taken from reference [12].

2. ESTIMATION OF MOLECULAR POLARIZABILITY ANISOTROPY

As it is well known, we need a molecular polarizability ellipsoid rather than the average polarizability to study the directional properties of the anisotropic crystals. In the calculation of the polarizability $\alpha_\|$ we take the molecular axis along the line joining the centres of the two benzene rings and assume the molecule to be rigid. The polarizability contribution parallel to the molecular axis of the polarizability ellipsoid of a polyatomic molecule is given by

$$\alpha_\| = \sum \bar{\alpha}_\| \cos^2\theta + \sum \alpha_\perp \sin^2\theta$$ (6)

(summed over all bonds) where θ is the angle between a bond and the molecular axis, $\bar{\alpha}_\|$ and $\bar{\alpha}_\perp$ are the parallel bond component and the perpendicular bond component of the polarizability.

In the absence of the conformed molecular structures of many of these substances, for the sake of uniformity and simplicity the bond angles are assumed to be 109°, for the bonds involving tetrahedral linkage and in all other cases as 120°. Standard values of bond lengths are assumed and the angle between the various bonds and the molecular axis were determined by drawing a figure of the molecule.

Using the value $\alpha_\|$ obtained eqn. (6) the molecular polarizability anisotropy can be calculated as

$$(\alpha_\| - \alpha_\perp) = \frac{3}{2}(\alpha_\| - \alpha)$$ (7)

where α is the mean polarizability obtained from the MLδP method. The $\alpha_\perp$ can be calculated as

$$\alpha_\perp = \alpha - \frac{1}{3}(\alpha_\| - \alpha_\perp).$$ (8)

From the polarizability anisotropy $\alpha_\parallel - \alpha_\perp$, the scaling factor $\alpha'/(\alpha_\parallel - \alpha_\perp)$ can also be estimated from this MLδP method.

3. ESTIMATION OF MEAN DIAMAGNETIC SUSCEPTIBILITY

The relation between diamagnetic susceptibility and mean polarizability is given as

$$-\chi = (\gamma m \sigma') \alpha \qquad (9)$$

where $\gamma = (0.9)^n$ gives the saturation state of the molecule with n denoting the number of unsaturated bonds and rings in the molecule; σ' is the degree of covalency of the characteristic group and is given as

$$\sigma' = [\sigma_1^{1/n_1} \cdot \sigma_2^{1/n_2} \cdot \ldots \cdot \sigma_p^{1/n_p}]^{1/2} \qquad (10)$$

where $\sigma_1, \sigma_2, \ldots, \sigma_p$ are Pauling's percentage of covalence characters of the bonds present in the characteristic group; $n_1, n_2, \ldots, n_p$ are the bond orders of the various bonds in the characteristic group, m is a constant which is equal to 0.72×10^{19}. The values of $\sigma_1, \sigma_2, \ldots$ are taken from reference [13].

4. ESTIMATION OF ORDER PARAMETER

The orientation order parameer S is defined as

$$S = \frac{1}{2}\{3\langle\cos^2\theta\rangle - 1\} \qquad (11)$$

where θ is the angle made by the long molecular axis with the preferred direction and the brackets denote an average over the molecules in a microscopic volume.

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium and the orientational order of the polarization field of nematic liquid crystals. For calculations of the polarizabilities of the molecules and of the order parameter S from birefringence data, the Lorentz-Lorentz formula cannot be employed because its validity is restricted to cases where there is spherical (or cubic) symmetry in connection with the molecular arrangement. According to the Vuks formula [14] the ratio of the average local electric field to the applied field is the same for the two cases when the applied field is (i) parallel and (ii) perpendicular to the optic axis of the medium. Neugebauer [15,16] has considered in detail the form of the polarization field in anisotropic media. In a nematic medium, as a result of the anisotropic distribution of the molecules, the average local electric field is of the form $E + \gamma p$ where E is the applied field, p the polarization and γ is a factor which is different from the directions parallel and perpendicular to the optic axis.

In the present study the order parameters of homologous series of n-alkyl-p-(4-ethoxybenzylidene amino)-α-methyl cinnamates have been evaluated by using the

isotropic internal field model of Vuks [17] and the anisotropic internal field model of Neugebauer [16]. In the Vuks method the order parameter is given by [18]

$$S = \frac{\alpha}{(\alpha_\parallel - \alpha_\perp)} \cdot \frac{n_e^2 - n_o^2}{n^2 - 1} \qquad (12)$$

where $n^2 = (n_e^2 + 2n_o^2)/3$. α is the mean polarizability $\alpha_\parallel$ and $\alpha_\perp$ are the principal polarizabilities in directions parallel and perpendicular to the optic axis. In the Neugebauer method the order parameter is given by [18]

$$S = \left[\frac{\alpha}{(\alpha_\parallel - \alpha_\perp)}\right] f(B) \qquad (13)$$

where

$$f(B) = \frac{9}{4B}\left[B^2 - \frac{10}{3}(B+1)^{1/2} + \frac{B}{3} - 1\right]$$

and

$$B = \frac{n^2 - 1}{n^2 + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2\,n_o^2 + 2}{n_o^2 - 1}\right].$$

III. RESULTS AND DISCUSSION

The mean polarizabilities and polarizability anisotropies of the above homologous series of liquid crystals are presented in Table 1 and 2 along with the reported values [19].

Table 1

Polarizabilities (× 10^{24}cm^3) of n-alkyl-(4-ethoxybenzylidene amino) -α-methyl cinnamates

n	$\sum \bar{\alpha}_{\parallel p}$	$\sum \bar{\alpha}_{\parallel n}$	$\sum 2\bar{\alpha}_\perp$	α Present method	α Reported values
1	86.19	1.28	43.36	43.42	43.0
2	90.62	1.28	45.21	45.41	44.9
3	94.51	1.28	47.19	47.10	46.7
4	97.62	1.28	49.01	48.96	48.6
5	100.13	1.28	51.42	50.62	50.4
6	103.11	1.28	53.12	52.21	52.3
7	105.26	1.28	55.26	53.81	54.1
8	107.43	1.28	57.51	55.11	55.9

Table 2

Polarizability anisotropy (× 10^{24} cm^3) of n-alkyl-p-(4-ethoxybenzylidene amino)-α-methyl cinnamates

n	$\Delta\alpha = \alpha_\parallel - \alpha_\perp$		$[\alpha/(\alpha_\parallel - \alpha_\perp)]$
	Present method	Reported values	
1	25.12	25.00	1.73
2	25.23	25.10	1.80
3	25.39	25.80	1.85
4	25.21	25.10	1.94
5	25.06	24.60	2.02
6	24.91	24.10	2.09
7	24.76	24.30	2.17
8	24.53	24.20	2.25

Table 3

Mean diamagnetic susceptibilities (× 10^5 CGS units) of n-alkyl-p-(4-ethoxybenzylidene amino)-α-methyl cinnamates

n	$-\chi$	
	Present method	Pascal method
1	18.43	18.56
2	19.51	19.62
3	20.49	20.51
4	21.60	21.58
5	22.61	22.54
7	23.52	23.68
8	24.48	24.92

The mean diamagnetic susceptibilities of the liquid crystals are presented in Table 3 along with the values determined by using the Pascal method [20 - 22]. The variation of the order parameter with temperature is presented in Fig. 1. Examination of the results presented in Tables 1, 2 and 3 indicates a close agree-
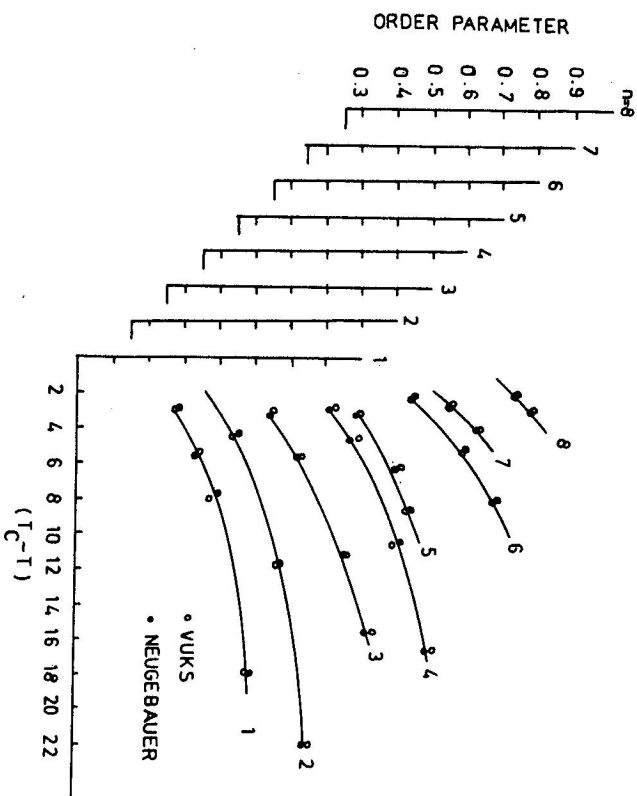

Fig. 1. The variation of order parameter with temperature of n-alkyl-p-(4- ethoxybenzylidene amino)-α-methyl cinnamates.

ment between the values estimated from the present method and the reported data. This confirms the applicability of the MLδP method to the liquid crystals exhibiting Smectic A and nematic phases. From Table 2, it is found that the values of polarizability anisotropy of all the members of the homologous series are nearly equal. This may be explained on the fact that a major portion of the polarizability anisotropy arises from the central rigid portion common to all the molecules and the polarizability anisotropy arising from the end groups is relatively small owing to their assumed conformations. It is also observed that, with increasing number of methylenes in the alkyl chain, the value of $\alpha/(\alpha_\parallel - \alpha_\perp)$ increases with further increase in the number of carbon atoms. This is due to the monotonic increase in α, and the almost constancy of $\alpha_\parallel - \alpha_\perp$ with increasing number of carbon atoms. It may be pointed out here that essentially similar features have been observed by Hanson and Shen [23] in their studies with homologous of p,p'-di-n-alkoxy-azoxy benzenes.

Acknowledgement

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