

Shape parameters and excited state dipole moments of some nematic liquid crystals from solvatochromic shifts

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Abstract : The solvent effect on the UV absorption (for S_1 band) spectra of some nematic liquid crystalline compounds is studied and the magnitude and direction of their electric dipole moments in the first electronically excited states is estimated. The shape parameters of these molecules are also determined

Keywords : Liquid crystal, UV absorption, solvatochromic shifts, dipole moment, shape parameter

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From a study of the solvent effect on the absorption spectrum of a molecule it is possible to determine its electric dipole moment in its electronically excited states. This parameter so determined gives some insight into electron distribution, reactivity, photochemical reactions etc., of the solute molecule in its electronically excited states. Apart from obtaining the permanent moment in the excited states it is also possible from these studies to determine the shape parameters, which is another important parameter that gives knowledge about the shape of the cavity in which solute molecule is supposed to lie.

Bearing the above considerations in mind UV absorption spectra of a single known concentration of each of the pure samples of p -(p -ethoxyphenylazo)-phenyl undecylate, p -(p -ethoxy phenyl azo)-phenyl heptanoate, 4, 4'-azo-diphenetole, 4, 4'-azoxy anisole and 4-n-octyloxy benzylidene-4'-butyl aniline, hereafter referred to as compounds N_1 , N_2 , N_3 , N_4 and N_5 , in a series of polar and non-polar solvents having different dielectric constants and refractive indices, are recorded using a Hitachi U3200 UV/VIS spectrophotometer with a cell path length of 1 cm. The concentration of the solute

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molecule in different solvents is in the range of 0.01 to 0.03 gm/litre.

The change in the permanent electric dipole moment (both magnitude and direction) of each of the compounds N_1, \dots, N_5 is determined using a procedure suggested from this laboratory [1] and the shape parameter is obtained in the light of a dielectric model proposed by Shibuya [2]. The relevant equations used are as follows.

Following Suppan and Tsiamis [3], the change in the permanent dipole moment ($\Delta\mu_{g-e}$) for a series of solvents of different dielectric constants (ϵ) but similar refractive indices (n) is related to the observed solvatochromic shift $\Delta\nu_{a-b}$ between solvents a and b by

$$-\Delta\nu_{a-b} = \frac{\mu_g \cdot \Delta\mu_{g-e}}{hca_o^3} \left[\Delta [f(\epsilon) - f(n^2)]_{a-b} \right] + \frac{\mu_e^2 - \mu_g^2}{hca_o^3} \Delta f(n^2)_{a-b}$$

and can be expressed as an equation of a straight line with intercept from [4] as

$$\frac{X}{C_1} + \frac{Y}{C_2} = 1$$

where, $X = \Delta [f(\epsilon) - f(n^2)]_{a-b} / \Delta\nu_{a-b}$, and

$$Y = \Delta f(n^2)_{a-b} / -\Delta\nu_{a-b}$$

and C_1 and C_2 are the intercepts ($C_1 = hca_o^3 / \mu_g \cdot \Delta\mu_{g-e}$; $C_2 = hca_o^3 / (\mu_e^2 - \mu_g^2)$) on the axes of X and Y respectively, when the quantity X is plotted versus Y . Other quantities contained in the equation, μ_g is the permanent electric moment in the ground state, h is the Planck's constant, C is the velocity of light, a_o is the radius of the cavity in which the solute molecule is supposed to lie. The quantities $f(\epsilon)$ and $f(n^2)$, referred to as polarity and polarizability functions are given by $f(\epsilon) = 2(\epsilon - 1) / (2\epsilon + 1)$; and $f(n^2) = 2(n^2 - 1) / (2n^2 + 1)$. By determining the two intercepts and with a pre-knowledge of other physical quantities in the equation, $\Delta\mu_{g-e}$ and its direction θ to μ_g axis can be estimated.

By performing separate set of dielectric measurements on the various solvents and dilute solutions of the compounds in these solvents, the static dielectric permittivity (ϵ) at 1 MHz with the help of a circuit similar to the one used by LeFevre *et al* [5] and dielectric permittivity at optical frequencies (refractive index n for sodium D line) using Abbe' refractometer, the ground state dipole moment μ_g is determined using a modified method due to Guggenheim [6]. The estimated percentages of accuracy in the quantities, ϵ , n , μ , are 1%, 0.03% respectively. The estimated accuracy in the case of $\Delta\nu_{a-b}$ is about ± 20 wave numbers. The quantity a_o is determined by the method of atomic increments [7] by treating each of the solute molecules as spherical for ease of calculation.

The values of static dielectric parameters of the solvents, the maximum of the absorption band $(\nu_{max})_{a-b} \text{ cm}^{-1}$ (treating CCl_4 as a reference solvent) are given in Table 1 whereas the values of μ_g , μ_{g-e} , θ and a_o are appended at the bottom of this same table.

Table 1. Physical contents of solvents, solvatochromic shifts etc..

Solvents	Θ	n	Δu_{\max} (cm ⁻¹)			
			N_1	N_2	N_3	N_4
Carbon tetra chloride (Ref. Solvent)	2.239	1.4590	28539*	28539*	28043*	28393*
Benzene	2.284	1.4980	89	202	196	355
<i>n</i> -Hexane	1.890	1.3751	-355	-329	-382	-542
<i>n</i> -Heptane	1.924	1.3877	-304	-304	-358	-551
Cyclo Hexane	2.025	1.4240	-255	-172	-254	-484
<i>P</i> -Xylene	2.273	1.5067	114	-	149	152
1,4-Dioxane	2.210	1.4200	-	57	-	-
Methyl Alcohol	32.700	1.3290	-123	89	-71	295
<i>n</i> Propyl alcohol	20.100	1.3850	-123	41	-86	264
iso-Propyl alcohol	19.920	1.3776	41	-106	-55	452
Amyl alcohol	15.300	1.4050	-155	-123	-39	264
Ethylene Dichloride	10.160	1.4422	106	-	180	343
Benzonitrile	25.200	1.5260	266	-	381	-
Dimethyl Formamide	36.710	1.4305	-	861	-	421
Butyl alcohol	17.100	1.3970	-	-106	-	-
$\alpha_D(\text{Å})$			4.69	4.45	3.98	3.88
$\mu_g(\text{D})$			3.36	3.62	2.62	1.79
$\mu_g \epsilon(\text{D})$			8.81	10.10	6.36	6.85
$\theta(\text{Degrees})$			64.00	61.00	70.00	-

* Indicate the value of ν_{\max} (cm⁻¹) in CCl₄

For the determination of the shape parameter(*s*) the linear relation between the oscillator strength of the solute molecule and the refractive index of the solvent as proposed by Shibuya [2] is used. The equation is —

$$\sqrt{nf''} = \sqrt{f} s (n^2 - 1) + \sqrt{f}$$

where, f'' is the apparent oscillator strength of the solute molecule measured in a solution of refractive index n , f is the oscillator strength of the solute molecule and s is the shape parameter. The oscillator strength f'' can be determined using the relation, [8].

$$f'' = 0.432 \times 10^{-8} \text{ MC}^{-1} \text{ l}^{-1} \int_{\nu_1}^{\nu_2} A(\nu) d\nu$$

where M is the molecular weight of the solute, C its concentration expressed in gm/litre, l is the cell length in cm $A(\nu)$ is the absorbance ($\log I_0 / I$).

In the present work, n is measured using Abbe' refractometer and the integration is performed by determining the area under the curve of Absorbance versus wave number plot. The relevant UV spectra of compounds N_1 N_5 for a known concentration of each of

them in a series of non-polar solvents are recorded. The results of these measurements are presented in Table 2.

Table 2. Oscillator strengths and shape parameters

Solvents	Apparent oscillator strengths (f'')				
	N_1	N_2	N_3	N_4	N_5
Carbon tetra chloride	0.5842	0.5398	0.4963	0.5423	0.5968
Benzene	-	0.5574	0.5174	0.6042	0.5492
<i>n</i> -Hexane	0.5224	0.6439	0.3541	0.5674	0.5087
<i>n</i> -Heptane	0.5083	0.5007	0.5349	0.5823	0.5261
Cyclohexane	0.5295	0.5099	0.6949	0.5992	-
<i>p</i> -Xylene	0.4873	-	0.5617	0.5746	-
1, 4-Dioxane	-	0.5359	-	-	-
Intercept : $\sqrt{\text{Oscillator strength}}$ $= \sqrt{f}$	0.6700	0.6100	0.5400	0.7700	0.6400
Slope : \sqrt{fx} Shape parameter $= \sqrt{f} s$	0.2021	0.2500	0.3000	0.1250	0.2300
Shape parameter : s	0.3017	0.4098	0.5556	0.1623	0.3594

It is observed from Table 1 that the observed solvatochromic shifts in all the cases with CCl_4 as reference solvent are well separated from solvent to solvent and that the dipole moments of these molecules in the excited electronic state in general follow the same trend of variation from one molecule to other as do their ground state dipole moment values within the experimental errors. Further the change in the value of the permanent dipole moment from ground state to the excited state is always positive and the angle of inclination μ_e to μ_g lies in first quadrant. Such a trend is observed in a variety of organic molecules reported in the literature [8-14]. Rather high values of the excited state dipole moments of these compounds may be taken to be indicative of considerable charge transfer contribution in each case to the excited state.

It is observed from Table 2 that the Shape parameter-value in all the cases is less than unity and that in the case of compound N_2 , N_3 and N_5 the s value is different from that corresponding to a sphere (transition moment in any direction) but approaches towards that corresponding to a long circular cylinder (transition moment along transverse direction) as given in the literature [15]. This trend may not be unexpected in view of the fact that the structure of these compounds is in the form of a long cylinder where two benzene rings are bridged by alkyl, alkoxy etc., groups. This trend is not observed in the case of N_1 and N_4 compounds although all these compounds belong to one class of liquid crystals.

In view of the fact that there are some inherent uncertainties in estimating the value

of a_0 , and also that this value may change on excitation, the observed results may merit to give only qualitative trends.

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