# PHYSICAL STUDIES OF HOMOLOGOUS
Di-n-ALKYL-4,4'-AZOXY-α- METHYL CINNAMATES

RANGA REDDY, R. N. V.[)], MURTHY, V. R.[)], Anantapur

The mean polarizabilities of homologous series of liquid crystals of di-n-alkyl4,4'- -azoxy-α-methyl cinnamates are evaluated by using the Modified Lippincott-δ- -Function Potential (MLδP) method. From these polarizabilities the mean diamag- netic susceptibilities of the liquid crystals are calculated. The anisotropy of molecular polarizability of these mesogens is also estimated. The orientational order parameters of these compounds are also evaluated using the Vuks and the Neugebauer methods. The variation of the order parameter with temperature is discussed.

I. INTRODUCTION

It is very well established that the order parameter of liquid crystals governs most of its physical properties [1—3]. It is possible to describe the order parameter by any one of the tensorial properties [3—5]. In the present paper the refractive index has been selected as a macroscopic property to represent the degree of ordering. Most of the practical applications of liquid crystals utilize the optical anisotropy of liquid crystals. The temperature dependence of the order parameter gives us an idea of the nematic phase. The physical behaviour of liquid crystals is remarkably subtle and is strongly influenced by the mole- cular structure and the contents of the mesogenic molecules. Polarizability studies are quite helpful in gaining a good understanding of the molecular and structural characteristics and their influence on the physical properties of mesogenic materials. In the present communication, we report the mean pola- rizabilities for the homologous series of di-n-alkyl 4,4'-azoxy-α-methyl cinnama- tes

$$C_nH_{2n+1}OOCC(CH_3)CHC_6H_4 = N-C_6H_4CHC(CH_3)COOC_nH_{2n+1}$$
$$\downarrow$$
$$O$$
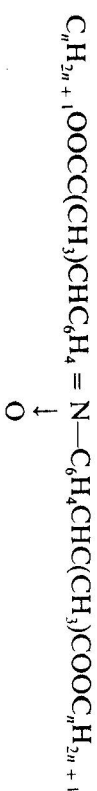
for $n = 4$ to 9 by using the modified Lippincott-δ-function potential method [6—11]. The mean diamagnetic susceptibilities of these compounds are eva-

[)] Department of Physics, Sri Krishnadevaraya University, ANANTAPUR 515003, INDIA.

luated from the polarizability data [8—11]. The molecular polarizability anisotropies of these liquid crystals are also estimated. The orientational order parameters of this homologous series are also evaluated using the Vuks and the Neugebauer methods.

II. METHOD

(i) Calculation of mean polarizability

The Lippincott-δ-function potential method is successfully applied for the evaluation of polarizabilities of simple and macro molecules by Murthy et al. [12—14]. But in the case of liquid crystals the method needs some modification due to the following reasons. In the crystalline state, there will be only pure brownian field alone acts on the condensed system, whereas in the liquid phase, both these fields will be acting. The resultant effect due to these fields is to decrease the potential on the electrons. In other words the shielding on the electrons will be less, thus contributing to more polarization. The behaviour is expressed empirically by the equation

$$A_{LC} = A \exp\left[\frac{T \sim T_c}{T_c}\right],$$ (1)

where T is the temperature pertaining to the study of the liquid crystal property and T_c is the liquid crystalline transition temperature. A and A_{LC} are the δ-function strengths in liquid and liquid crystalline phases.

Now the modified expressions for the parallel bond component ($\Sigma\bar{\alpha}_{\|p}$), the perpendicular bond component ($\Sigma\bar{\alpha}_\perp$) and the non-bond region electron contribution ($\Sigma\bar{\alpha}_{\|n}$) can be written as

$$\alpha_i = \frac{1}{3}(\Sigma\bar{\alpha}_{\|p} + \Sigma\bar{\alpha}_{\|n} + \Sigma 2\bar{\alpha}_\perp),$$ (2)

where

$$\Sigma\bar{\alpha}_{\|p} = \frac{4nA[\exp(T - T_c)/T_c]}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_R^2}\right]^2 \exp\left[-\left[\frac{(X_A - X_B)^2}{4}\right]\right].$$ (3)

Here n is the bond order, A the one-electron δ-function strength, a_0 is the radius of the first Bohr orbit of the atomic hydrogen, R the bond length, C_R is the geometric mean molecular δ-function strength, X_A, X_B are Pauling's electronegativities for the atoms A and B in the bond $A—B$,

$$\Sigma\bar{\alpha}_{\|n} = \Sigma f_j \alpha_j,$$ (4)

where $Y = (0.9)^n$ gives the saturation state of the molecule with n denoting the

Table 1
Polarizabilities ($\times 10^{24}$ cm³) of di-n-alkyl 4,4'-azoxy-α-Methyl cinnamates

(R)	$\Sigma\bar{\alpha}_{\|p}$	$\Sigma\bar{\alpha}_n$	$\Sigma 2\bar{\alpha}_\perp$	α Present method	α Refractivity method
Butyl	112.46	1.97	52.84	55.72	56.87
Amyl	121.16	1.97	57.36	60.13	60.89
Hexyl	129.86	1.97	61.89	64.54	64.57
Heptyl	138.56	1.97	66.41	68.97	69.21
Octyl	147.25	1.97	70.93	73.36	74.12
Nonyl	155.95	1.97	75.45	77.71	78.42

where f_j is the fraction of the non-bonded electrons of the jth atom and α_j is its atomic polarizability.

$$\Sigma 2\bar{\alpha}_\perp = n_{df}\left[\frac{\Sigma x^2 \alpha}{\Sigma x^2}\right],$$ (5)

where 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 bonds in the liquid crystals.

$$\alpha = \alpha_l\left[1 - \frac{m}{\varrho_l}(T - T_l)\right],$$ (6)

where m is the slope of the ϱ versus the t curve, T_l is the transition temperature, ϱ_l is the density in the liquid phase and α is the mean polarizability in the liquid crystalline phase. Details of the derivation of Eq. (6) are discussed in our previous paper [6].

The necessary data on bond lengths are taken from Ref. [15]. The transition temperatures of this systems are taken from Ref. [16]. The mean polarizabilities of the liquid crystals calculated using Eq. (6) are presented in Table 1 along with the values estimated from the refractivity method [7] using the refractive indices data of Ref. [16].

(ii) Calculation of diamagnetic susceptibility

The semi-empirical relation between the diamagnetic susceptibility and mean polarizability of liquid crystals is given as [8—11]

$$-\chi = (Ym\sigma')\alpha,$$ (7)

Table II

Diamagnetic Susceptibilities ($\times 10^5$ CGS units) of Di-n-Alkyl 4,4'-azoxy-α-Methyl cinnamates

(R)	χ	
	Present method	Pascal's method
Butyl	28.15	27.98
Amyl	30.38	30.36
Hexyl	32.71	32.68
Heptyl	34.95	35.05
Octyl	37.18	37.42
Nonyl	39.41	39.80

number of unsaturated bonds and rings in the molecule; σ' is the degree of covalency of the characteristic group and is given as

$$\sigma' = (\sigma_1^{1/n_1} \sigma_2^{1/n_2} \dots \sigma_p^{1/n_p})^{1/2}, \qquad (8)$$

where $\sigma_1, \sigma_2 \dots \sigma_p$ are Pauling's percentage of covalence characters of the bonds present in the characteristic group, $n_1, n_2 \dots n_p$ are the bond orders of the various bonds on the characteristic group; m is a constant which is equal to 0.72×10^{19}. The values of σ_i are taken from Ref. [18].

The mean diamagnetic susceptibilities of these mesogens calculated from Eq. (7) are presented in Table II along with the values estimated from the Pascal method [19, 20].

(iii) Calculation of the 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 $\alpha_\parallel$ 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

$$\alpha_\parallel = \Sigma \bar{\alpha}_\parallel \cos^2 \Theta + \Sigma \alpha_\perp \sin^2 \Theta \qquad (9)$$

(summed over all bonds), where Θ is the angle between a bond and the molecular axis, $\bar{\alpha}_\parallel$ 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 angles

between the various bonds and the molecular axis were determined by drawing a figure of the molecule (Fig. 1).

Using the value $\alpha_\parallel$ obtained from Eq. (9) the molecular polarizability anisotropy can be calculated as

$$(\alpha_\parallel - \alpha_\perp) = \frac{3}{2}(\alpha_\parallel - \alpha), \qquad (10)$$

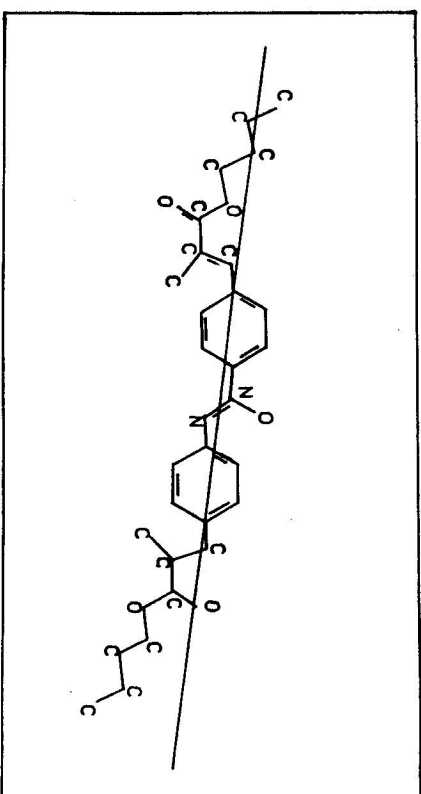where α is the mean polarizability obtained from the MLδP method.

Fig. 1. The shape of the molecule di-n-butyl 4,4'-azoxy-α-methyl cinnamate.

The $\alpha_\perp$ can be calculated as

$$\alpha_\perp = \alpha - \frac{1}{3}(\alpha_\parallel - \alpha_\perp). \qquad (11)$$

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

(iv) Calculation of the order parameter

The orientation order parameter S is defined as

$$S = \frac{3}{2}\langle \cos^2 \Theta \rangle - \frac{1}{2}, \qquad (12)$$

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 macroscopic volume.

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium and the orientational order parameter S determine the birefringence of nematic liquid crystals. For calculations of the polarizabilities of the molecules and of the order parameter S from birefringence data, the Lorenz–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 [21] the ratio of the average local electric field to the applied field is the same for the two cases when the applied fields is (i) parallel and (ii) perpendicular to the optic axis of the medium. Neugebauer [22, 23] 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 $E + YP$, where E is the applied field, P the polarization, and Y is a factor which is different from the directions parallel and perpendicular to the optic axis.

In the present study the order parameters of the homologous series of di-n-alkyl 4,4′-azoxy-α-methyl cinnamates have been evaluated, both the isotropic internal field model of Vuks [24], and the anisotropic internal model of Neugebauer [22] are compared. In the Vuks method the order parameter is given by [25]

$$S = \left[\frac{a}{a_\parallel - a_\perp} \right] \left[\frac{n_e^2 - n_0^2}{n^2 - 1} \right],$$

where $n^2 = 1/3\,(n_e^2 + 2n_0^2)$. a is the mean polarizability, $a_\parallel$ and $a_\perp$ are the principal polarizabilities in directions parallel and perpendicular to the optic axis. The scaling factor $(a/a_\parallel - a_\perp)$ can be determined from a plot of

$$\log[n_e^2 - n_0^2/n^2 - 1] \text{ versus } \log[1 - T/T_c].$$

Using this scaling factor and mean polarizability obtained from the refractivity method we can also estimate $a_\parallel$, $a_\perp$ and the anisotropy $(a_\parallel - a_\perp)$.

In the Neugebauer method, the order parameter is given by [25]

$$S = \left[\frac{a}{a_\parallel - a_\perp} \right] \cdot f(B),$$

where

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

and

$$B = \frac{n^2 - 1}{n^2 + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_0^2 + 2}{n_0^2 - 1} \right].$$

(13)

(14)

Table III

Anisotropy of the molecular polarizability for homologous Di-n-alkyl 4,4′-azoxy-α-Methyl cinnamates in units of 10^{24} cm³

(R)	$(a_\parallel - a_\perp)$*	$(a_\parallel - a_\perp)_V$**	$(a_\parallel - a_\perp)_N$***
Butyl	40.0	41.9	33.4
Amyl	43.4	45.9	36.7
Hexyl	45.2	46.2	37.2
Heptyl	48.4	48.5	39.0
Octyl	50.3	49.1	40.0
Nonyl	53.7	51.6	40.2

* Obtained from the present method
** Obtained from using the isotropic model of Vuks
*** Obtained from using the anisotropic model of Neugebauer.

Table IV

Principal Molecular Polarizabilities for Homologous Di-n-alkyl 4,4′-azoxy-α-Methyl cinnamates in units of 10^{24} cm³

(R)	$a_\parallel$	$a_\perp$	$(a_\parallel)_V$	$(a_\perp)_V$	$(a_\parallel)_N$	$(a_\perp)_N$
Butyl	82.4	42.4	84.8	42.9	79.2	45.7
Amyl	89.0	45.7	91.5	45.6	85.3	48.7
Hexyl	94.6	49.5	95.5	49.3	89.5	52.3
Heptyl	101.3	52.8	101.6	53.0	95.2	56.2
Octyl	106.8	56.6	106.9	57.8	100.8	60.8
Nonyl	113.5	59.8	112.8	61.2	105.6	64.9

The scaling factor in this method can be determined by plotting $\log f(B)$ as a function of $\log(1 - T/T_c)$. Using this scaling factor and mean polarizability obtained from the refractivity method we can estimate $a_\parallel$, $a_\perp$ and the anisotropy $(a_\parallel - a_\perp)$.

The molecular anisotropies and the principal molecular polarizabilities obtained from the extrapolation procedures mentioned above as well as those calculated from the present method are given in Tables III and IV.

III RESULTS AND DISCUSSION

From Table I, it is clear that the mean polarizability values calculated by the MLδP method agree well with the values obtained by the refractivity method. Similarly the mean diamagnetic susceptibility presented in Table II agree well with the one estimated from the Pascal method. As seen in Table III, the

$(\alpha_\perp - \alpha_\perp)$ values calculated using the present method are in better agreement with the $(\alpha_\parallel - \alpha_\perp)_I$ values than with the $(\alpha_\parallel - \alpha_\perp)_N$ values, which is consistent with the studies of Van Hecke [26].

Though the Vuks and the Neugebauer methods are known to give different values for the polarizability anisotropy, the former has an edge on the latter. Haller et al. [27] concluded that the assumptions involved in the Vuks method are more sound than those in the Neugebauer method. Blinov et al. [28] who measured the dichroism of dye molecules in a nematic solvent found that their results are consistent with an isotropic local field, thus further supporting the Vuks assumption. The validity of the Vuks model has also been checked by Pines et al. [29] by measuring the NMR chemical shifts of ^{13}C spectra from which the order parameter can be deduced. All these facts support the reliability of the present results.
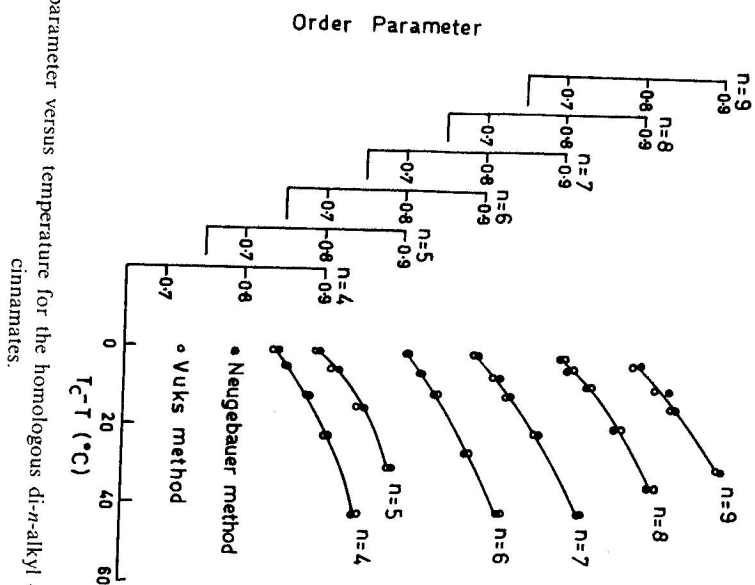
Order Parameter

Fig. 2. Order parameter versus temperature for the homologous di-n-alkyl 4,4'-azoxy-α-methyl cinnamates.

The variation of the order parameter with temperature is shown in Fig. 2. Relatively high values in the order parameter may be attributed to the error in the estimation of the scaling factor in the extrapolation procedure. Here however the scaling procedure suggested by Haller [30] has been adopted,

which relies on the plausible assumption that if a liquid crystal could be cooled to zero without undergoing any phase transitions, S would become equal to unity. While such a long-range extrapolation can never be entirely convincing, we estimate that the intercept on the vertical axis is determined within 0.04, an uncertainty of 10% in scaling the order parameter.

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ФИЗИЧЕСКОЕ ИССЛЕДОВАНИЯ ТИПОВЫХ di-n-ALKYL-4,4'-AZOXY-α-ЦИННАМЯТОВ МЕТИЛА

В работе приводится оценка средней поляризуемости типового ряда жидких кристаллов di-n-alkyl-4,4'-azoxy-α-циннаматов метила с применением MLSP метода. С поляризуемостей вычислены средние диамагнитные проницаемости жидких кристаллов. С поляризуемостей молекулярная поляризуемость анизотропии показаных мезогенов. Тоже оценена молекулярная поляризуемость анизотропии показаных мезогенов. С применением метода Вукс—Нойгебацера оценены также параметры порядка выстросности. Обсуждаются параметра порядка с температурой.