Short Communication

Perturbation of spectra properties of 3,4-diphenyl thiophene by polar and non polar solvents

Adeogun, A. I.[1]*, Egwuonwu, N. W[1]. and Bello O. S.[2]

[1]Department of Chemistry, University of Ibadan, Ibadan. Nigeria.
[2]Chemistry Department, Ladoke Akintola University of Technology, Ogbomoso. P.M.B. 4000. Ogbomoso, Oyo State, Nigeria.

The UV/visible spectra of 3,4-diphenyl thiophene were obtained in various solvents (both polar and non polar). The wave number of transition energies, corresponding molar absorp-tivities and oscillation frequency were determined. Three bands were obtained in solvents such as cyclohexane, propan-2-ol, methanol and ether. Two bands are obtained in n-hexane and 1,2- dichloroethane, while 1,4-dioxane give a single band. Transitions are assigned to these bands according to their shift due to the effect of solvents.

Key words: 3,4-diphenylthiophene, fluorenone, frank-condon, excited state, polar and non polar solvent, electronic transitions.

INTRODUCTION

Electronic spectroscopy is concerned with electron transi-tion between orbital of different energy, usually from the occupied orbital of highest energy to vacant orbital of lowest energy (Kemp, 1987). The excitation is as a result of absorption of light, the quantum energy (E) of which is a function of frequency (v). However not all absorption of radiation by organic molecules result in electronic excita-tion, the probability of excitation depends on the wave functions of both the ground and excited states of orbital concerned. The rules about which a transition is allowed or forbidden, is a functions of symmetry and multiplicity of the ground and excited state of the orbital concerned (Crandall and Gilbert, 1970). The electronics excitation in a molecule is accompanied by change in vibrational and rotational quantum numbers; therefore what supposes to be absorption lines becomes a broad peak containing vibrational and rotational fine structures. However, the interaction of solute and solvent molecules blurred out the fine structures and a smooth curve is observed (Wil-liams and Flemmings, 1973). The position of maximum absorption is often greatly affected by the solvent nature in which the spectrum was determined. The shift in the

position of maximum absorption band upon varying the solvent from polar to non-polar or dielectric variation has been used to establish empherical classification of elec-tronic spectra into either blue shift or red shift, depending on whether the shift is higher or lower wave number (Unguade, 1953).

Solvent effect on the absorption spectra had been both quantitative and qualitative. Quantitatively, the spectra shifts relative to the refractive index have been derived by Baylis and McRae (1954). The qualitative and compre-hensive treatment of solvent effect have been sought to interpret spectra shift in term of combination of dipole-polarization of solute molecule and hydrogen bonding effect. Brealey and Kasha (1955) correlates hydrogen bonding of solute by the solvent with the blue shift pheno-menon of n→π* electronic transition, in changing from non-polar to polar solvent. Frequency shift are usually att-ributed to specific solute-solute and solute-solvent inter-action in form of hydrogen bonding or bulk solvent pro-prieties. The statistical theory according to Weigang (1960) interpreted spectrum shift as due to unequal per-turbation of light absorber in its ground and excited sta-tes, when surrounded by a particular solvent molecule configuration.

In this study, the spectra of 3,4-diphenylthophene was studied in various solvents ranging from polar to non-

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*Corresponding author. E-mail: abuaisha2k3@yahoo.com.
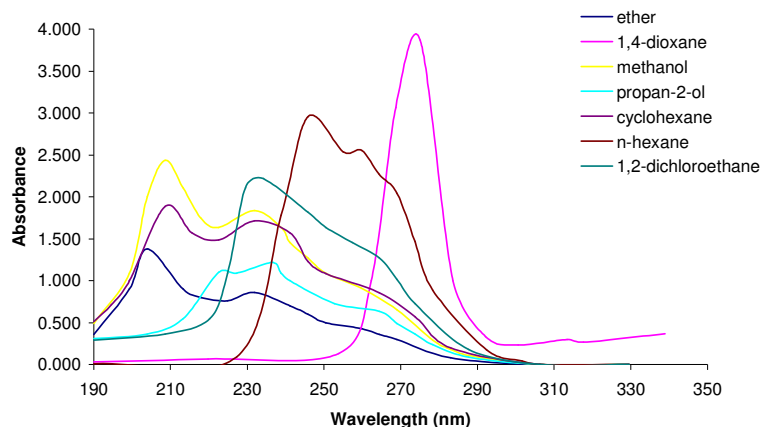
Figure 1. The electronic spectra of 3,4-diphenyl thiophene in polar and non polar solvents.

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	38759.7	35958.3	10466.7	0.20
Cyclohexane	39682.5	36284.5	10510.3	0.23
1,2-dichloroethane	39370.1	35958.3	16638.5	0.36
Propan-2-ol	39682.5	35803.8	10259.9	0.27
Methanol	40000.0	38363.9	15012.3	0.17
1,4-Dioxane	38461.5	35688.5	8250.2	0.15
Diethyl ether	40000.0	38797.9	18351.3	0.15

polar solvents. The effect of solvent media on the observed transitions, oscillator strength, intensities and other absorption parameter were reported.

MATERIALS AND METHOD

Prof. I. Iweibo kindly provided 3,4-diphenyl thiophene and the solvents, which are all product of British Drug House Limited, except the solute. The solvents are spectroscopic grade and were distilled twice at their boiling point. 3,4-diphenyl thiophene was used as provided without further purification. The absorption spectra were run on single beam Unicam (Helios γ) uv/visible spectrometer interfaced with computer and printer.

EXPERIMENTAL

Preparation of solution

Solute of mass between 0.1 - 0.2 mg was carefully weighed and transferred quantitatively into 10 ml volumetric. The solvent was added and total dissolution was ensured. The solution was then made up to mark.

Spectra running

The baseline was calibrated by pipeting 2 cm^3 of blank solvent into a 1.0 cm silica cell. The absorption was scanned between 190 – 600 nm. Definite amount of solution of 3,4 diphenyl thiophene in µL

was added to the blank and the absorption run with instrumental bandwidth set at 1.0 nm and scan speed of 1 or 2 nms^{-1}.

RESULTS AND DISCUSSION

The spectra of 3,4-diphenyl thiophene consists of three bands in cyclohexane, propan-2-ol, methanol and ether. Two bands were obtained in n-hexane and 1,2-dichloroethane, while in 1,4-dioxane a single band was obtained as shown in the Figure 1. The band were designated I, II and III in order of increasing energy.

Tables 1 to 3 summarize the average wave number of transition energies, corresponding molar absorptivities and value of oscillator strength of 3,4-diphenyl thiophene in different solvents. The high values of oscillator strength in all solvents indicate that the transitions are symmetry allowed. Band I shows a shift to a shorter wavelength as the solvent was changed from n-hexane to methanol and this may be assigned to n→π* transitions. Band II is not strongly affected by the change in solvents. Band III shifts to longer wavelength as the solvent changed from n-hexane to propan-2-ol and this may be assigned to π →π* transitions.

Abu-Etitah and Hilal (1975) had reported earlier that steric hindrance is significant in the spectrum of 3,4-di-

Table 2. The spectra properties of Band II.

Solvents	ν_{max} (cm^{-1})	$\nu_{1/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	F
n-Hexane	40650.4	42087.5	12100.3	0.12
Cyclohexane	42735.0	46253.5	16590.3	0.38
1,2-Dichloroethane	42372.9	44306.6	26009.7	0.32
Propan-2-ol	42735.0	45998.2	17530.4	0.38
Methanol	42735.0	40000.0	25157.2	0.48
1,4-Dioxane	-	-	-	-
Diethyl ether	42735.0	40000.0	30896.4	0.32

Table 3. The spectra properties of Band III.

Solvents	ν_{max} (cm^{-1})	$\nu_{1/2max}$ (cm^{-1})	ε_{max} M^{-1}cm^{-1}	F
n-Hexane	-	-	-	-
Cyclohexane	47619.0	50735.7	18250.2	0.37
1,2-Dichloroethane	-	-	-	-
Propan-2-ol	45045.0	47303.7	15082.9	0.24
Methanol	48076.9	49505.0	33155.6	0.33
1,4-Dioxane	-	-	-	-
Diethyl ether	49019.6	49751.2	48696.8	0.24

phenylthiophene and that the spectrum of the composite molecule will be the additive spectra of the subsystem, they also obtained three bands in cyclohexane (Abu and Hillal, 1975). It could be inferred that n-hexane and 1,4-dioxane are not transparent at some part of wavelengths under consideration, hence lesser band were obtained in them. The values of oscillating strength in polar and non polar solvent range between 0.12 and 0.48, which in agreement with literature show that the transition is symme try allowed. The value of intensities shown in Tables 1 to 3 allowed band I to be assigned $^1L_a(S_o-S_1)$, band II assigned ^1L_b (S_o-S_2) while band III is assigned B_b (S_o-S_3).

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