Estimation of excited state electric dipole moment of some substituted benzonitriles

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Abstract : The electric dipole moments in the excited state of S_1 band system of 2,3-, 2,4-, 2,5-, 2,6- and 3,4-difluorobenzonitriles (DFBN) have been estimated using solvatochromic shift measurements. The old procedure adopted by others and a new method proposed from this laboratory have been applied for the estimation of dipole moment in the excited state of these molecules. Two methods have been discussed and compared in the light of the results obtained.

The ground state electric dipole moment of these molecules which are pre-requirement in the determination of excited state electric dipole moment, were also determined experimentally.

I. Introduction

In continuation of the on-going work in our laboratory (Ayachit *et al* 1986, 1988, Shashidhar *et al* 1976, Deshpande *et al* 1981, Tonannavar *et al* 1987) in the area of solvatochromic shift measurements and estimation of excited state electric dipole moments of molecules using these measurements, we have measured the solvato-chromic shifts of S_1 electronic band system of 2,3-, 2,4-, 2,5- 2,6- and 3,4-difluorobenzonitriles (DFBN) and estimated the electric dipole moments of these molecules in their excited states of this system. The estimation of excited state electric dipole moments of these molecules has been carried out as these give an insight into the molecular structural parameters in their excited state such as electronic charge distribution etc.

Ledger and Suppan (1967) had earlier suggested a method for determining the excited state electric dipole moment of a molecule, using its solvatochronic shifts from Mc Rae's equation (Mc Rae 1957). Since then the method has been modified by several workers (Suppan and Tsiamis 1980, Suppan 1975, Prabhumirashi *et al* 1983). A new approach (Ayachit *et al* 1986) to this problem with a new method

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has been proposed from this laboratory. The earlier method and the new method suggested from this laboratory were applied to the S_1 band system of the above mentioned molecules and the results are presented and discussed here.

The pre-requisite values of ground state electric dipole moments in the calculation of excited state electric dipole moments of these molecules were also determined by the well-known modified Guggenheim's method (Guggenheim 1951).

2. Experimental

The electronic absorption spectra (S_1 band) of pure samples (Supplied by Aldrich Chemical Co., USA) of 2,3-, 2,4-, 2,5-, 2,6- and 3,4-DFBN in different solvents of spectroscopic grade given in Table 1, were recorded using a Hitachi Model 150-20 UV/VIS spectrophotometer with a cell pathlength of 1 cm. The concentration of the solute molecule in different solvents was in the range of 0.01 to 0.02 gm/litre.

The data required in the determination of ground state electric dipole moments, namely, the change in capacitance and refractive indices of the various dilute solutions of these polar substances in dioxane were measured respectively using a crystal controlled oscillator [1 MHz] and Abbe's refractometer.

3. Results and discussion

In the old method, Mc Rae's equation was reduced to two straight line equations, namely,

$$\nu_a = \nu_v - \frac{\mu_g . \Delta \mu_{g,e} f(D)_s}{hca_0^3} \qquad\qquad . \tag{1}$$

$$\nu_s = \nu_u - \frac{\mu_e|^2 - |\mu_g|^2}{hca_0^3} f(n^2)_s \tag{2}$$

where eq. (1) holds good for a set of polar solvents of nearly the same refractive index while eq. (2) holds only for non-polar solvents.

In the new method proposed from this laboratory, the Mc Rae's equation has been re-written in the form of an equation of a straight line in the intercept form,

$$\frac{X}{C_1} + \frac{Y}{C_2} = 1 \tag{3}$$

with

$$X = \Delta[f(D) - f(n^2)]_{1-2} / - \Delta\nu_{1-2}.$$

$$Y = \Delta f(n^2)_{1-2} / - \Delta\nu_{1-2}$$

$$C_1 = hca_0^3 / \mu_g . \Delta\mu_{g,e}$$

$$C_2 = hca_0^3 / \{ |\mu_e|^2 - |\mu_g|^2 \}$$

Table I.

Solvents	n	D	Position of ν_{max} (cm^{-1})				
			2,3-DFBN	2,4-DFBN	2,5-DFBN	2,6-DFBN	3,4-DFBN
Cyclohexane	1.426	2.024	36326	36180	34520	36470	36077
Carbontetrachloride	1.459	2.236	36221	36168	34472	36432	36038
n-Pentane	1.358	1.837	36486	36221	34615	36592	36116
n-Heptane	1.387	1.920	36486	36205	34568	36550	36142
1,4-Dioxane	1.421	2.233	—	—	34143	36326	36116
Hexane	1.375	1.883	36432	36225	34568	36575	36181
Methanol	1.329	5.700	36221	36255	34663	36273	36140
n-Propanol	1.384	21.246	36326	36200	34615	36326	36103
Iso-Propanol	1.377	20.317	36326	36250	34615	36379	36129
Ethanol	1.360	3.471	36260	36260	34712	36260	36168
Chloroform	1.446	4.810	36247	36255	34563	36273	36142
Dimethylformamide	1.428	36.710	36169	36225	34627	36221	36116
Dichloromethane	1.424	9.080	36169	36235	34675	36260	36129

and which holds for any set of solvents.   In eqs. (1), (2) and (3), ν_s, $| \mu_e |$, $| \mu_g |$, a_0 are respectively, position of maximum (in cm^{-1}) of a band system in a solvent, the excited state electric dipole moment, the ground state electric diopole moment and cavity radius of solute molecule. The other quantities have the same significance as in our earlier paper (Ayachit et *al* 1986).   Here

$$\mu_0 . \Delta\mu_{g,e} = \mu_0 . (\mu_g - \mu_e)$$

$$= | \mu_g |^2 - | \mu_e | \, | \mu_g | \cos \theta$$

θ is the angle between $| \mu_e |$ and $| \mu_g |$.

The values of ν_{max} in different solvents for all the molecules studied are given in Table 1, along with refractive indices and dielectric constants of solvents (Aldrich 1985, CRC hand book 1973-74).

According to the old method, by choosing two sets of solvents one polar of nearly the same refractive index and another non-polar, the spectra were recorded.
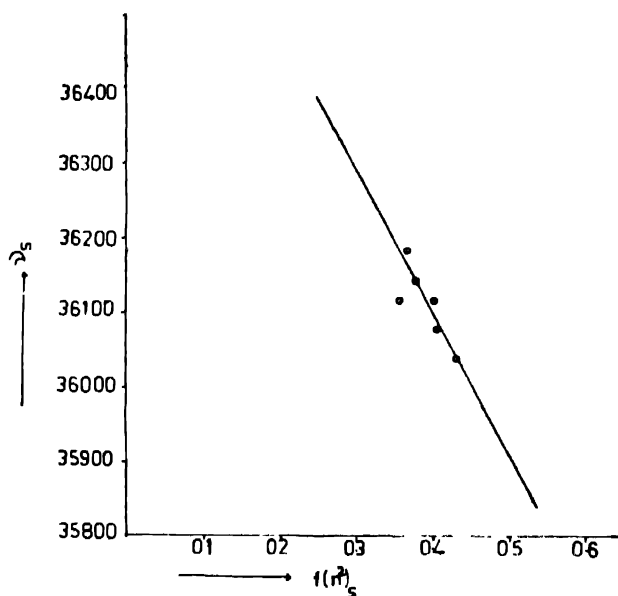

Figure I.   Plot of ν_s vs $f(n^2)_s$ of 3,4-difluorobenzonitriles.

For solvents of the first kind, a plot of ν_s against $f(D)_s$ and for second kind, ν_s against $f(n^2)_s$ were made.   By calculating the slopes (using least-square method for both the plots) $| \mu_e |$ and θ were calculated with a prior knowledge of ν_0 and a.   Figures 1, 2 give the illustrative plots of ν_s against $f(n^2)_s$ and ν_s against $f(D)_s$ in the case of 3,4-DFBN.

The method developed by us is independent of the nature of the solvents used, that is whether it is non-polar or polar and this is not the case with the other

methods mentioned earlier. Further it makes use of only one equation, namely, eq. (3). The other methods in the literature are essentially equivalent to the old
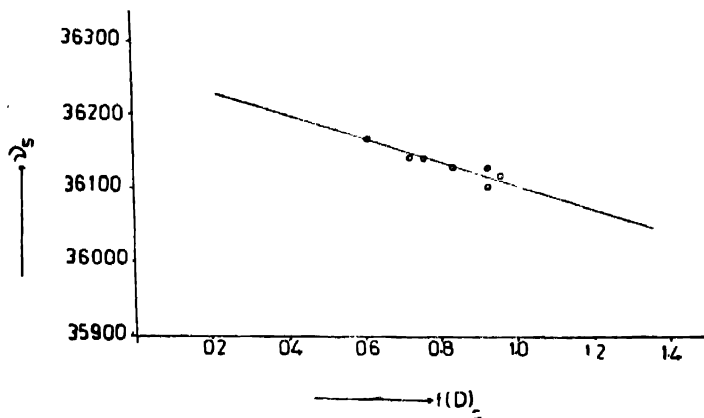

Figure 2. Plot of ν_s vs $f(D)$, of 3,4-difluorobenzonitrile.

method of Mc Rae and they also use two eqs. (1) and (2). Therefore, it would not be very useful to use these methods and compare the results.

Using the same data given in Table 1, the values of X and Y were calculated for each molecule from eq. (3) in different solvents. By plotting X against Y and
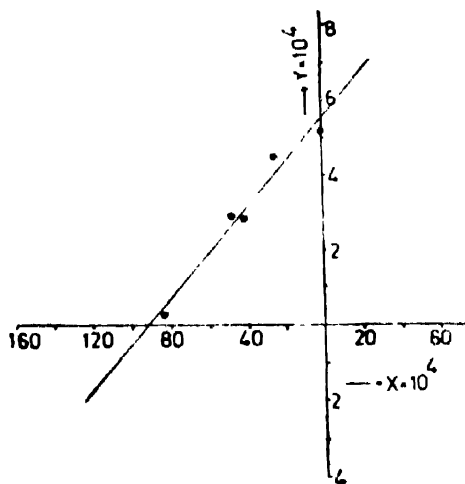

Figure 3. Plot of X vs Y of 3,4-difluorobenzonitrile.

calculating C_1 and C_2 (using least square fit method) $|\mu_e|$ and θ were calculated with a prior knowledge of μ_g and a_0. Figure 3 gives an illustration of a plot of X against Y in the case of 3,4-DFBN.

The two methods mentioned above, do not take into account the other interactions such as, solvent-solvent interaction (dispersive) hydrogen bonding, effect of

any complexes that may be formed etc. The effect of these factors can be minimised by a proper choice of the solvents, non-polar and polar as has been done in the present study.

The estimated values of $| \mu_e |$ and θ using both the methods are given in Table 2, along with μ_g values calculated by the modified Guggenheim's method.

As for the molecular radius a_0, the molecules were assumed to be spherical in shape and was estimated using the method of atomic increments and the value of the cavity radius in each molecule is 3.03 Å (Edwards 1956).

The difference in the μ_e values obtained by two methods is essentially because of the way the methods have been formulated from Mc Rae's equation. It can be

Table 2.

Molecule	μ_g in D	μ_e in D	θ in degrees
1 2,3-DFBN	4.35	7.47 (6.97)	60 (56)
2 2,4-DFBN	3.21	4.46 (3.91)	42 (40)
3 2,5-DFBN	4.06	6.64 (6.09)	59 (52)
4 2,6-DFBN	4.04	6.63 (6.27)	61 (56)
5 3,4-DFBN	2.39	3.97 (3.99)	48 (48)

The values in the parentheses are estimated values of the μ_e and θ, using Mc Rae's method.

shown that the eq. (3) can be reduced to eqs. (1) or (2) under with solvents suitably chosen. Eq. (3) can be reduced to eq. (1), by taking solvents of nearly same refractive indices, while by taking non-polar solvents it can be reduced to eq. (2). This means that eq. (3) is a more general way of representing Mc Rae's equation. Further, in eqs. (1) and (2), we neglect the contributions due to the dispersion term, namely, $(A+B)f(n)$ and other quantities which are small, while in eq. (3) we neglect quantities which are differences of such small quantities, namely, $(A+B) f(n^2)_{1-2}$ and etc. In view of these, naturally, the second method may be expected to give a better estimation of $| \mu_e |$ and θ.

Table 2 shows that the dipole moments in the excited state of these molecules are higher than their ground state values indicating the observed band system in these molecules is due to $\pi^* \leftarrow \pi$ transition which is consistent with literature (Jaffe and Orchin 1962) more on the basis of the solvent effect on system.

These molecules exhibit S_1 band system In the region around λ 2800 Å. The vapour spectra of these molecules show a prominent absorption band system in this region (Rao et al 1989) and the analysis of this system in each molecules is a $\pi^* \leftarrow \pi$ system analogous to $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene. Hence, the present results are consistent with our earlier observations.

Acknowledgments

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