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Short Communication

Solvents effect on n→π*and π→π* transition of 9-fluorenone

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Absorption spectra of 9-fluorenone had been studied in polar and non-polar solvents. Maximum of four bands were observed; the shift in these band as the solvents were changed from polar to non-polar were noted. The quantitative treatments of the shifts allowed the transition to be assigned as n→π*or π→π*.

Key words: Fluorenone, electronic absorption, transition, excited state polar and non polar solvent.

INTRODUCTION

Anomalous shifts of electronics absorption bands of unsaturated molecules to shorter wavelength on changing from the solvent of low dielectric constant to one of higher dielectric constant and vice versa had been a subject of several studies (Lee and Boo, 1996; Caldwell and Gagewski, 1970; Leonard et al., 1978; Richard, 1969; Baylis and Johnson, 1968). These shifts were named as blue and red shifts respectively. McConnell (1952) had catalogued the solvents blue or red shifts of certain electronic absorption of solute molecules and assigned them as n→π*or π→π* transition respectively.

Blue shift transition originates from the fact that the solvent molecules are oriented around the solute molecules to fit with the ground state charge distribution of the solute molecules. On excitation, if the charge distribution changed markedly as in n→π* transitions, the solvents molecule would not have position and orientation to bind with the excited state charge distribution. Blue shift will therefore be observed since in relation to non-polar solvents, a polar solvent will give greater solvation energy for the ground state of the solute than for the excited state (Baylis and McRae, 1954).

Solvents and functional group substitution dependence of the absorption and florescence spectra of fluorenone had been studied. Keityaro and David (1966) in their studies distinguishes between n→π*and π→π* transitions of fluorenone by oxime formation test on the spectra. The disappearance of n→π* transition was attributed to oxime formation which has no effect on the π→π* transition. Józefówich et al. (2002) also confirmed that the wave number difference of absorption and excitation spectra are solvents dependent and that bathochromic shift is larger in non-polar solvent than in polar solvent.In this study, we present the effect of solvent polarity on the absorption spectra of 9-fluorenone.The effect of solvent media on transition energies, oscillator strength and other absorption parameter are presented. Based on the shifts,the transition are assigned to either n→π*or π→π*.

Experimental

The solvents were all analytical grades and are products of British Drug House Limited London. Prof. I. Iweibo of Chemistry Department University of Ibadan provided the solvents and fluorenone, which is a product of sigma chemicals. The solvents were distilled twice before use, while the solute was used without further purification.

Preparation of solution

The solution of 9-fluorenone was prepared by dissolving 0.1 - 0.2 mg of the solid solute in the solvent and made up to 10 ml. Thorough shaking or application of heat may be required for effec-

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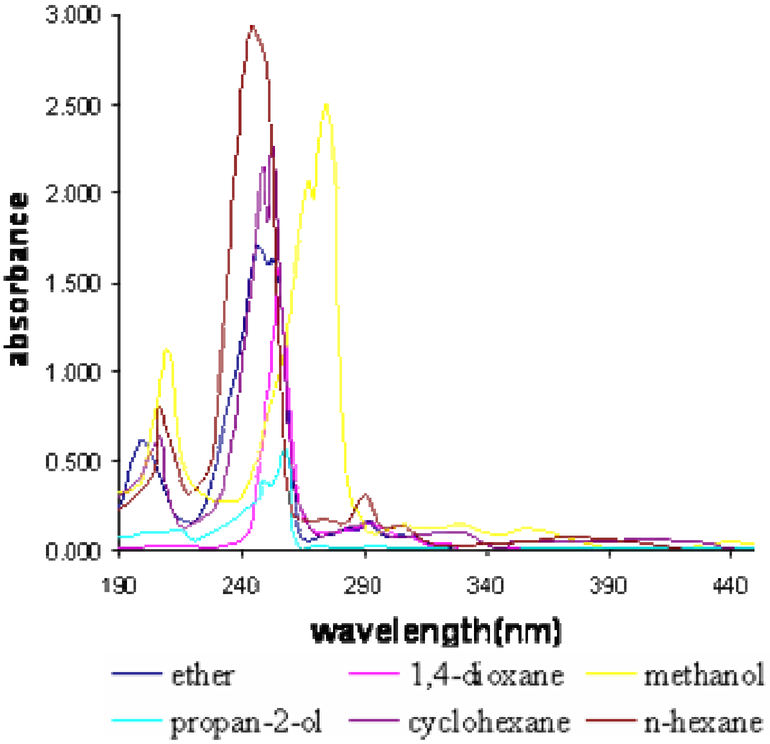

Figure 1. Absorption spectral of flurenone in polar and non-polar solvent.

Table 1. The spectra properties of Band I.

Solvents	υ_{max} (cm^{-1})	$\upsilon_{1/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	f
n-hexane	26990.6	24588.1	263.8	0.004
Cyclohexane	27027.0	24539.8	345.6	0.006
Propan-2-ol	26595.7	23855.0	220	0.004
Methanol	26455.0	26940.6	230	0.004
1,4-dioxane	26595.7	23866.3	182.3	0.003
Diethyl ether	-	-	-	-

Table 2. The spectra properties of Band II.

Solvents	υ_{max} (cm^{-1})	$\upsilon_{1/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	f
n-hexane	34246.6	36968.6	3196.9	0.058
Cyclohexane	-	-	-	-
Propan-2-ol	34013.6	32457.0	435.2	0.005
Methanol	34013.6	31575.6	1824.9	0.03
1,4-dioxane	34013.6	32258.1	1386.7	0.02
Diethyl ether	34246.6	36791.8	548.9	0.01

tive dissolution especially in non-polar solvents.

Spectra runs

The absorption spectra were run on single beam Unicam (Helios γ) uv/visible spectrometer interfaced with computer and printer. The baseline was first calibrated with blank solvents after which about 40 – 50 µL of the solution will be added and the absorption is scanned through the desired wavelengths.

RESULTS AND DISCUSSION

The spectra of fluorenone revealed four major bands designated I, II, III and IV in order of increase energy (Figure 1). Band III is the most intense in all solvents investigated, probably due to the fact that it is quantum mechanically and overlap allowed. Band IV is absent in 1,4-dioxane due to non-transparency of the solvent at its absorption wavelength.

Tables 1 - 4 show the average wave number of the transition energies, the corresponding molar absorptive-ties and the oscillator strength of 9-fluorenone in various solvents. The f-values of band IV in all the solvents suggested that its intensity is sensitive solvent perturb-bation. Band II in both polar and non-polar solvents, is characterised by a well-resolved fine structure, while fine structure is observed in band I only in non-polar literature (McConnell, 1952) may be assigned $\pi \rightarrow \pi^*$.

Blue shift is however observed for band IV as the solvent is changed from non-polar to polar solvents and therefore this band is assigned $n \rightarrow \pi^*$.

The intensities of the bands as shown by the f-values in

Table 3. the spectra properties of Band III.

Solvents	υ_{max} (cm^{-1})	$Y_{/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	f
n-hexane	40650.4	42735.0	35217.3	0.49
Cyclohexane	39370.1	41666.7	16265.5	0.24
Propan-2-ol	39062.5	41050.9	4439.5	0.06
Methanol	39370.1	41528.9	11496.5	0.17
1,4-dioxane	39062.5	40000.0	35041.4	0.21
Diethyl ether	40485.8	38610.0	6701.6	0.09

Table 4. The spectra properties of Band IV.

Solvents	υ_{max} (cm^{-1})	$\upsilon_{1/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	f
n-hexane	48076.9	48543.7	9567.8	0.03
Cyclohexane	48543.7	51334.7	4646.2	0.08
Propan-2-ol	46729.0	45248.9	843.4	0.008
Methanol	49019.6	50251.3	5193.3	0.04
1,4-dioxane	-	-	-	-
Diethyl ether	48780.5	50735.7	5867.3	0.05

the Tables 1 to 4 suggested that bands II and I are probably forbidden. The values of their molar absorptivities suggested ^1L_a ($S_0 - S_1$) transition for band I, ^1L_b ($S_0 - S_2$) transition for band II, while bands III and IV are assigned B_b ($S_0 - S_3$) and B_a ($S_0 - S_4$) transition respectively.

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REFERENCES

Baylis NS, Johnson W (1968). Solvent effects on intensities of a weak UV spectra of ketones and nitro paraffin-I. Spectrochim Acta 24A, 551.

Baylis NS, McRae EG (1954). Solvent effect in organic spectra-dipole force and Frank-Condom principle, J. Am. Chem. Soc. 58: 1002-1006.

Caldwell RA, Gagewski A (1970). Fluorenone photosensitised isomerization of trans stillbene inefficiencies both in intersystem crossing and in triplet excitation transfer, Tetrahedron 26: 1303.

Józefówich M, Heldt JR, Heldt J (2002). The red-shift in spectra of fluorenone and 4-hydroxyl fluorenone in alcohol solutions Z. Narutureforsch 57a: 787-796.

Keityaro T, David RK (1966). Spectroscopic properties of low lying excited state of fluoreno, J. Chem. Phys. 45: 1991-1999.

Lee SY, Boo BH (1996). Molecular Structure and Vibrational Spectra of 9-fluorenone, density functional theory studies, Bull. Korean Chem. Soc. 17: 760-764.

Leonard JA, Atkins D, Henry L (1978). Photophysical process in fluorenone, J. Phys. Chem. 82(21): 2304-2309.

McConnell H (1952). Effect of polar solvent in absorption in absorption spectra frequency of n→π* electronic transition, J. Chem. Phys. 20: 700-704.

Richard AC (1969). The quenching of fluorenone fluorescence by trimethylamine, medium effect on lifetime, Tetrahedron Letter 26: 2121-2124.