Substituent and solvent effect on the solvatochromic properties of some thiophene derivatives

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ABSTRACT

In this paper, a variant of solvatochromic frequency shift equation that accommodates intensity parameters such as solvent molecular polarizability (α), the molar refraction (R), stark term (μ/r^3) and Einstein Coefficient (k) and oscillator intensity (f) had been developed. This was applied to the study of photo-physical properties of three thiophene derivatives: 3, 4-diphenylthiophene; 3, 4-dicarboxylic-2, 5-diphenylthiophene and benzo[b] thiophene in order to determine their transition polarizability ($\Delta\alpha$), transition dipole moment ($\Delta\mu$) and other molecular properties using UV-visible spectrophotometer. The magnitudes of both the experimental oscillator strength in solution and vapour phase were calculated using Lorentz- reaction field model while the frequencies of the transitions in polar and non-polar solvents were used to characterize the observed bands. The spectra behaviours of these molecules in the different solvents in terms of dipole moments in the ground and excited states and calculated values $\Delta\alpha$ have been interpreted and related to the transition energies, intensities and the molecular structures of the compounds.
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KEYWORDS

Solvatochromic;
Photo-physical;
Intensity;
Transition polarizability;
Transition dipole moment;
Vibrational fine structures.

INTRODUCTION

Heterocyclic and hetero aromatic substances are known to play important roles in the metabolism of all living cells, and their ever increasing large scale production are finding important new uses in fine chemical industries as starting materials or intermediates to many products for pharmaceuticals, agrochemicals, dyestuffs, and electronic applications; and in researches as UV-stabilizers and biological probes[2,16]. Thiophene and its derivative, benzothiophene exhibit a broad spectrum of biological and pharmacological activities as selective oestrogen receptors and modulators for treatment or prophlaxis for prostatic cancer, benign hyperplasis and nervous disorder but, pure thiophene administered to mice through inhalation were found to be distinctly more toxic than benzene[5,15]. For proper understanding of the activity and for further application of these biologically active compounds, it is necessary to investigate their photo-physical properties.

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The studies of the spectra behaviour of five membered hetero-aromatic systems and their derivatives in various solution show that the choice of adequate solution influences the structures of these compounds, which implies the change in their spectroscopic properties[19,23]. This effect could be as a result of either direct interaction between the solvent and the compound or through the influence of solvent interaction with the substituents on the molecule or the substituents interacting with each other. This phenomenon has been observed in organic solute and in polar solutions, especially in the case of thiophene moieties[4].

The aim of this work was to investigate the influence of solvent polarity and substituent types, position and numbers on the photo-physical properties of three thiophene derivatives: 3, 4-diphenylthiophene (DPT); 3, 4-dicarboxylic-2, 5-diphenylthiophene (DCDPT) and benzo[b]thiophene (BT). The varying degrees of perturbation of the potential energy surfaces of ground and excited state by these factors manifests itself by the observed differences in the electronic polarizability (α) and dipole moment (μ) of the excited state relative to ground state of any compound[3]. This is as a result of the changes in charge distribution of the excited molecule due to absorption or emission of radiation.

The understanding of photo-physical processes of electronically excited molecules in solution present a challenging problem as the electronic structures of the excited state is transient and complex because of the high degree of electron correlation. Therefore, the generation of qualitative and quantitative acceptable description of the excited states properties has been a demanding task and different approaches had been used[10]. Owing to the setbacks encountered in the operation and applicability of various approaches to the theoretical and experimental determination of the qualitative and quantitative description of the photo-physical properties of the excited states of molecules[2,22], this investigation decided to use a quantum-mechanical perturbation theory that accommodates intensity parameters such as solvent molecular polarizability (α), the molar refraction (R), stark term (μ/r^3) and Einstein Coefficient (k) and oscillator intensity (f), using the scope of Iweibo *et. al*; (1991) and adopting partly, the Louguett – Higgins and Salem[6] mode of intermolecu-

lar forces, which is effective in revealing the factors governing intensity enhancement. Through this, a linear regression model was developed. This was then applied to determining the transition polarizabilities ($\Delta\alpha$) and transition dipole moment ($\Delta\mu$) of DPT; DCDPT and BT with the principle of absorption spectro-photometry. This research also correlates the properties of the solvated solutes of interest to that of the vapour and in part identifies the key terms that contribute to oscillator parameter in solution based on the rigorous formulation developed by. The effect of substituents on the transition energies of the compounds was also investigated.

EXPERIMENTAL SECTION

Material and methods

The selected solvents n-hexane, dichloromethane and methanol were obtained from British drug House Limited (BDH). These were further purified by re-distillation twice under reduced pressure before use while the solute 3, 4-diphenylthiophene; 3, 4-dicarboxylic - 2, 5-diphenyl thiophene were products of British drug house Limited (BDH) and benzo[b]thiophene was obtained from Aldrich Chemical Company limited. All these were of spectroscopic grade and were used without further purification. All weighing were carried out on Mettler H18 chemical balance.

Ultraviolet-visible measurements

The electronic absorption spectra analysis of the dilute solution of the compounds were carried out in each of the solvents choice in the concentration range of 10^{-6} to 10^{-4} using a highly computerized Shimadzu UV-1650 double beam spectrophotometer coupled with UV-probed 2.31 versions (software) and operated in the wave length range of 190 nm to 400 nm. The optical excitation was done with deuterium lamp as light source in the UV region and tungsten lamp in the visible region. The spectra were scanned at 25ºC, recorded with the instrumental band set at 0.2-1.0 nm and scan speed of 2 nm per second.

Computation of oscillator strength

The experimental oscillator strength in solution $f_{(s)}$ and the molar extinction coefficient $\varepsilon_{(v)}$ for each absorption band in the spectra of the molecules studied

were calculated as a measure of the intensity of absorption of the molecules by means of equation 1.

$$\mathbf{f_{sol}^{expt}} = \frac{4n\left(10^3\ln 10 m_e c^2\right)}{(1+n)^2\left(\pi e^2 N_0\right)}\int \varepsilon_{(v)}\partial v \qquad (1)$$

The integral $\varepsilon_{(\bar{v})}\,\partial v$ were calculated using the assumptions of symmetrical bands in conformity with Gaussian distribution as reported by Iweibo[18]. The vapour phase oscillator strength $f_{(v)}$ values were also computed using the modified Onsager-Abe reaction field model of equation 2

$$\mathbf{f_{aio(s)}}\Big/\mathbf{f_{aio(v)}} = \phi \qquad (2)$$

where $\Phi = \dfrac{9n^3}{\left(2n^2+1\right)^2}$, the correction factor on changing from solution phase to vapour phase.

Determination of ground state polarizability and ground state dipole moments

Using Lorentz-Lorentz expression of equations 3 and 4 below, the theoretical ground state electric polarizability (α_g) for the solutes were calculated from the molar refraction of bond atoms in a molecule of compound in different solvent[11], while the theoretical ground state electric dipole moment (μ_g) of the selected solvent used were computed where necessary from the measurement of stark effect in the microwave spectrtroscopy of gas[17].

$$\mathbf{R} = (^{n^2-1}\big/_{n^2+2})\frac{\mathbf{M}}{\mathbf{d}} \qquad (3)$$

$$\alpha = \frac{3}{4\pi N_0}(\mathbf{R}) \qquad (4)$$

where n is the refractive index of the solvent of choice, R is the molar refraction, N_0 the Avogadro's number (mol^{-1}), M being the molecular weight of the molecule under investigation and d, the density of solvent in which the molecule is dissolved.

Determination of transition dipole moment ($\Delta\mu$) and transition polarizability ($\Delta\alpha$)

The expression in *5,* its rearranged form of *6* and equation 7, developed from the intensity perturbation approximation relate the square root of oscillator strength in solution $f_{(s)}^{1/2}$ to that of the vapour $f_{(v)}^{1/2}$ to the stark

terms (X_2), integral Einstein co-efficient (K), electric polarizability of the solvent, transition dipole moment $(\Delta\mu)$ and transition polarizability $(\Delta\alpha)$ as well as, the ratio of the change in the transition energies of the solute to that of the solvent $\left(\Delta E_{solute}\big/\Delta E_{solvent}\right)$.

$$\mathbf{f_{(s)}^{\frac{1}{2}}} = \mathbf{f_{(v)}^{\frac{1}{2}}} + \frac{3x}{1-x^2}\mathbf{f_{(v)}^{\frac{1}{2}}}\left(\frac{\alpha_b}{r_{\alpha\beta}^3}\right) + \Delta\alpha_{\alpha io}\mathbf{k}\left(\frac{\mu_{\beta 00}}{r_{\alpha\beta}^3}\right) \qquad (5)$$

$$\frac{\mathbf{f_{(s)}^{\frac{1}{2}}} - \mathbf{f_{(v)}^{\frac{1}{2}}}}{\mathbf{X_1}} = \frac{3x\mathbf{f_{(v)}^{\frac{1}{2}}}}{1-x^2} + \Delta\alpha_{\alpha io}\mathbf{K}\frac{\mathbf{X_2}}{\mathbf{X_1}} \qquad (6)$$

$$\mathbf{f_{(s)}^{\frac{1}{2}}} = \mathbf{f_{(v)}^{\frac{1}{2}}}\left(1 + \frac{3x}{1-x^2}\mathbf{X_1}\right) + \Delta\alpha_{\alpha io}\mathbf{k}\left(\mathbf{X_2}\right) \qquad (7)$$

where $\dfrac{\alpha_b}{r_{\alpha\beta}^3} = \mathbf{X_1}$, $\dfrac{\mu_{\beta 00}}{r_{\alpha\beta}^3} = \mathbf{X_2}$ and $r_{\alpha\beta}$, the inter-nuclear distance between the solute and the solvent molecule. These show that a number of data on the solvent and the solute were required to permit the researchers to use these equations reliably in determining the change in the transition dipole moment and polarizability of molecules, from where the excited state dipole moment $\left(\mu^*\right)$, the excited state polarizability $\left(\alpha^*\right)$ can be determined. TABLE 1 summarizes the data used in this way.

RESULT AND DISCUSSION

Presented in Figures 1, 2 and 3 are the representative spectra of the studied thiophene derivatives: DPT, DCDPT and BT in the representative solvents (methanol, dichloromethane and heptanes), while Figures 4, V and VI show the plots of data on intensity perturbation of the different bands associated with each compound in polar solvent using equation 6 above. TABLEs 1 and 2 are the summary of the properties of the band peaks, that is, oscillator strength, energies in wave numbers (full band width), and molar absorptivities of the different transitions for the compounds in the solvents of choice.

3, 4- diphenylthiophene (DPT)

As shown in Figure 1 and TABLE 1, the electronic

TABLE 1 : Summary of the transition energies $\overline{v}_{max}$ (cm^{-1}), molar absorptivities, $\varepsilon_{max}(M^{-1}cm^{-1})$ and other transition properties for the observed absorption bands of DPT, DCDPT and BT in polar and non-polar solvents

Compounds and Transitions	Methanol			Dichloromethane			Heptane		
	$\overline{v}_{max}$ (cm^{-1})	ε_{max} $(M^{-1}cm^{-1})$	$f_{(s)}$	$\overline{v}_{max}$ (cm^{-1})	ε_{max} $(M^{-1}cm^{-1})$	$f_{(s)}$	$\overline{v}_{max}$ (cm^{-1})	ε_{max} $(M^{-1}cm^{-1})$	$f_{(s)}$
DPT									
S_0-S_1	-	-	-	-	-	-	33,784	-	0.021
S_0-S_2	-	-	-	-	-	-	34,722	-	0.027
S_0-S_3	39,063	12,535	0.23	38,911	15,474	0.49	39,370	-	0.18
S_0-S_4	43,103	23,103	0.54	42,373	34,688	0.70	44,248	8,730	0.70
S_0-S_5	49,020	36,285	0.53	-	-	-	50,000	5,560	0.61
DCDPT									
S_0-S_1	-	-	-	-	-	-	33,786	3,589	0.030
S_0-S_2	35,714	11,315	0.30	35,336	14,093	0.13	39,063	4,693	0.095
S_0-S_3	43,103	25,975	0.43	42,077	28,255	0.32	44,248	13,665	0.23
S_0-S_4	49,020	42,088	0.65	-	-	-	50,000	10,836	0.15
BT									
S_0-S_1	33,784	5,754	0.013	33,298	1,222	0.010	-	-	-
S_0-S_2	34,722	3,274	0.020	34,602	1,022	0.015	-	-	-
S_0-S_3	39,063	10,000	0.13	38,960	2,822	0.011	-	-	-
S_0-S_4	44,248	52,480	0.71	42,553	3,550	0.10	43,943	8,730	0.0092
S_0-S_5	49,505	33,925	0.40	-	-	-	48,302	5,560	0.042

spectra of DPT consist of two to five bands, depending on the solvent of choice. In dichloromethane, two prominent bands were observed; three bands were observed in polar-protic methanol while five were observed in heptane. The shapes of these bands are virtually the same in the three solvents of choice and are designated as $S_0{\rightarrow}S_1$, $S_0{\rightarrow}S_2$, $S_0{\rightarrow}S_3$, $S_0{\rightarrow}S_4$ and $S_0{\rightarrow}S_5$ in order of increasing transition energies. The high values of oscillator strength (except for band I or $S_0{'}{!}S_1$ transition in heptane) for the observed bands show that these transitions are symmetry or overlap allowed.

The absence of $S_0{\rightarrow}S_2$ and $S_0{\rightarrow}S_3$ transitions in the spectrum of this compound in dichloromethane and methanol may be ascribed to the non transparency of these solvents to DPT at the wavelength under consideration. Also, $S_0{\rightarrow}S_3$ peak is not strongly affected by solvent while Bands IV and V show a shift to a longer wavelength as the solvent were changed from less polar to a more polar ones and this may be assigned π -π^* transitions. Moreover, Abu Ettitah and Hilal had earlier reported that steric hindrance which is significant in the spectrum of 3, 4-diphenyl thiophene and the specrum

of its composite molecule will be additive spectra of its subsystem.

2, 5-dicarboxylic-3, 4-diphenylthiophene (DCDPT)

Three prominent Bands were observed in the spectrum of this compound in methanol while two and four bands were observed in dichloromethane and heptane respectively. The filter effect of methanol on the compound caused greater distortion of Band IV and in methanol, there is probability of the existence of hydrogen bonding between this solvent and the compound as the compound has greater dipole moment. It interaction with this protic solvent (methanol) is a specific dipole-dipole interaction. Moreover, these peaks lack vibrational fine structure in all the solvents of choice, attesting to greater interaction between the solvents and the compound. The disappearance of Band I in the spectra of the compound in all solvents except in heptane is due to the overlap of this Band with Band II as a result of the mixing of their excited state. The little influence on the position of Band III and IV (Red shift), with increasing dielectric constant of solvent in addition to

M.D.Adeoye *et al.*

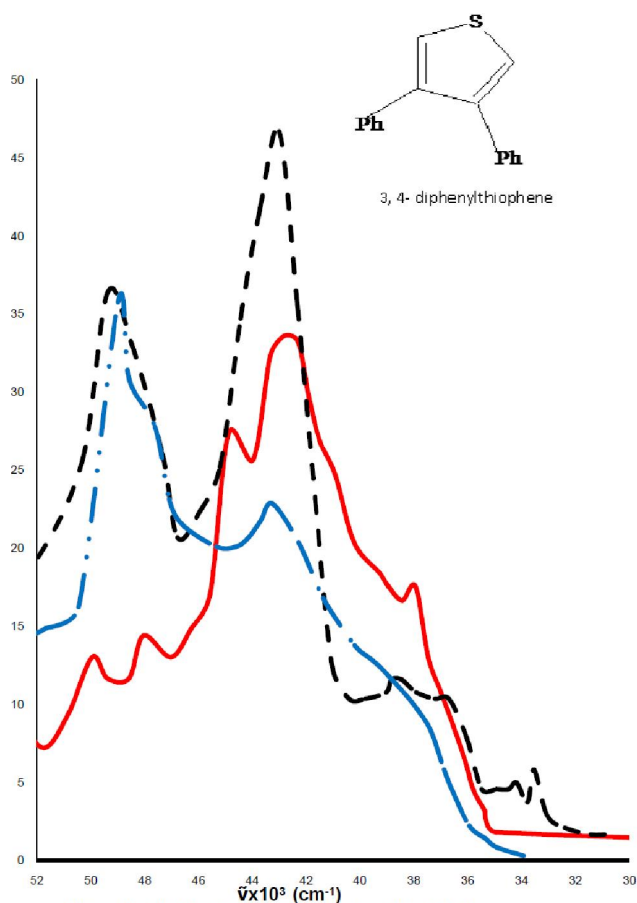their high molar absorptivities suggest their π-π^* nature.

Figure 1 : Electronic absorption spectra of 3,4-diphenylthiophene in dichloromethane(___),heptane (------) and methanol (-.-.-.-)

Benzo[b]thiophene (BT)

As shown in the representative spectra of BT and the summary of the spectral properties of this compound in various solvents of choice in Figures 3 and TABLE 1, there are five distinct observable bands in methanol and heptane as solvents, while four bands were observed in dichloromethane. These bands are designated as $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ in order of increasing energies. The intensities follow the order $S_o \rightarrow S_4 > S_o \rightarrow S_5 > S_o \rightarrow S_3 > S_o \rightarrow S_2 > S_o \rightarrow S_1$. From the evidence of single and double excitation configurational interaction (S-CI and D-CI) using Platt's notation, $S_o \rightarrow S_1$ can be assigned ^1L_a, $S_o \rightarrow S_2$ can be designated as ^1L_b, $S_o \rightarrow S_3$ corresponds to ^1B_b, while $S_o \rightarrow S_5$ and $S_o \rightarrow S_4$ are assigned the ^1C_b and ^1B_a respectively. The band features of thiophene ($v_{max} = 42,000$ cm^{-1}) and benzene ($v_{max} = 39,370$ and $49,019$ cm^{-1}) are

retained in BT with slight shift in the absorption band maximum due to the increasing conjugation as a results of the condensation of the benzene ring system to position b of the thiophene ring[7]. The appearance of extra bands in the benzo[b]thiophene relative to thiophene and benzene moieties is opened to the interpretation expected from the prediction of free electron molecular orbital theory (FEMO). The enlargement of the pi electron system of benzene ring causes the electronic bands to be remarkably shifted to the red, as a result of which a band occurring in the far ultraviolet region now appears as extra bands in the near ultraviolet.
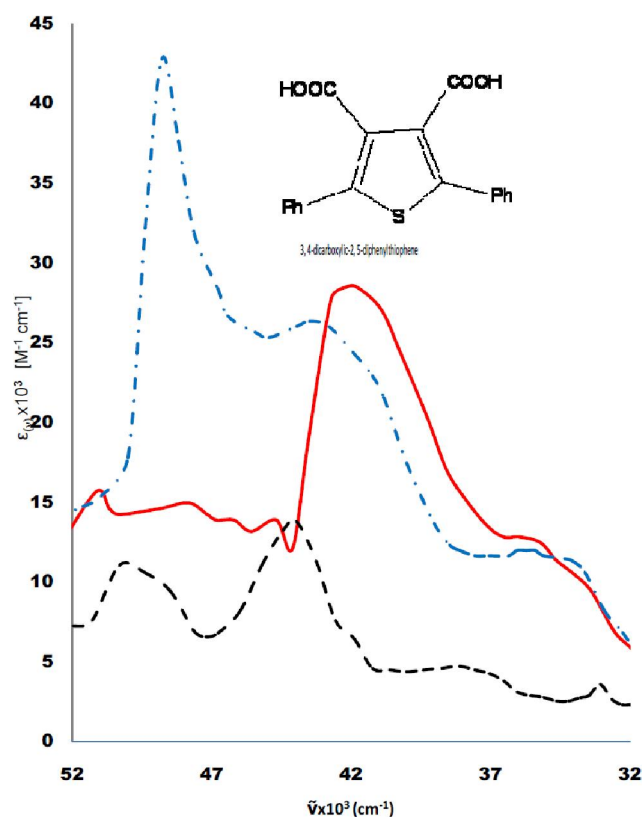

Figure 2 : Electronic absorption spectra of 3,4- dicarboxylic-2,5-diphenylthiophene in dichloromethane(___),heptane (--------) and methanol (-.-.-)

Bands I ($S_o \rightarrow S_1$) and II ($S_o \rightarrow S_2$) are not strongly affected by change in solvent polarity, while positive solvatochromic shift (bathochromic shift) is observed for Bands III ($S_o \rightarrow S_3$) and V ($S_o \rightarrow S_5$) with solvent of increasing dielectric constant, attesting to their π-π^* transitions nature. Negative solvatochromic shift is observed in band IV ($S_o \rightarrow S_4$) as the solvent polarity increases showing that it is of n-π^* origin. These transitions suggest a specific solute-solvent interaction viz,

dipole-dipole or hydrogen bonding interaction in the molecule. The appearance of four bands in some solvent is as results of overlap or mixing of the excited state of the forbidden transitions of the compound with its more allowed transitions and the non transparency of the solvent to the ultra-violet light at which they occurred.
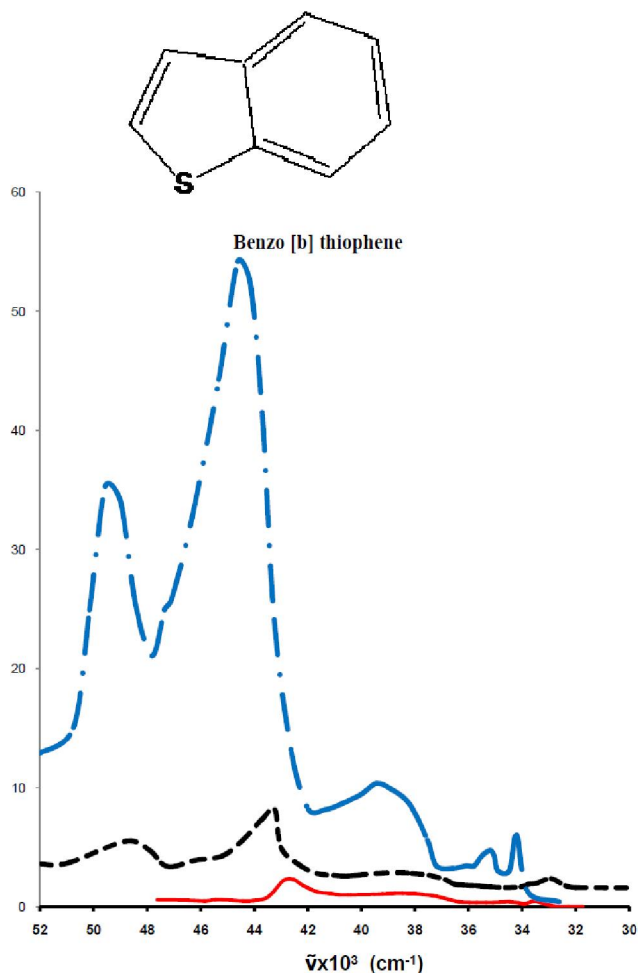
tronic transitions for the given compounds studied. This trend is in harmony with expectation, as in polar solvent, all the Van- der Waals interaction forces between the solute and the solvent (the dispersion interaction included) are in operative in the perturbation of the oscillator strength. These are also positive and additive contributions to the oscillator strength in the vapour phase but in non polar solvent, only the dispersion interaction exist.
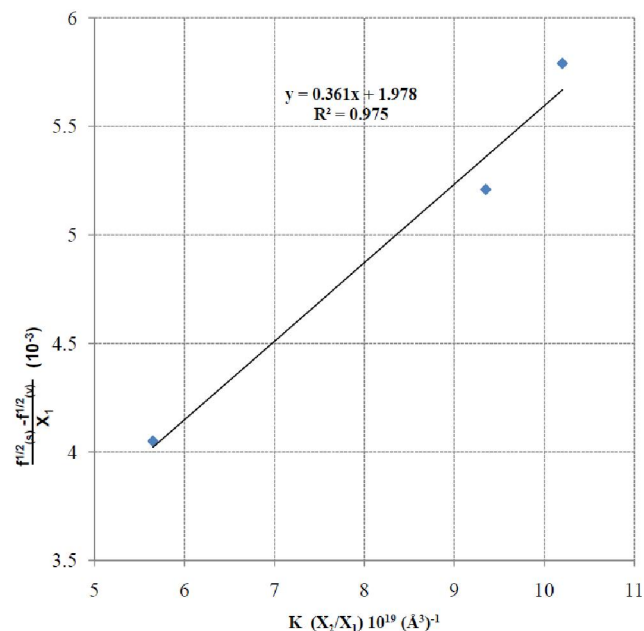

Figure 3 : Electronic absorption spectra of benzo[b]thiophene in dichloromethane(___), heptane (---------) and methanol (-.-.-.-)

Figure 4 : Plots of data on intensity perturbation of the bands 3,4-diphenylthiophene in methanol

Oscillator intensity

(a) Solvent effect on the oscillator strength

Presented in TABLE 1 is the summary of the transition intensities which are recorded in the form of oscillator strength in different solvents for the various transitions of the compounds studied. Generally, the oscillator strength of an electronic transition of any given compound in a series of solvents increases with increase in solvent polarity. This is particularly true for most elec-
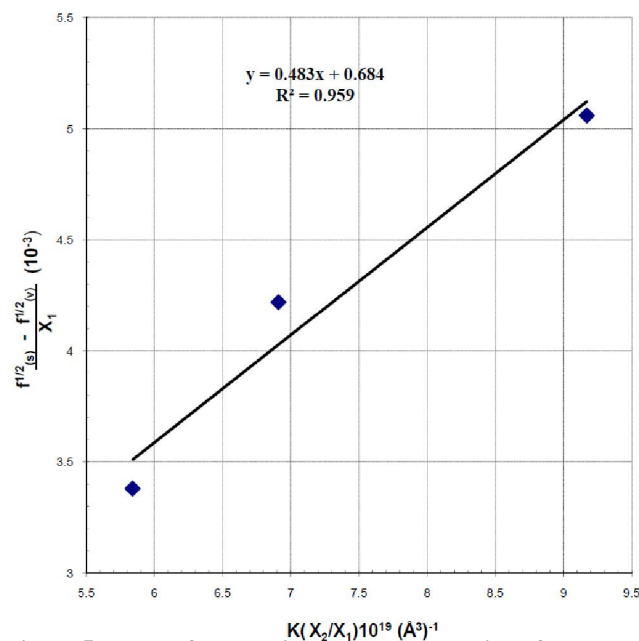

Figure 5 : Plots of data on intensity perturbation of the bands of 3,4-dicarboxylic-2,5-diphenyl thiophene in methanol

TABLE 2 : Summary of the ground state polarizability, transition dipole moment and transition polarizability for the observed absorption bands of DPT, DCDPT and BT in polar and non-polar solvents

Compounds	Methanol				Dichloromethane			
	α (Å^3)	$\Delta\alpha$ (Å^3)	$\Delta\mu$ (D)	$\dfrac{\Delta E_{solute}}{\Delta E_{solution}}$	α (Å^3)	$\Delta\alpha$ (Å^3)	$\Delta\mu$ (D)	$\dfrac{\Delta E_{solute}}{\Delta E_{solution}}$
DPT	0.16	0.30	1.86	11.75	-	-	-	-
DCDPT	0.34	0.50	2.20	0.005	-	-	-	-
BT	0.14	0.40	2.35	0.10	0.11	0.40	0.87	0.018

The oscillator strength values for all the compounds studied in vapour phase in all the choice solvents, when compared with the corresponding ones in solution, reveals that for any given transition, the vapour phase oscillator strength values are lesser than those in solution except in few cases where they are equal. This is in agreement with the expectation from the prediction of equations *2* and *3*, showing that these equations have adequately correlated the spectral properties of the molecules in solution with those of the vapour. It was also observed from TABLEs 1 and the representative spectra of these compounds in different solvents that in general, for the various electronic transitions in a given compound, the magnitude of the oscillator strength (which ranged from 9.20×10^{-3} for the forbidden electronic transition to approximately 0.71 for allowed transition) does not follow the trends described by the theoretical predictions and the molecular orbital calculations of the oscillator strength. The experimentally determined oscillator strength for the compounds in solution and those calculated in vapour phase generally follow the trend

$$f_{(S_0 \to S_1)} < f_{(S_0 \to S_2)} < f_{(S_0 \to S_4)} < f_{(S_0 \to S_3)} \text{ or}$$

$$f_{(S_0 \to S_1)} < f_{(S_0 \to S_3)} < f_{(S_0 \to S_4)} < f_{(S_0 \to S_2)}$$

$$\text{instead of } f_{(S_0 \to S_1)} < f_{(S_0 \to S_2)} < f_{(S_0 \to S_3)} < f_{(S_0 \to S_4)}$$

The solvent correction factors ϕ to oscillator intensity which is attributed to the optical set–up in the spectrophotometer and described by the equation *3* has varied contributions to the oscillator strength (*f*) of different electronic transitions[7]. The fractional contribution of solvent correction factor to the intensity, *q*, as expressed by Abe and Iweibo[20] in the form $q = \dfrac{\Delta f}{f_s}$, generally follows the trend $q\,(S_0 \to S_1) > q\,(S_0 \to S_2) > q\,(S_0 \to S_4) > q\,(S_0 \to S_3)$ showing that the correction factor becomes less important, the more allowed a tran-

sition is. For example, for benzo[b] thiophene, the fractional contribution of the solvent factor to the intensities of the bands observed in methanol are as follows: $q\,(S_0 \to S_1) = 5.0\%$, $q(S_0 \to S_2) = 3.0\%$, $q(S_0 \to S_3) = 2.8\%$ and $q(S_0 \to S_4) = 2.5\%$. The percentage contributions of this correction factor in different compounds vary with solvents but the same trends were observed.

y = 3.136x + 3.131
R² = 0.969
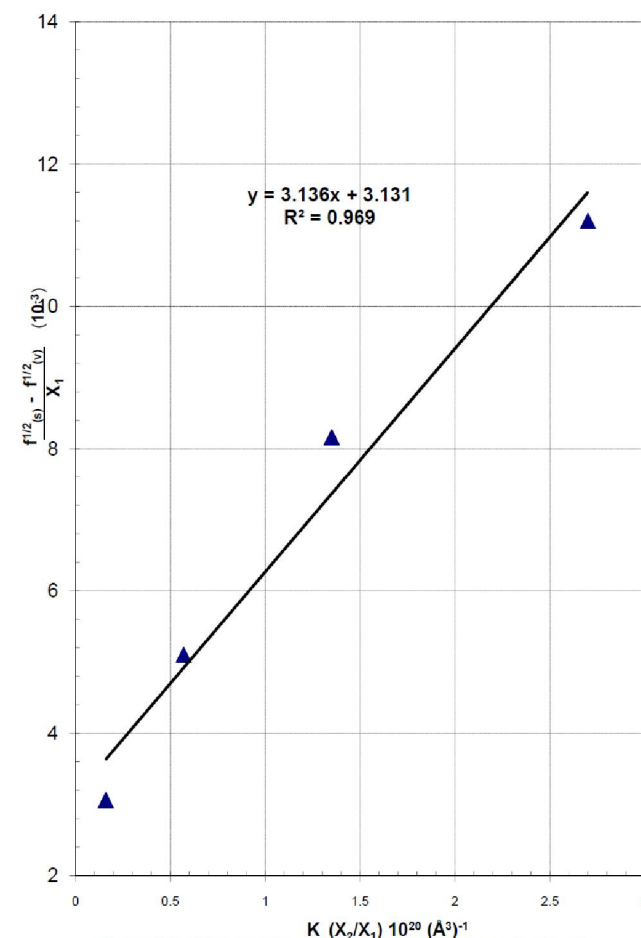
Figure 6 : Plots of data on intensity perturbation of the bands benzo[b] thiophene in methanol

The small values of the oscillator strength are generally in conformity with the degree of forbiddance of the transitions and the proximity of the Bands to the transition from which it can borrow intensity. The $S_0\text{–}S_1$

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or ^1L_b transitions are forbidden both quantum mechanically and by parity while the $S_o–S_2$ or ^1L_a transition is quantum mechanically forbidden but parity or overlap allowed. The observation of these bands in these compounds especially in benzo[b] thiophene and 3,4-diphenylthiophene is normal for most benzene derivatives, but the deviation of the magnitudes of the oscillator strength for the different transitions from the theoretical descriptions are associated with the vibrational borrowing of intensity from more allowed transitions, the removal of the overlap forbiddance by substitution which mixes the higher adjacent states and sometimes changes the symmetry and intensity borrowing from solvent transitions[7].

The intensity of any given transition is given by the square of transition moment as seen in equation 9 where ψ_i and ψ_j are the perturbed wave function for the ground and excited state respectively. The more allowed a transition, the greater the probability that the transition moment will be greater than zero. Thus, the transition moment integral usually show a gradation of values; being smallest for weak and forbidden transitions but approaches a theoretical values of unity for fully allowed transitions.
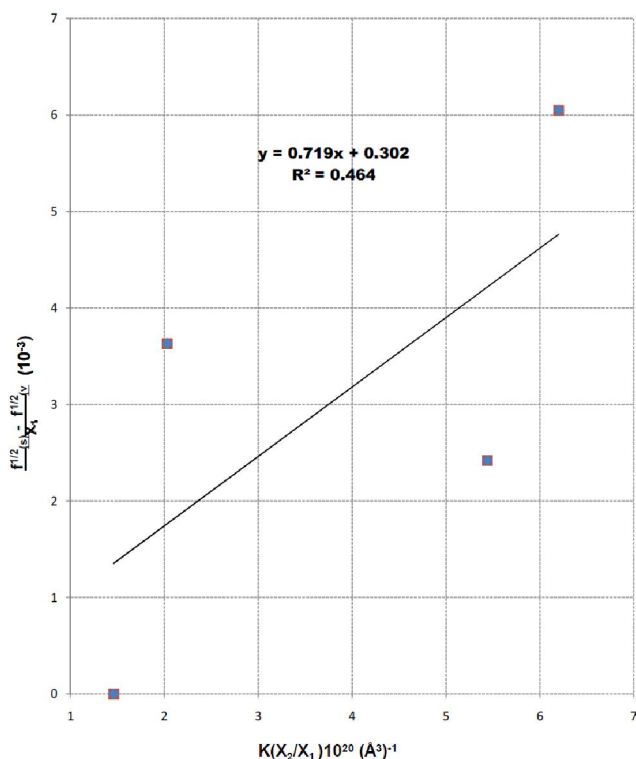

Figure 7 : Plots of data on intensity perturbation on the bands of benzo[b]thiophene in dichloromethane

(b) Substituents effect on the oscillator strength

In the light of the present study, thiophene derivatives studied form the basis of comparison in discussing the effect of substituents on the electronic absorption spectra properties of the molecules. The perturbation of electronic absorption spectra of a given compound by the introduction of substituent (s) into its structural skeleton produces effects that manifest itself in term of changes in the band intensity, frequency shift and band profile and width. These effects are as a result of coulombic interaction of the nuclei and the electrons of the substituents with those of the parent molecules. The outcome of which is an extension of inductive effect and the electromeric or mesomeric effect. The second interaction is by changing the symmetry of the parent molecules which causes a forbidden band to appear as an allowed component of the transition moment in the modified symmetry as seen in group theory, while the third is substituent steric hindrances which results in nuclear configurational changes with its consequences being on the previous effects. In these compounds, these three effects manifest themselves and one or more of it is dominants in each compound.

The spectra displays depict the effects of different substituents on the absorption frequencies of thiophene derivatives studied. And, from the summary of the transition energies ($\upsilon\ cm^{-1}$) and oscillator strength of these compounds in TABLEs 1 and 2, it could be seen that the electronic perturbation introduced by the electron withdrawing substituents (-COOH) at the positions 3 and 4 of thiophene moiety, in addition to the electron donating substituents (-Ph ring) at positions 2 and 5 of thiophene has profound effect on the absorption maximum of DCDPT relative to DPT and fused ring BT molecules. The presence of three to-five band systems in the spectra of BT in different solvents of choice is due to the enlargement of the pi electron system of thiophene system by the benzene ring. These results in bathochromic shifts of λ_{max} and a decrease in the oscillator strength of the various transitions observed for the compound in most solvent relative to other two substituted thiophene compounds. This trend is also observed in the spectra of DCDPT relative to those of DPT. The bathochromic shifts in the peaks wavelength of the compound are due to the extended π- electron manifolds of the two –COOH in conjugation with the substituted thiophene moiety.

Moreover, the strongest transitions in this push – pull molecules have more charge transfer character than their parent thiophene molecule as observed from the literature[9]. It can therefore be inferred from this observation that the greater the number of substituents, the greater the oscillator strength, showing the interplay of all the three effects earlier mentioned.

Furthermore, with Platt's Free Electron Molecular Orbital theory[12], the expansion of the size of π-electron system with a greater number of substituents will not only cause greater ease of shift of an electronic charge (e_i) on a π-electron atom but increases the distance (r) through which such charge is transferred to another atom. This indicates that as the magnitude of transition moment increases, the oscillator strength which is proportional to the square of the transition dipole moment also increases i.e $I \propto / \mu_{ij} /^2 = \sum e_i r_{ij}$. In protic solvents (methanol), there is tendency of hydrogen bonding with the DCDPT. And, since the compound has greater dipole moment, it interaction with this solvent caused the observed transitions of Band III and IV for the compound to be of the same wavelength as those of DPT.

Transition polarizabilty

As observed from the TABLES 1 and 2, for the solvents where the spectra of the compound is having more than three bands, the transition polarizabilities (a measure of sensitivity of different transition to applied electric field) follow the order oscillator strengths of each transition. This trend conforms to the expectations as submitted by Iweibo *et. al.*[7] and supported by the approximate theory which relates the polarizability of any state *ij* to the transition frequency between the state *i* and *j*, and the oscillator strength by:

$$\alpha_{ij} = \frac{e^2}{m_e} \sum_j \frac{f_{ij}}{\omega_{ij}} \qquad (8)$$

where *e* and denote the electronic charge and mass respectively, and $= 2\pi\upsilon_{ij}$ denoting the circular frequency. These trends are reflective of the oscillator strength values for these transitions, and also confirms the positive correlation between the transition polarizabilities $(\Delta\alpha)$ and the integral Einstein coefficient *B*. Besides, in line with the FEMO theory, the polarizability is proportional to the molecular volume (i.e. $\Delta\alpha \alpha a^3$, where *'a'* denotes molecular radii). Consequently, compounds with larger molecular radii show greater transition polarizability. For instance, the molecular radii increase from 3,4-diphenylthiophene and benzo[b]thiophene to 3,4-diphenyl-2,5-dicarboxylicthiophene so do the transition polarizability. The present observation agrees favourably with that of Abe and Iweibo[20] but disagrees with that of Morale. This marked difference probably arises because Morale considered only the dispersion forces in deriving his expression while the present study takes into consideration all possible interaction modes. As expected, the excited state values also follow the order of change in polarizabilities of the various transitions in the given compounds.

The transition polarizabilities $(\Delta\alpha)$ are positive and very small (less than one) for the thiophene derivatives studied. The small values of the transition polarizabilty of these compounds which represent little or no change in the potential energy surface of the ground and the excited state is in agreement with the conclusion that the equilibrium nuclear position (from the consideration of shape of Franck- Condon envelop) of the excited states is only a little shifted relative to that of the ground state, showing that there is only a slight reorientation of the solvent molecule to produce a reaction field which in turn results in a shift between the energies of ground and the excited states. These results are consistent with the reaction field formulation of Liptay (1969, 1976). Moreover, the observed positive values for the transition polarizabilities $(\Delta\alpha)$ show that the excited states of the compounds studied are more polar than their corresponding ground states.

Electronic transition dipole moments

TABLE 2 shows the transition moment (measure of amount of charge transfer associated with transitions) of the compounds in this study. It follows similar trend like that observed for the oscillator strength and transition polarizabilties. This order conforms to the expectation as it agrees perfectly with the expression that relates the intensity *I*, of a transition to the square of integral of transition moment, *M* i.e

$$I \alpha \left| M_{ij} \right|^2 = <\mu_i |e_i r_i| \mu_j>^2 \qquad (9)$$

This implies that the more allowed a transition is, the higher the probability that transition dipole moments $(\Delta\mu)$ will be greater than zero.

Hence, the transition moment integral shows a gra-

dation of values, being smallest for the weak and forbidden transitions but increases considerably for the fully allowed transitions. The small values of $\Delta\mu$ observed for all the transitions in these compounds point to the conclusion that the equilibrium nuclear position of the excited state is a little shifted relative to that of the ground state. This result confirms the selection rule which states that for electronic transition to occur, transition moment integral must not be zero.

CONCLUSION

This work has successfully used a variant of solvatochromic frequency shift equation that accommodates intensity parameters to determine the transition dipole moment and transition polarizability simultaneously for the compounds studied in polar solvents. This provides insight into the nature of electrostatic interactions between these solvents and the compounds studied. The values of oscillator strength in vapour and solution phase have also verified the facts on intensity borrowing from solvents and substituents phenamena. The method gave results that showed minimal dispersion in the values of transition polarizabilities and transition moments. It is expected that the results obtained will form a database for comparison with the results of future determination by electro-optical and molecular orbital calculation methods for these parameters.

Moreover, the solvents perturbation allows the assignment of the transitions to be n→π* and π→π* transitions and confirm that these thiophene derivatves are active, with their excites state been more polar than their ground states.

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