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Anisotropic properties of some nematic liquids

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Abstract : In the present communication, magnetic anisotropies of some nematic phenyl ester liquids are reported The diamagnetic susceptibilities are calculated using a molecular vibration approach of Murthy *et al* and by a semiempirical relation of Rao *et al*, from the polarizabilities that are available in literature. The mean polarizability values have also been calculated from additive rule of polarizability.

Keywords : Diamagnetic susceptibility, polarizability, nematic liquids

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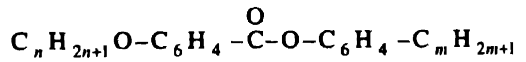
The molecular ordering of liquid crystals governs all their physical properties. According to de Gennes [1], any of the bulk tensorial properties like electric and magnetic susceptibilities, elastic constants, refractive indices, *etc*, can be used to determine the macroscopic parameters. In the present communication, we have reported the mean molecular diamagnetic susceptibilities three 4,4'-disubstituted benzoic acid phenylester compounds by molecular vibration approach [2–4] using force constants and mean amplitudes of vibration as parameters and by a semiempirical relation of Rao *et al* [4–6] from polarizabilities reported in literature [7]. The mean polarizability values have also been calculated from the additive rule of bond polarizability. The selected nematic liquids and their structural formulae are

(I) 4-Methoxy-benzoic acid-[4'-n-pentyl-phenyl ester],

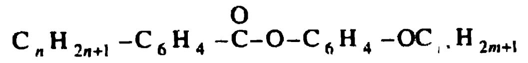
(II) 4-n-Hexyloxy-benzoic acid-[4'-n-pentyl-phenyl ester],

(III) 4-n-Butyl-benzoic acid-[4'-n-hexyloxy-phenyl ester],



$$C_nH_{2n+1}O-C_6H_4-\overset{O}{C}-O-C_6H_4-C_mH_{2m+1}$$

$[m = 5, n = 1, 6–(I,II)]$,



$$C_nH_{2n+1}-C_6H_4-\overset{O}{C}-O-C_6H_4-OC_mH_{2m+1}$$

$[m = 6, n = 4$ (III)].

1997 IACS

Diamagnetic susceptibilities from molecular vibration approach :

The method provides a relatively more easy way of calculating bond-, principal-, and mean molecular diamagnetic susceptibilities of any molecular system using the data available on molecular vibration parameters, force constants and mean amplitudes of vibration. The algebraic expressions used in the molecular vibration approach of Murthy *et al* [2–4] which has proved its validity to different molecular aggregates such as biomolecules, nucleic acid bases, *etc*, are

$$(\chi_L - \chi_T) = A\gamma m L'\left[(X_B X_C)^{1/2}\left[aN/(K-b)\right]^{2/3}\right]^S . \qquad (1)$$

$$(\chi_L + 2\chi_T) = m\gamma L' C P^J (j)^{n\tau} \sigma_e^{1/2} , \qquad (2)$$

where χ_L and χ_T are longitudinal and transverse bond susceptibility coefficients of a bond B–C in the molecule, K is the stretching force constant, $\sigma_e^{1/2}$ is the mean amplitude of vibration, L' is the degree of covalency [8] defined as $e^{-l(X_B - X_C)2]/4}$, where B and C are the bonded atoms with electronegativities X_B and X_C and other terms in the eqs. (1) and (2) have the usual meaning as in reference [2].

The expressions (1) and (2) give χ_L and χ_T separately, which can be used to calculate anisotropic susceptibilities and mean molecular diamagnetic susceptibility. The mean molecular diamagnetic susceptibility is given by

$$\chi = 1/3 \Sigma n_i (\chi_L + 2\chi_T), \qquad (3)$$

where n_i gives the number of identical sets of bonds of kind 'i' and $(\chi_L + 2\chi_T)$ gives the total contribution of each such bond.

The determination of mean diamagnetic susceptibility however, needs some correction [3,4] which can be attributed to the fact that the outer valence electrons attached to an atom do not completely feel the impact of impressed external magnetic field, but will be screened to some extent due to the neighbouring electrons in the atom. This screening is estimated to a first order approximation by a parameter λ' called 'Screening Parameter' given as

$$\lambda' = \sigma' \exp -(\gamma/2), \qquad (4)$$

where $\sigma' = \left[\sigma_1' \sigma_2' \sigma_3' \sigma_4' \ldots\ldots\ldots \sigma_j'\right]^{1/2}$ and $\left[\sigma_1' \sigma_2' \sigma_3' \sigma_4' \ldots\ldots\ldots \sigma_j'\right]$ refers the covalency factor of characteristic group and γ is the saturation factor equal to $(0.9)^n$, where 'n' is the number of unsaturated bonds or rings. Such screening constants were also suggested as chemical shielding tensor [9].

If χ_M' is the diamagnetic susceptibility of a chosen system by molecular vibration approach, then the diamagnetic susceptibility χ_M after applying the above correction becomes

$$\chi_M = [\chi_M']\lambda' \qquad (5)$$

The necessary force constants and mean amplitudes of vibration of the chosen system are evaluated using Wilson's and Cyvin's methods [10,11] respectively from vibrational frequency data as given below :

$$|FG - E\lambda| = 0, \tag{6}$$

$$(\Sigma G' - E\Delta) = 0, \tag{7}$$

where $\lambda = 4\Pi^2 C^2 v^2$ and $\Delta = [h / 8\Pi^2 cv][\coth(hcv / 2KT)]$,

v is the vibrational frequency of each bond expressed as wave numbers.

The necessary data on vibration frequencies are taken from vibrational spectral data of nearest free environmental values [assumed to be proximate] from Landolt-Börnstein Tabullen [12].

Diamagnetic susceptibility from polarizability :

The semiempirical relation between the diamagnetic susceptibility and mean polarizability given as [4–6]

$$-\chi_M = (\gamma m \sigma')\alpha_M, \tag{8}$$

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

$$\sigma' = \left[\sigma_1^{1/n1}\, \sigma_2^{1/n2}\, \sigma_3^{1/n3}\, \sigma_4^{1/n4} \qquad \sigma_p^{1/np}\right]^{1/2}$$

where [$\sigma_1\ \sigma_2\ \sigma_3\ \sigma_4$ .... σ_p] are Pauling's percentage covalence characters of the bonds present in the characteristic group, $n_1\ n_2$ .... 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 are taken from Pauling [13].

Table 1. Molecular parameters.

Bond	Force constant $k \times 10^5$ dyne/cm	Mean amplitude of vibration 10^{-10} cm	Percentage of covalency l.′
C–H	05.14	07.67	0.984
C–C	03.49	05.35	1.000
C=C	09 07	04 17	1 000
C–O	04.90	03 74	0 778
C=O	11.70	03.79	0.778

The molecular parameters and mean diamagnetic susceptibilities of the various bonds are presented in Table 1. The bond diamagnetic susceptibility coefficients are presented in Table 2. The mean molecular diamagnetic susceptibilities calculated by molecular vibration approach along with screening parameter, the diamagnetic susceptibilities from polarizabilities by Rao *et al* method using reference values calculated by Vuk's approach from refractivity studies by Ibrahim [7] and the values from Pascal's method [14,15] are presented in the Table 3. The polarizabilities calculated by additive rule [16,17] are also presented in the same table.

Table 2. Bond diamagnetic susceptibility coefficients.

Bond	χ_L	χ_T	χ_M Mean diamagnetic susceptibility 10^{-5} CGS units
C–H	0.480	0.472	0.475
C–C	0.839	0.783	0.802
C=C	0.721	0.642	0.668
C–O	0.700	0.635	0.657
C=O	0.727	0.639	0.669

Table 3. Anisotropic properties of selected nematic liquids

	Diamagnetic susceptibilities $-\chi_M \times 10^6$ CGS units			Polarizabilities $\alpha_M \times 10^{24}$ cm^3	
Compound	Present method screening parameter 0.644	Rao *et al* method	Pascal's method	Reference values	From bond polarizabilities
$m = 5, n = 1$	17.62	18.60	17.63	35.46	34.43
$m = 5, n = 6$	23.27	23.33	23.72	44.48	44.13
$m = 6, n = 4$	22.15	22.38	22.54	42.66	42.19

From the Table 3 it can be seen that the diamagnetic susceptibility values calculated by molecular vibration approach are in good agreement with those obtained from different methods.

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