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Polarizabilities and Diamagnetic Susceptibilities of some Liquid Crystalline Compounds

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ABSTRACT

The mean polarizabilities of some liquid crystalline compounds "N-(n-p-alkoxy benzylidene)-p-n-alkoxy anilines" are evaluated using MLδP method and Molecular vibration method and compared with the reported data. The diamagnetic susceptibilities of above compounds are also estimated from mean polarizabilites. A close agreement is found between the values estimated from the theoretical methods and the reported data, which confirms the applicability of these methods for the study of liquid crystals.

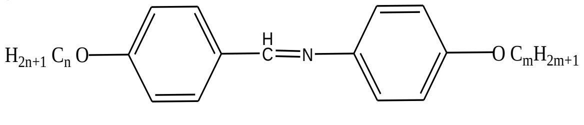
Keywords: Liquid Crystals, Molecular Polarizabilities , Diamagnetic Susceptibilities.

1. 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 polarizabilites 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. There are different methods to estimate the molecular polarizabilities. The methods are refractivity method, the magneto-optic method of Faraday, the method based on the modified Lippincott-δ potential model and the molecular vibration method are a few ones.

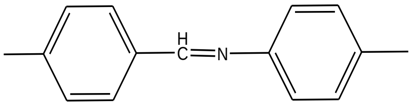
In the present investigation we are reporting the molecular polarizabilities of liquid crystalline compounds whose structure is of nO.Om form, using the last two theoretical methods.

The molecular formula of these compounds is given below



$H_{2n+1}C_nO$ and $H_{2m+1}C_mO$ - Flexible chains

O- Bridging group



-Rigid core

2. EXPERIMENTAL

2.1 Estimation of mean polarizability from Modified Lippincott δ- function method

The MLδP has been used to estimate the mean polarizability in terms of parallel bond components($\sum \alpha \parallel_p$), perpendicular bond contribution ($\sum 2\alpha \perp$) and non-bond region electron contribution ($\sum \alpha \parallel_n$). The expression for the mean polarizability is given as

$$\boldsymbol{\alpha_1} = \frac{1}{3}\left(\sum \alpha \parallel_p + \sum \alpha \parallel_n + \sum 2\alpha \perp\right) \tag{1}$$

Where the parallel bond component is given as

$$\sum \alpha \parallel_p = \frac{4\mathrm{nA}\left[\frac{\exp(\mathrm{T}-T_C)}{\mathrm{T}_C}\right]}{a_0}\left[\frac{R^2}{4}+\frac{1}{2\mathrm{C}_{R^2}}\right]\exp\left[-\frac{(\mathrm{x}_A-\mathrm{x}_B)^2}{4}\right] \tag{2}$$

Here n is the bond order A, δ-function strength or reduced electro negativity. R is the bond length, X_A and X_B are the Pauling's electro negativities of atoms A and B in the bond AB 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. For the second term on the right hand side of the equation (1), we have

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

Here f_j is the fraction of the non-bonded electrons of the jth atom and α_j is its atomic polarizability. For the third term in the equation (1)

$$\sum 2\alpha \perp = \boldsymbol{n_{df}} \frac{\sum x^2{}_j \alpha_j}{\sum x^2{}_j} \tag{4}$$

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

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$$\alpha = \alpha_1[1 - m/\rho_l(T - T_c) \qquad (5)$$

Here m is the slope of the ρ versus T curve. T_C is the transition temperature, ρ_l is the density in liquid phase and α is the mean polarizability in liquid crystalline phase. The necessary data on bond lengths are taken from reference [7]. The density data and transition temperature for the system are taken from reference [16].

2.2 Molecular Vibration Method

The mean molecular polarizability α_M is calculated by the expression

$$\alpha_M = \sum_i \frac{n_i\left(\mathrm{b_L} + 2\mathrm{b_T}\right)_i}{3} \qquad (6)$$

Rao and Murthy[8] have developed the following relations between bond polarizabilities and force constants of various chemical bonds. These relations completely empirical one and the proposed equations are connected to the above parameters which reads as

$$\mathrm{b_L} - \mathrm{b_T} = \mathrm{A}[(\mathrm{X_1X_2})^{s/2}[\frac{a\,N}{k-b}]^{2s/3}] \qquad (7)$$

$$\mathrm{b_L} + 2\mathrm{b_T} = [\mathrm{Cp}^{j}\,(j)^{n\beta}\sigma_e^{1/2}] \qquad (8)$$

various terms in the above equations are explained in the reference[9].

Utilizing the expressions (6), (7) & (8) the bond polarizability coefficients b_L and b_T and mean molecular polarizability α_M are evaluated. In order to facilitate the evaluation of b_L , b_T individually b_L values are taken from the estimation of bond polarizabilities of Denbigh[10] and Le Fevere[11]. Where b_L and b_T are longitudinal and transverse polarizabilities of i^{th} and n_i is the number of bonds of i^{th} kind in molecule.

2.3 Estimation of mean diamagnetic susceptibility

Diamagnetic susceptibilities and mean molecular polarizabilities depends upon the effective number of free electrons which will be free to take part in magnetic and optical interactions. In view of these considerations a semi empirical relation was proposed by Rao et al., which is given as

$$\chi_M = \left(\gamma m\, \sigma^{l}\right)\alpha_M \qquad (9)$$

$\gamma = (0.9)^n$ represents saturation state of the molecule with n denoting the number of unsaturation rings and bonds present in the molecule. $\sigma'$is the degree of the covalency of the characteristic group and is given as

$$\sigma' = \left(\sigma_1{}^{1/n_1}\sigma_2{}^{1/n_2}\text{---}\sigma_p{}^{1/n_p}\right)^{1/2} \qquad (10)$$

Where $\sigma_1,\sigma_2,\ldots.,\sigma_p$ are the 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 $\sigma_1,\sigma_2,\ldots.,\sigma_p$ are taken from reference[12].

3. RESULTS AND DISCUSSIONS

The mean polarizabilites of "N-(n-p-alkoxy benzylidene) -p-n-alkoxyanilines" compounds calculated from MLδP method are presented in Table 1. The necessary data on vibrational frequencies of different bonds are taken from Landolt-Bornstein Tabellen [14] and the necessary data on refractive indices are taken from[16]. The bond polarizabilites of various bonds of compounds are presented in Table 2.

The mean diamagnetic susceptibilities obtained from Rao et al's method agrees with the results obtained from Pascal's method. As the applicability of Pascal's method is already established by Bahadur et al.[17], De Jeu et al.[18] the agreement with this method indicates the general applicability in evaluating the diamagnetic susceptibilities of liquid crystals.

A review of the comparison data in Table 3. shows that the polarizabilites determined from MLδP method and Molecular vibration method are in good agreement with the experimental reported values[16]. From the table 3, it is clear that mean polarizability increases linearly with increase of chain length for the homologous series studied. It can also be observed that the mean diamagnetic susceptibilities presented in table IV also increases linearly with the number of carbon atoms in the alkyl chain. These factors support the additive nature of mean polarizability and the mean diamagnetic susceptibility in the liquid crystals homologous series studied in the present investigation.

4. CONCLUSIONS

In this paper we estimated the mean molecular polarizabilities of nO.Om liquid crystal compounds using MLδP method and Molecular vibration method. In these methods molecular vibration method is superior to the MLδP method since any small deviation in intermolecular forces due to changes in chemical environment will be truly represented in their force constants and vibrational frequencies. Therefore, the molecular vibration method can be treated as superior to MLδP model which requires only bond lengths and atomic delta functions and reduced electronegatvities. Both bond lengths and reduced electronegativities are less sensitive to conformational changes than vibrational frequencies. The reasonably good agreement found in polarizabilities evaluated by the theoretical methods and the experimental reported data [16] confirms the applicability of these methods in evaluating molecular polarizabilities. The mean diamagnetic susceptibilities from Rao etal. method are also in close agreement with Pascal’s method which is already established by many authors in evaluating the diamagnetic susceptibilities of liquid crystals. These theoretical methods can be adopted to estimate mean molecular polarizabilities and mean diamagnetic susceptibilities when the best instrumentation is not available readily.

Table 1: Polarizabilities [α x 10^{24} cm^3] of “N-(*n*-*p*-alkoxy benzylidene)-*p*-*n*-alkoxy anilines” Lippincott δ - function potential model.

n	Name of the compound	$\sum \alpha_{11p}$	$\sum \alpha_{11n}$	$\sum 2\alpha_{\perp}$	α_M
1	N-(*p*-*n*-ethloxy benzylidene)-*p*-*n*-pentyloxyaniline, 2O.O5	81.60	10.86	35.38	39.35
2	N-(*p*-*n*-propoxy benzylidene)-*p*-*n*-pentyloxyaniline, 3O.O5	85.32	10.86	37.63	41.34
3	N-(*p*-*n*-octyloxy benzylidene)-*p*-*n*-propoxyaniline, 8O.O3	96.46	10.86	44.35	47.30
4	N-(*p*-*n*-octyloxy benzylidene)-*p*-*n*-butoxyaniline, 8O.O4	99.79	10.86	46.58	49.15
5	N-(*p*-*n*- octyloxy benzylidene)-*p*-*n*-hexyloxyaniline, 8O.O6	106.44	10.86	51.05	52.86
6	N-(*p*-*n*- octyloxy benzylidene)-*p*-*n*-heptyloxy aniline, 8O.O7	109.77	10.86	53.29	54.71

Table 2: Bond polarizability values for various bonds b in units of [10^{-23} cm^3]

Bond	b_L	b_T	$(b_L + 2b_T)/3$
C – C	0.1870	0.0908	0.1228
O – H	0.1350	0.0420	0.0730
C – H	0.0588	0.0472	0.0510
C = C	0.1690	0.0838	0.1122
C = N	0.1480	0.0533	0.0848
N – C	0.1660	0.0470	0.0866

Table 3: Diamagnetic susceptibilities of nO.Om compounds [$-\chi_M \times 10^6$cgs emu mol^{-1}]

n	**Name of the compound**	**Pascal’s method**	**Rao et al. method**
1	N-(*p*-*n*-ethloxy benzylidene)-*p*-*n*-pentyloxyaniline, 2O.O5	185.66	165.90
2	N-(*p*-*n*-propoxy benzylidene)-*p*-*n*-pentyloxyaniline, 3O.O5	197.52	175.51
3	N-(*p*-*n*-octyloxy benzylidene)-*p*-*n*-propoxyaniline, 8O.O3	233.10	204.31
4	N-(*p*-*n*-octyloxy benzylidene)-*p*-*n*-butoxyaniline, 8O.O4	244.96	213.92
5	N-(*p*-*n*- octyloxy benzylidene)-*p*-*n*-hexyloxyaniline, 8O.O6	268.68	233.14
6	N-(*p*-*n*- octyloxy benzylidene)-*p*-*n*-heptyloxy aniline, 8O.O7	280.54	242.74

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5. REFERENCES

[1].W. H. De Jeu, (1980) Physical properties of Liquid crystalline Materials in relation to their applications, ***Mol. Cryst. Liquid Cryst.***, **63:** 83-109.

[2].S. Chandrasekhar, N. V. Madhusudana, (1969) ***J. Physque.*, 30:**. 24.

[3].H. S. Subrahmanyam, D. Krishnamurthi, (1973) Polarization Field and Molecular Order in Nematic Liquid Crystals, ***Mol. Cryst. Liquid Cryst.*, 22:** 239-248.

[4].W. H. De Jeu, P. Bordewijk, (1978) Physical studies of Nematic azoxybenzenes I.Magnetic susceptibilities and the order parameters, ***J. Chem. Phys.*, 68:** 109.

[5].I. H. Ibrahim, W. Haase, (1981) On the Molecular Polarizability of Nematic Liquid Crystals, ***Mol. Cryst. Liquid Cryst.*, 66:** 189-198.

[6].P. Palffy Muhoray, D. A. Balzarini, (1981) The Clausis-Mossotti relation for anisotropic molecular fluids, ***Can. J. Phys.*, 59:** 375-377.

[7].Handbook of Physics and Chemistry 59th ed.,(1979): **CRC Press**.

[8].B. P. Rao, V. R. Murthy, (1979) Molecular Polarizabilities from molecular vibration studies, ***Ind. Chem.J.*, 13:** 17-21.

[9].Y. N. Murthy, V. R. Murthy, R. N. V. Ranga Reddy, (1997) Molecular vibration approach to polarizabilities of Methyl Cinnamate

Liquid Crystal ccopounds, ***Acta Physica Polonica A.*,** **91:** 1069-1079.

[10]. K. G. Denbigh, (1940) The Polarizabilities of bonds-I, ***Trans. Faraday Soc.*,** **36:** 936-948.

[11]. R. J. W. Le Fevree (1970) ***Rev. pure and Appl. Chem.*,** **20:** 67.

[12]. L. Pauling, (1969) The Nature of chemical bond: **Oxford and IBH Pub.,** New Delhi.

[13]. Y. N. Murthy, Ph.D. Thesis, (1997) S. K. University, Anantapur, India.

[14]. Landolt-Bornstein Tabellen, (1951) Molekulen Teil 1: **Springer Verlag,** pp 479-551.

[15]. P. Pascal, (1913) ***Ann. Chim.et Phys.*,** **29:** 218.

[16]. K. Fakruddin, Ph.D. Thesis, (2007) S. K. University, Anantapur, India.

[17]. B. Bahadur, (1977) Magnetic Susceptibilities studies of the liquid crystal N(p-hexyloxybenzylidene0-p-toluidine(HBT), ***J. Chem. Phys.*** **67:** 3272-3273.

[18]. W. H. De Jeu, W. A. P. Classen, (1978) Physical studies of Nematic azoxybenzenes II. Refractive indices and the internal field, ***J. Chem. Phys.*** **68:** 102-108.

Bibliographical Sketch

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