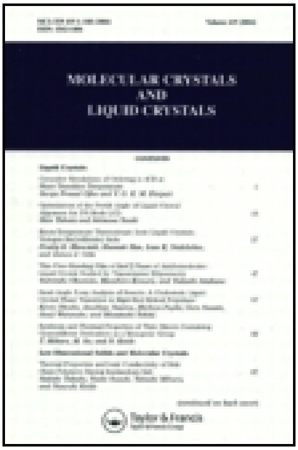

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Polarizabilities of a Few Nematic Liquid Crystals

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Polarizabilities of a Few Nematic Liquid Crystals†

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The parallel, perpendicular and the mean polarizabilities of two series of nematogenic homologous series have been evaluated using modified method of Lippincot-δ-function potential model. The results are discussed in relation to reported values. The fair agreement between calculated and reported value of α lends support to the applicability of Lippincot-δ-function model to liquid crystals.

INTRODUCTION

The liquid crystals play a considerably important role partly because of their applications in display technology. The study of their optical properties such as circular dichroism, optical rotatory power and polarizabilities have gained much momentum and recent articles of Lebodov *et al.*[1] and Chandrasekhar[2] give an account of the same. The polarizability is particularly useful in the sense that it gives an estimate of order parameter and helical content. The importance of polarizability to stereo-chemical problems of simple molecules has long been established and its application to conformation of biopolymers has been worked out recently by Rao *et al*,[3] Murthy *et al.*[4,5] The present investigation deals with the evaluation of polarizability of two series of nematogenic homologous series of *p,p'*-di-*n*-alkoxy-azoxy benzenes and *p*-((*p*-alkoxy phenyl)azo)phenyl esters by a method based on Lippincot-δ-function potential model. The polarizability and its anisotropic behaviour of this series of liquid crystals have been worked out theoretically by

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Sashidhar Prasad[6] starting from the concept of additivity of bond polarizabilities. But a survey of literature seems to suggest that Lippincot-δ-function potential model has not been used for evaluation of polarizability of liquid crystals, though its application to simple and macromolecules is made by several investigators.[7,8] Hence the utility of Lippincot-δ-function potential model for the evaluation of polarizability of these liquid crystals is attempted successfully in this present investigation.

THE METHOD

Lippincot-δ-function potential model is based on the Quantum mechanical approach to the study of eigen state of the system and polarizability forms one of the fine criterion for testing suitability of such wave functions. It gives an easy and fair reliability for the polarizability determination.

Relevant equations to calculate the mean polarizability α in terms of the parallel bond component ($\Sigma\alpha_{\parallel p}$), perpendicular bond contribution ($\Sigma 2\alpha_{\perp}$) and non-bond region electron contribution ($\Sigma\alpha_{\parallel n}$) are given as [Eq. (1) to Eq. (4)]

$$\alpha = \tfrac{1}{3}[\Sigma\alpha_{\parallel p} + \Sigma\alpha_{\parallel n} + \Sigma 2\alpha_{\perp}] \tag{1}$$

where

$$\alpha_{\parallel p} = \frac{4nA}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_R^2}\right]^2 \exp\left[-\frac{(x_1 - x_2)^2}{4}\right] \tag{2}$$

Here n is the bond order, A, the δ-function strength or reduced Electronegativity, R, the bond length, X_1 and X_2, the Pauling's electronegativities of atoms A and B in the bond A—B. The values of delta function strengths A's and C_R's for various bonds are taken from Refs. (9) and (10).

$$\Sigma\alpha_{\parallel n} = \Sigma f_j \alpha_j \tag{3}$$

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

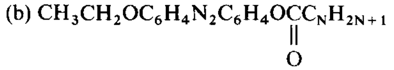
$$\Sigma 2\alpha_{\perp} = n_{df}\left[\frac{\Sigma x_j^2 \alpha_j}{\Sigma x_j^2}\right] \tag{4}$$

Here n_{df} is the number of degrees of freedom given by the equation $n_{df} = 3N\text{-}2n_b/N$ where N is the number of atoms and n_b is the number of bonds in the liquid crystal. n_{df} for phenyl ring is taken as 19.

The bond lengths are taken from the *Handbook of Physics and Chemistry*, Rubber publishing Company Edition, 1979. The values of $\Sigma\alpha_{\parallel p}$, $\Sigma\alpha_{\parallel n}$, $\Sigma 2\alpha_{\perp}$ and α are presented in Table I along with the reported values of α (Refs. 6).

TABLE I

Polarizabilities (X 10^{24} cm^3) of (a) $C_NH_{2N+1}OC_6H_4N_2OC_6H_4OC_NH_{2N+1}$

N	$\Sigma\alpha_{\parallel p}$	$\Sigma\alpha_{\parallel n}$	$\Sigma 2\alpha_{\perp}$	$m \times 10^3$	T_c°C	α calc.	α Exptl.	α Prasad.
5	94.27	1.43	51.16	1.12	120	48.96	49.50	47.367
6	105.58	1.43	55.68	8.48	127	54.23	51.00	51.053
7	114.71	1.43	60.27	10.57	122	58.80	57.40	54.739
(b)  $CH_3CH_2OC_6H_4N_2C_6H_4O\underset{\underset{O}{\parallel}}{C}C_NH_{2N+1}$								
4	78.35	1.23	43.20	3.82	128	40.93	—	42.160
5	83.11	1.23	45.46	4.33	126	43.27	—	44.000
6	86.99	1.23	47.71	4.47	119	45.31	—	45.850

RESULTS AND DISCUSSION

In mesomorphic state the two fields due to crystalline and liquid phases will be there but their net resultant will only reduce the potential on the electron and hence the δ function strengths show a remarkable increase. As such $\alpha_{\parallel p}$ contribution will be more. An empirical fitting for this behaviour can be given as

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

The expression for A_{LC} is used in place of A in Eq. (2) for evaluating $\alpha_{\parallel p}$ and hence α. The calculation of polarizabilities in the crystalline, nematic and liquid phases can be done by using Neugebauer's relation and Lorenz–Lorentz relation and the method is outlined below.

If N_1 and N_{1c} are the number of molecules per unit volume in the liquid and liquid crystalline phases and α_1 and α_{1c} are the respective polarizabilities they are related by the equation,

$$\frac{n_1^2 - 1}{n_1^2 + 2}\cdot = \frac{4\pi N_1}{3}\cdot\alpha_1 \tag{5}$$

and

$$\frac{1}{3}\left[\frac{n_e^2 - 1}{n_e^2 + 2} + \frac{2(n_0^2 - 1)}{n_0^2 + 2}\right] = \frac{4\pi N_{1c}}{3}\cdot\alpha_{1c} \tag{6}$$

The quantity on the R.H.S. in Eq. (6) can be simplified to $[n_{1c}^2 - 1/n_{1c}^2 + 2]$.

From the observations of refractivities of 4,4′-bis(pentyloxy) azoxy benzene[12] and 4,4′-bis(hexyloxy) azoxy benzene[13] it can be inferred that the average refractivity does not depend very much on temperature so that the R.H.S. of Eq. (5) and (6) will almost be equal and hence,

$$\frac{4\pi N_1}{3}\alpha_1 = \frac{4\pi N_{1c}}{3}\alpha_{1c}$$

or

$$\frac{N_1}{N_{1c}} = \frac{\alpha_{1c}}{\alpha_1} \tag{7}$$

But N_1 and N_{1c} are related by the expressions

$$N_1 = \frac{N\rho_1}{M} \quad \text{and} \quad N_{1c} = \frac{N\rho_{1c}}{M}$$

Hence

$$\frac{N_1}{N_{1c}} = \frac{\rho_1}{\rho_{1c}} \tag{8}$$

(Since N and M are constants). From a graph of ρ versus t, ρ_{1c} is related to ρ_1 as

$$\frac{\rho_{1c}}{\rho_1} = 1 + \frac{m}{\rho_1}(T_c - T) \tag{9}$$

Where m is the slope of the ρ versus t graph, and T_c is the transition temperature.

Substituting Eq. (9) in Eqs. (7) and (8) and simplifying we get

$$\alpha_{1c} = \alpha_1\left[1 - \frac{m}{\rho_1}(T_c - T)\right] \tag{10}$$

α_1 is the mean polarizability in liquid state obtained from Lippincot-δ-function model.

Using Eq. (10), the mean polarizability in liquid crystalline state is evaluated. The calculated values of polarizability are compared with that of reported values of Prasad[6] and Hanson *et al.*[11] The agreement is found to be very good.

Thus the applicability of Lippincot-δ-function potential model with the above modification to liquid crystals is proved beyond doubt. But one serious limitation to this is the sensitivity of this method (Lippincot method) is rather limited. Nonetheless an *a priori* estimate of polarizability can be had by this method.

The application of this method to the calculation of order parameter and helical content in case of cholesteric liquid crystals is in progress.

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