

Determination of excited state electric dipole moment of the isomeric fluorophenylisocyanates from solvatochromic shift measurements

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Abstract. The excited state electric dipole moments of three isomeric fluorophenylisocyanates are determined using the method of solvatochromic shift measurements recently suggested from our laboratory.

Keywords. Excited state dipole moments; fluorophenylisocyanates; solvatochromic shifts.

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1. Introduction

Ledger and Suppan (1967) had suggested a method to determine the excited state electric dipole moment of a molecule using its solvatochromic shifts from McRae's (1957) equation. This method has since been modified (Suppan 1975; Suppan and Tsiamis 1980; Prabhumirashi *et al* 1983). Recently a new method has been proposed from our laboratory (Ayachit *et al* 1986) and applied for some substituted benzenes. This method has now been applied to the S_1 band of a few more molecules, namely, the three isomeric fluorophenylisocyanates (FPICs).

2. Experimental

The ultraviolet absorption spectra (S_1 band) of pure samples (Aldrich Chemical Co., USA) of the three isomeric FPICs in different solvents of spectroscopic grade purity viz (i) cyclohexane, (ii) tetrahydrofuran, (iii) *n*-propanol, (iv) *iso*-propanol, (v) ether, (vi) hexane, (vii) *t*-butanol and (viii) *n*-heptane were recorded using a ratio recording spectrophotometer (DK-2A) with a cell thickness of 1 cm. The concentration of each of the solute molecules in different solvents was in the range of 0.01 to 0.02 g/litre.

3. Method, results and discussion

In the method suggested earlier (Ayachit *et al* 1986), McRae's equation (McRae 1957) was put in the form of an equation for a straight line (intercept form),

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$$(X/C_1) + (Y/C_2) = 1, \quad (1)$$

where

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

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

$$C_1 = hca_0^3/(\mu_g \cdot \Delta\mu_{g-e}) \quad \text{and} \quad C_2 = hca_0^3/(|\mu_e|^2 - |\mu_g|^2).$$

Here, $\Delta\nu_{1-2}$ is the difference in position (in cm^{-1}) of the band of maximum intensity (ν_{max}) of a solute molecule in two solvents 1 and 2 and $|\mu_e|$, $|\mu_g|$ are respectively the ground and excited state dipole moments of a molecule under study. The other part of the expression represents the same quantities as given earlier (Ayachit *et al* 1986). In obtaining (1), it is assumed that the induced shifts in the position of ν_{max} due to complex formation, charge transfer and hydrogen bonding etc., are negligible.

A plot of X vs Y for different solvents yields a straight line in the intercept form, the intercepts being C_1 and C_2 . From C_2 and C_1 one can calculate respectively $|\mu_e|$ and the angle between $|\mu_e|$ and $|\mu_g|$, θ

$$(\mu_g \cdot \Delta\mu_{g-e} = |\mu_g|^2 - |\mu_g||\mu_e| \cos \theta)$$

using the predetermined values of a_0 (molecular radius) and $|\mu_g|$. The frequency ν is chosen in each solvent for a particular band system where the intensity is maximum.

The ν_{max} identified for S_1 band system in the case of the three isomeric FPICs in different solvents are given in table 1 and have been used to estimate $|\mu_e|$ and θ for these molecules. In this table are given the values of the static dielectric constants (D_s) and the refractive indices (n_s) of the solvents used which are taken from the literature (CRC Handbook 1973; Aldrich Catalog 1985).

The ground state values of the dipole moments of these molecules were estimated by compounding vectorially the group moments of the substituents, namely, isocyanate and fluoro groups (2.29 D and 1.46 D respectively) taken from the literature (Audsley and Goss 1941; Jolliffe and Smyth 1958). It is assumed that both the dipoles act towards the centre of the ring. However, the method of vectorial addition of moments does not consider the possible induced effects and therefore the estimated dipole moment values may differ from the actual experimental values to that extent. Since the inclination of the —NCO group (Bouchy and Roussy 1977; Balfour *et al* 1982) to the linkage of the carbon atom of the ring is neglected and since these group moments act towards the centre of ring, the estimated values may be taken to be approximate but will, however, be of the right order of magnitude.

As regards the value of the molecular radius a_0 , the molecules are assumed to be spherical in shape to make the calculation simpler and using the method of atomic increments (Edwards 1956) the value of the quantity is 3.01 Å.

The relevant plots of X vs Y for the three molecules are given in figure 1. The accuracy in the values of X and Y are $\pm 5\%$. Obtaining intercepts from the plots, $|\mu_e|$ and θ have been calculated and are presented in table 2, which also gives the values of $|\mu_g|$ of these molecules calculated as indicated earlier.

Table 2 shows that the dipole moments in the excited state of these molecules are higher than their ground state values indicating that the observed band system in the molecules studied is due to $\pi^* \leftarrow \pi$ transition, which is consistent with published observations (Jaffe and Orchin 1962; Shashidhar *et al* 1976; Deshpande *et al* 1981; Prabhumirashi 1983).

Table I. Excited state dipole moment of three isomeric FPICs.

Solvent	n_s	D_s	$f(n_s^2)$	$f(D_s)$	$\nu_{\max}(\text{cm}^{-1})$		
					<i>o</i> -FPIC*	<i>m</i> -FPIC	<i>p</i> -FPIC
Cyclohexane	1.4260	2.0240	0.4079280	0.4057052	37094	36353	36485
Tetrahydrofluran	1.4070	7.390	0.3950756	0.8098859	34237	33773	35450
<i>n</i> -propanol	1.3837	21.24	0.378784	0.93100275	36552	34591	35450
<i>Iso</i> -propanol	1.3770	20.317	0.37399	0.9279435	35577	—	—
Ether	1.3506	4.2294	0.3545945	0.6828350	36090	35831	—
Hexane	1.3749	1.8836	0.3724768	0.3706997	—	34354	36352
<i>t</i> -butanol	1.3975	13.63	0.3885058	0.8230714	35450	35450	36388
<i>n</i> -heptane	1.3870	1.920	0.3811291	0.3801652	—	37302	36753

*FPIC, fluorephenylisocyanate.

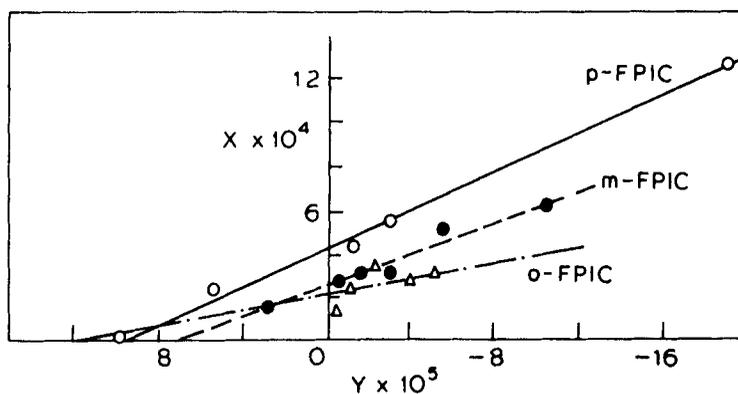


Figure 1. X vs Y plots for three isomeric fluorophenylisocyanates.

Table 2. Values of electric dipole moments and θ .

Molecule	$ \mu_g $ (in D)	$ \mu_e $ (in D)	θ (in deg)
<i>o</i> -fluorophenylisocyanate	3.26	7.06	59
<i>m</i> -fluorophenylisocyanate	2.03	8.58	29
<i>p</i> -fluorophenylisocyanate	0.83	7.40	77

As regards the calculated θ values, particularly that in *p*-FPIC, which has been shown to belong to symmetry group, planar C_s (Balfour *et al* 1982) in which the linear NCO group makes an angle of $\approx 134^\circ$ with the relevant C_2 axis of the phenyl ring in the plane of the ring, the change in the orientation of the dipole moment upon electronic excitation seems to be rather large, although there is no change in the symmetry of the molecule, but we feel that there may be no inconsistency in the orientation of the dipole moment of the molecule changing upon electronic excitation, without change in its symmetry. Further, the θ value may be considered as only approximate since it depends on the dipole moment value of the molecule in the ground state which, as mentioned earlier, is again only approximate.

The three isomeric FPICs exhibit this S_1 band in the region around 2800 Å. The vapour spectra of these three molecules show prominent absorption band system in this region (Huralikoppi *et al* 1983, 1985) and an analysis of this vapour system in these molecules has shown that this system in each molecule is a $\pi^* \leftarrow \pi$ system arising from a ${}^1A' \leftarrow {}^1A'$ transition analogous to ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition in benzene. Hence the present results are consistent with our earlier observations.

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