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Structural Characteristics and Reactivity Relationship of Some Thiophene Derivatives

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ABSTRACT

The application of many hetero-aromatic compounds in pharmaceutical and dye industries make the theoretical study of their dipole moment (μ) oscillator strength (f) and other photo-physical properties worthwhile. These properties determine the solubility of many compounds; predict the relationship between their structures, properties and performance. The f, μ, α, transition dipole moment ($\Delta\mu$), vertical Excitation Energies (EE) and the frontier orbitals energy gap ($\Delta E_{LUMO\text{-}HOMO}$) of the optimized structures of 3, 4-diphenylthiophene (DPT); 3, 4-dicarboxylic-2, 5-diphenylthiophene (DCDPT); and benzo[b] thiophene (BT) were determined in solvents of different polarity functions (ΔP) by Time-Dependent Density Functional Theory, using Becke's three parameter with Lee-Yang-Parr modification and 6-31G* basis set theory (TD- DFT- B3LYP/6-31G*). The associated quantum chemical descriptors of $\Delta E_{LUMO\text{-}HOMO}$ such as: Ionization Potential (IP) and global hardness (η) for the compounds were also determined with the same level of theory. The μ of the molecules increases with increasing ΔP, but highest for DCDPT. Bathochromic shifts associated with decreasing EE were recorded for the electronic transitions in DCDPT compare with those observed for DPT and BT. The IP and η increased as ΔP increases, suggesting high stability of these compounds in polar solvents. The energy gaps, its associated parameters and positive $\Delta\mu$ suggested strong activity of the molecules, with DCDPT being the highest. This is in reasonable agreement with the experimental results for the molecules particularly if the experimental uncertainties are considered.

Keywords: Polarizability; photo-physical; excitation energy; oscillator strength; Time Dependent-Density Functional Theory

1. INTRODUCTION

The synthesis and physical characterizations of many hetero-aromatic derivatives have been studied by several authors due to their various applications in industries and pharmaceuticals [1, 2, 3]. Some of their derivatives also constitute important class among Π-conjugated materials that are promising for electronic and nonlinear optical technology [1, 4, 5]. Thus, for proper understanding of the activities and the applications of these biologically active compounds, it is necessary to investigate their electrostatic properties (dipole moment, μ and polarizability, α). The electrostatic properties of molecules in their electronically ground and excited states determine many of their observable structural properties and various applications. The conformational or geometrical changes of chemical substances (especially organic molecules) are important subject for the understanding of many chemical and biochemical

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phenomena, and reactions involving them [6, 7]. The slight changes in the structure of molecules lead to great variations in their physical properties: solubility, stability in ambient air, optical and electronic properties such as energy gap, electron affinity and electron transfer efficiency. Even, the stability of the cation(s) or anion(s) produced by such molecules after electron donation or acceptance depends on structural changes at the molecular level. This because the assumed configurations of many compounds and their corresponding derivatives are governed by different factors: the type, number and position of the substituents whose effects can be mesomeric (delocalization), inductive and or steric; solvent preferential stabilization of a particular configuration or set of configurations; charge transfer and structural change through the process of absorption of photon [1, 6, 8].

Moreover, the photo-physical behaviours of compounds: intensity, shape and wavelength of absorption bands depend on the nature of their environment i. e solute and solvent –solute interaction. In relation to non-polar solvents, polar solvents provide greater solvation energy for the ground state of the solute than the excited state. It could also affect the geometry, as well as, the molecular properties of molecular systems via long range interactions with the solute molecules thereby stabilizing their frontier molecular orbitals [Highest Occupied Molecular Orbitals (HOMO) and lowest Unoccupied Molecular Orbital (LUMO)] [9]. These reactivity indices (HOMO and LUMO energies) and associated parameters: electronegativity, chemical potential ($^{\chi}$), global chemical hardness (η) and electrophilicity index (ω) have also attracted considerable attention in this research. The detailed information about them helps in the understanding of the photophysics and photochemistry of molecules [10, 11, 12, 13]. Theoretical investigations into these properties are of important in the study of the relationship between structures, properties and performance; and in the development and synthesis of derivatives of new compounds with improved properties. However, few works have been reported in this area, especially in the comparative molecular calculations of photo-physical properties for better understanding of the molecular structures, along with using such information to predict the chemical stabilities and activities of compounds [12].

In this present study, the theoretical treatment using Time-Dependent Density Functional Theory using Becke’s three parameter with Lee-Yang-Parr modification and 6-31G* basis set of theory (TD-DFT-B3LYP/6-31G*) was employed to calculate the electronic properties: oscillator strength; *f*, absorption wavelength, transition energies ($\Delta\bar{\upsilon}$), number of transitions, the ground state dipole moment, μ_g, the transition dipole moment, $\Delta\mu$, transition polarizability $\Delta\alpha$, bond length, bond angles, torsion angles, the frontier orbitals energy gap ($\Delta E_{LUMO-HOMO}$) and associated parameters such as: Ionization Potential (IP) global softness and global hardness (η) of the optimized structures of 3, 4-diphenylthiophene (DPT), benzo[b]thiophene (BT) and 3,4-dicarboxylic-2,5-diphenylthiophene (DCDPT). These sets of molecules were chosen to allow the assessment of the donor-acceptor substituents and steric inhidrance on the hetero-aromatic (thiophene) ring. In addition, the study of benzo[b]thiophene serve to describe the effect of increasing conjugated system by linear benzo-annelation (fused benzene ring).

TD-DFT-B3LYP/6-31G* accepted by the ab initio quantum chemistry community is a cost-effective general procedure for studying and treating excitation energies, the physical properties and effect of solvations on the spectra properties of many organic compounds compare with other methods. It has also been reported to always show reliable and promising results that conform with experimental results [1, 14, 15]. Literature survey reveals that to the best of our knowledge, no ab-initio TD-DFT-B3LYP/6-31G* absorption spectra calculations of DPT, BT, DCDPT have been reported so far.

2. THEORETICAL / COMPUTATIONAL METHOD

Computational studies of the compounds: 3, 4-diphenylthiophene; 3, 4-dicarboxylic-2, 5-diphenylthiophene and benzo[b] thiophene were initiated by drawing their molecular structure with 2D-MODEL program. Following the drawing, Gaussian'03 [16] was employed for the ground-state geometry and energy optimization of these molecules in the different solvent, leading to the energy minima [17] and determination of the convergence properties of the molecules [18, 19] without any symmetry constraints; using the hybrid density form of Becke's three-parameter hybrid exchange functional with the Lee, Yang, and Parr's correlation functional (TD- DFT- B3LYP). This method has been reported to give results with respect to geometric parameters that show better agreement with experimentally determined values [1, 3, 14] for many compounds while the basis set permits the molecular wave function the flexibility to distort away from the spherical symmetry in the neighbourhood of each atom in a molecule thereby augmenting the determination of the degree of distortion or polarization in the molecule.

After optimization, energies of electronic transitions and corresponding oscillator strength (for the structures optimized in the ground state) were calculated using the same method. All the calculations in this work have adopted the 6-31G* basis set. The properties investigated for the stable structures included bond length, bond angles, transition dipole moment, transition polarizability, highest occupied molecular orbital (HOMO) and lowest un-occupied molecular orbital LUMO energies, vertical ionization energies and associated properties.

3. RESULTS AND DISCUSSION

The optimized structures of the investigated compounds are as shown in Figures 1. Greater geometric changes are observed for the compounds in solvents of different polarities, measured by the polarity functions $\Delta P = \left(\frac{\boldsymbol{\varepsilon-1}}{\boldsymbol{2\varepsilon+1}} - \frac{\boldsymbol{n^2-1}}{\boldsymbol{2n^2+1}}\right)$. The constant $\boldsymbol{\varepsilon}$ and n required for the calculation of ΔP of these solvents were obtained from the handbook of chemistry and physics [20].

The most widely used measure of polarity for polar covalent bond is dipole moment. DPDCT has the highest dipole moment which decreases with increasing ΔP for the studied compounds. This trend may be due to the high tendency of intra and intermolecular hydrogen bonding of DPDCT in polar solvent and the high tendency of charge delocalization from phenyl ring and lone pair of electron on S atom of the thiophene moiety in it. This observation supports the experimental findings on the studies of the spectra properties of these molecules [21]. The lone pairs of electrons on S atom and phenyl rings are electron donors while the carboxylic groups are electron withdrawing. The intramolecular charge redistribution in DPDCT could be the driven by the large change in dipole moment between DPDCT and polar solvent [23].

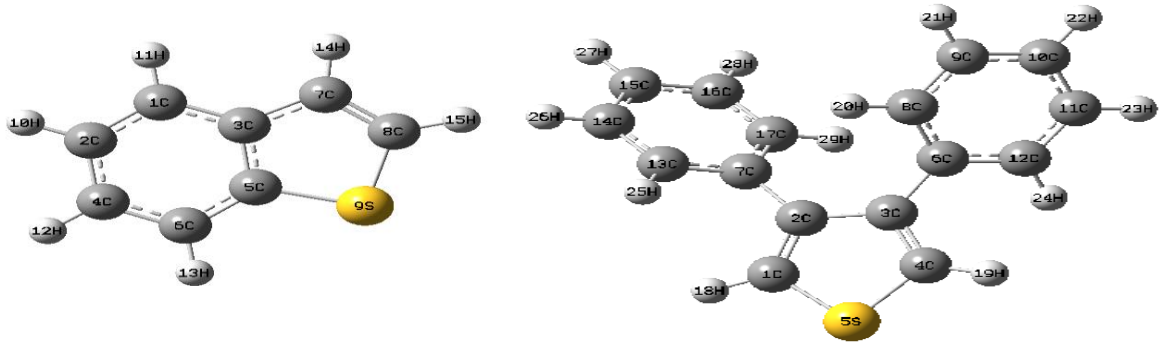
Onsager radius (a) was calculated using the equation:

$$a^3 = \frac{3M}{4\pi N_0 d} = \frac{3M_R}{4\pi N_0}\left(\frac{n^2+2}{n^2-1}\right)$$

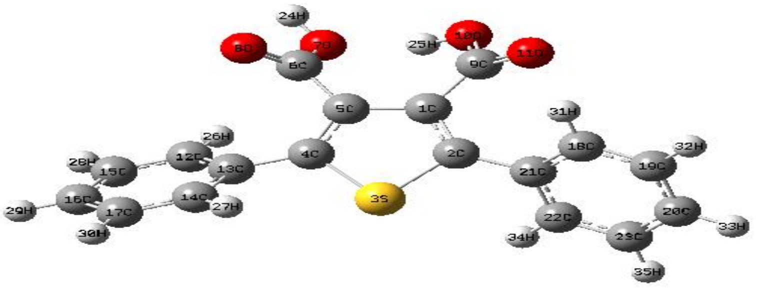
M is the molecular weight, d density of solvent, M_R molar refraction, n solvent refractive index and N_0 the Avogadro's constant [20].

Table 1. Solvent polarity index and calculated Onsager radius (a) for the investigated compounds in different solvents

Polarity index		**Onsager radius** (a) **for the investigated compounds**		
Solvent	**(ΔP)**	**BT (10^{-8}) cm**	**DPT (10^{-8}) cm**	**DCDPT (10^{-8}) cm**
Methanol	-1.191	4.965	4.908	5.456
Dichloromethane	0.218	3.423	4.133	4.593
n-heptane	0.309	4.268	5.154	5.727



Benzo[b]thiophene **3, 4-diphenylthiophene**



3, 4- dicarboxylic-2, 5-diphenylthiophene

Fig. 1. Optimized structures of the studied molecules.

Table 2. TD-DFT-B3LYP/6-31G* computed singlet state excitations for benzo[b]thiophene

		EXCITED STATES						
Solvents		**1**	**2**	**3**	**4**	**5**	**6**	**7**
	ν(cm^{-1})	38,504	41,191	44,506	45,756	48,716	49,142	51,797
Methanol	*f*	0.0955	0.088	0.0001	0.2726	0.0001	0.3006	0.1024
	EE (eV)	4.7739	5.107	5.5179	5.6734	6.040	6.0929	6.4220
	ν(cm^{-1})	38,413	41,102	44,413	45,623	48,629	48,979	51,720
DCM	*f*	0.1041	0.0919	0.0001	0.2951	0.0001	0.3126	0.1031
	EE (eV)	4.7626	5.096	5.5065	5.6564	6.0291	6.0727	6.4124
	ν(cm^{-1})	38,314	40,963	44,201	45,550	48,450	48,842	51,624
n- heptanes	*f*	0.0999	0.0806	0.0001	0.3037	0.0001	0.2991	0.1007
	EE(eV)	4.7449	5.0787	5.4801	5.6473	6.0071	6.0557	6.4005

f : Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 3. TD-DFT-B3LYP/6-31G* computed singlet state excitations for 3, 4-diphenylthiophene

		EXCITED STATES									
Solvent		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	ν(cm^{-1})	38,217	39,725	41,145	41,246	41,925	43,142	43,952	44,543	44,982	44,998
Methanol	*f*	0.1562	0.0013	0.0606	0.0000	0.1127	0.4133	0.0068	0.0091	0.0028	0.0422
	EE(eV)	4.7384	4.9252	5.1014	5.1139	5.1982	5.3489	5.4494	5.5226	5.5771	5.5790
	ν(cm^{-1})	38,158	39,695	41,086	41,234	41,857	43,034	43,937	44,547	44,936	44,960
DCM	*f*	0.1718	0.0014	0.0709	0.0001	0.1112	0.4341	0.0078	0.0103	0.0020	0.0462
	EE(eV)	4.7309	4.9215	5.0941	5.1124	5.1896	5.3342	5.4473	5.5232	5.5714	5.5743
	ν(cm^{-1})	38,153	39,725	40,958	41,215	41,703	42,965	43,900	44,623	44,845	44,859
n-heptane	*f*	0.1667	0.0009	0.0838	0.0004	0.0976	0.4278	0.0139	0.0108	0.0026	0.0443
	EE(eV)	4.7304	4.9252	5.0780	5.1100	5.1706	5.3269	5.4430	5.5326	5.5600	5.5618

f : Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4. TD-DFT-B3LYP/6-31G* computed singlet state excitations for 2, 5-diphenyl-3, 4-dicarboxylicthiophene

		EXCITED STATES									
Solvent		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	ν(cm^{-1})	30,951	33,618	35,841	36,088	36,316	38,311	39119	39,394	39,928	40,522
Methanol	*f*:	0.3246	0.1499	0.0066	0.0190	0.0091	0.0034	0.1576	0.0092	0.0411	0.0922
	EE(eV)	3.8375	4.1680	4.4437	4.4744	4.5027	4.7500	4.8501	4.8830	4.9505	5.0256
	ν(cm^{-1})	30,787	33,629	35,708	35,991	36,311	38,165	39,020	39,316	39,742	40,476
DCM	*f*	0.3284	0.1666	0.0092	0.0213	0.0097	0.0092	0.1551	0.0054	0.0387	0.1078
	EE(eV)	3.8171	4.1695	4.4273	4.4623	4.5019	4.7319	4.8378	4.8745	4.9275	5.0185
	ν(cm^{-1})	30,540	33,882	35,399	35,885	36,649	37,636	38,662	39,279	39,524	40,269
n-heptanes	*f*	0.2958	0.1773	0.0254	0.0333	0.0089	0.0348	0.0938	0.0328	0.0090	0.0800
	EE(eV)	3.7865	4.2009	4.3890	4.4492	4.5440	4.6663	4.7935	4.8700	4.9004	4.9927

f: Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 5. Theoretically computed transition dipole moment (D) of the compounds

	TRANSITION STATES									
Solvents	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Benzo[b]thiophene										
Methanol	0.903	0.839	0.0203	1.400	0.023	1.419	0.801			
DCM	0.945	0.858	0.020	1.459	0.024	1.449	0.807			
n-heptane	0.927	0.805	0.199	1.482	0.025	1.419	0.810			
3,4-diphenylthiophene										
Methanol	1.156	0.102	0.696	0.015	0.941	1.776	0.225	0.260	0.141	0.556
DCM	1.194	0.107	0.754	0.024	0.935	1.810	0.241	0.276	0.122	0.570
n-heptane	1.218	0.086	0.821	0.058	0.878	1.823	0.323	0.283	0.138	0.582
2,5-diphenyl-3,4-dicarboxylicthiophene										
Methanol	1.786	1.211	0.292	0.417	0.287	0.172	1.152	0.213	0.582	0.936
DCM	1.858	1.277	0.246	0.441	0.297	0.281	1.143	0.278	0.566	0.866
n-heptane	1.874	1.313	0.888	0.553	0.282	0.552	0.894	0.524	0.275	0.809

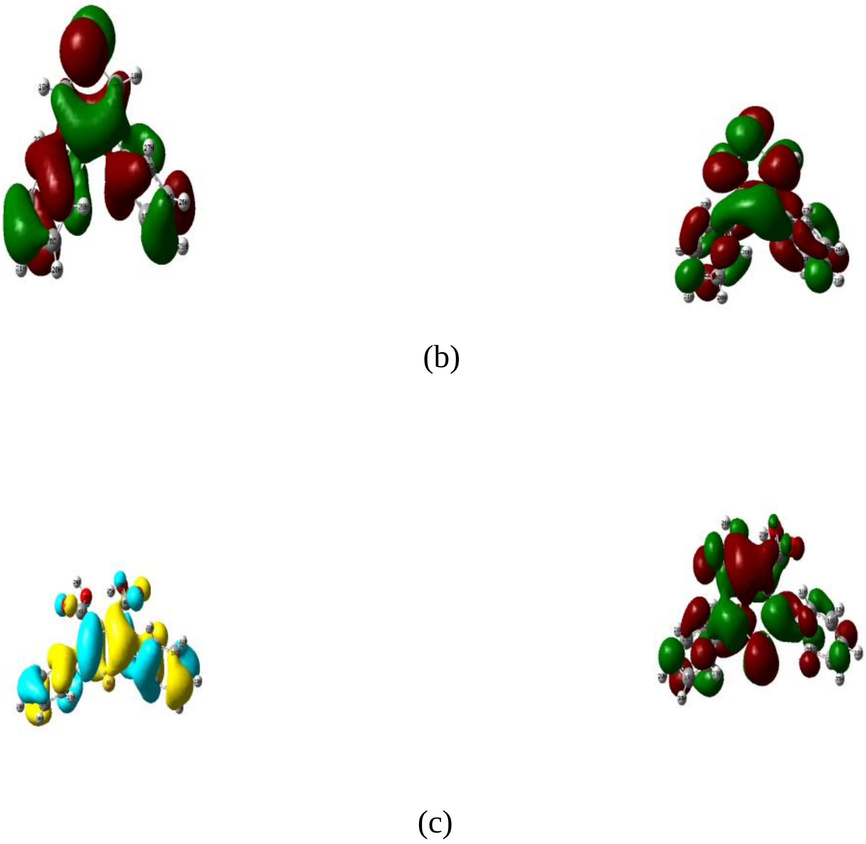
Table 6a. HOMO, LUMO, energy gaps (LUMO - HOMO) and related molecular properties of molecules

Solvents	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**$E_{(LUMO HOMO)}$ (eV)**	**ϗ (eV)**	**ω (eV)**	**IP (eV)**	**EA (eV)**	**η (eV)**	**S (eV)**	**μ (D)**	**α (Å^3)**	**E_S (a.u)**
Benzo[b]thiophene												
Methanol	-6.056	-0.752	5.304	-3.404	2.185	6.056	0.752	2.654	0.190	1.0954	56.18	-706.6610
DCM	-6.042	-0.742	5.299	-3.392	2.171	6.042	0.742	2.650	0.189	1.0430	55.64	-706.6598
n-heptane	-6.011	-0.729	5.282	-3.370	2.150	6.011	0.729	2.641	0.189	0.8576	55.47	-706.6560
3,4-diphenylthiophene												
Methanol	-6.132	-0.813	5.319	-3.473	2.267	6.132	0.813	2.660	0.188	0.9710	99.51	-1015.126
DCM	-6.117	-0.080	5.317	-3.099	1.807	6.117	0.080	2.658	0.188	0.963	99.80	-1015.124
n-heptane	-6.086	-0.775	5.310	-3.430	2.216	6.086	0.775	2.655	0.188	0.848	100.67	-1015.119

Table 6b. HOMO, LUMO, energy gaps (LUMO - HOMO) and related molecular properties of the compounds

Solvents	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**$E_{(LUMO-HOMO)}$ (eV)**	**ϗ (eV)**	**ω (eV)**	**IP (eV)**	**EA (eV)**	**η (eV)**	**S (eV)**	**μ (D)**	**α (Å^3)**	**E_S (a.u)**
3,4 dicarboxylic-2,5 diphenylthiophene												
Methanol	-6.321	-1.922	4.399	-4.122	3.862	6.321	1.922	2.200	0.227	6.035	131.36	-706.6609
DCM	-6.324	-1.935	4.389	-4.130	3.885	6.324	1.935	2.195	0.228	6.378	130.40	-706.6598
n-heptane	-6..332	-1.974	4.358	-4.153	3.958	6.332	1.974	2.179	0.230	5.106	130.10	-706.6560

(a)


(b)

(c)

Figure 2: HOMO (left) and LUMO (right): Electronic densities of (a) benzo[b] thiophene (b) 2, 3-diphenylthiophene and 3, 4-dicarboxylic-2, 5-diphenylthiophene calculated at the TD-DFT/6-3IG* level of theory.

3.1 Electronic Properties

Tables 2-4 show the TD-DFT-B3LYP/6-31G* computed singlet state excitations for the studied compounds in the solvent of choice. The molecular orbital calculations on the excited singlet states of the compounds whose optimized electronic structures are as shown in Figures 1 were performed in order to confirm on theoretical basis the experimental findings [21] on their reactivities and the charge transfer phenomena of their excited states. The foremost step of any photo-induced process is the formation of a collective excited state whose properties (electronic energy levels, oscillator strength, dipole moment and others) depend on the structures of the constitutive molecules [12].

From the raw output data of the excited state quantum descriptor of the molecules in the representative solvents (dichloromethane, methanol and n-heptane) in Tables 2-4, seven to ten excited states were observed for the UV-absorption spectra of the molecules. This is in contrast to the experimental results where one to five bands were recorded in different solvent in the UV- region of the spectrum [21]. This is likely due to the absence of solvent interactions which might perturb the energy levels of the transitions, making most bands to be well resolved computationally [3]. The oscillator strength values of each excited state correlate with the intensity of the peaks at its wavelength. It was observed that the higher level excited states (except in 2,5-dicarboxylic-3,4-diphenylthiophene) contributed most to the intensity of the peaks.

3.5- diphenylthiophene

This recorded ten excited states in the UV-region of its spectra (Table 3). Hypsochromic (blue) shifts were observed for all transitions in this molecule with solvent of increasing ΔP except for the excited state 2 where the wavelength are retained while red shifts were recorded for the excited state 8 in polar solvent relative to non-polar solvent. This signifies that both n- π* and π-π* transitions occur in the compound as reported in the experimental findings [21]. The π-π* transitions which occur as a result of red shift can be ascribed to an increase in contribution of the lone pair of electrons on the electronegative S-atom to the delocalized π-electron system [24]. For this transition, the excited states are more solvated than the corresponding ground state, and the dipole-dipole interaction with the solvent molecules lowers the excited state energy more than the ground state [9]. The bands in the wavelength (in wave-number) at 43,103cm^{-1} and 43,103cm^{-1} (in Methanol); 39,370 cm^{-1} (in n-heptane) and 38,991 cm^{-1} (in dichloromethane) recorded in the experimental results [21] are also retained in the theoretical results but with slight shift to shorter wavelength theoretically due to solvent interactions.

2, 5-dicarboxylic-3, 4-diphenylthiophene

The computational studies of the UV-studies on this compound recorded bathochromic shift associated with decreasing vertical excitation energies (EE) for all the observed transitions except the excited states 2 and 5. This indicate greater charge distribution and increasing delocalization of electrons as a result of extension of conjugation (Figure 1) and greater charge transfer phenomena in this compound relative to other thiophene derivatives studied. The low intensity and blue shift of most of the observed bands (except bands 2, 4 and 5) in polar solvent relative to non-polar solvent supports the n- π* nature of these bands, since in polar and hydroxylic solvent, the n-electrons are blocked by the solvent hydrogen ions (H^+) through inter and intra-molecular hydrogen bonding (from adjacent carboxylic groups on the thiophene system). Consequently, the excitation of n-electron is difficult i. e; the n band will appear as ill-defined band in polar solvent as attested to by the high excitation energies for the molecule in polar solvents [25, 9].

Benzo[b]thiophene

Seven singlet excited states were recorded for the UV spectra band studies of this compound (Table 4). The highest peaks are in the wavenumber range of 45,510 cm^{-1} - 49,142cm^{-1} with excitation energies in the range of 5.33eV-5.35eV. The strongest transition observed at 49,142 cm^{-1} in methanol, 48,979 cm^{-1} in dichloromethane and 48,842 cm^{-1} in n-heptane suggest a blue shift (hypsochromic shift) in solvent of high dielectric constant (methanol). This transition is therefore assigned n- π* transition as a result of solvent interaction (intermolecular hydrogen bonding) with the lone pair of electron on the S- moiety on the molecule. This was also observed for other transitions. Associated with the blue shifts are high excitation energies, suggesting that the ground state of the transitions being more polar than their corresponding ground states in polar solvent relative to non-polar solvent. Moreover, the transition intensities (*f*) of all the bands recorded in the UV-region is low in heptane relative to other solvents. This was also observed experimentally [21], attesting to the low solubility of this molecule in heptane and its nontransparency in the spectra region of interest. There π- π* transitions or red shifts recorded experimentally were absent computationally but the band feature of benzene (49,019cm^{-1}) and thiophene (42,101 cm^{-1}) reported in the experimental findings are also recorded computationally but with slight shift to longer and shorter wavelength respectively.

3.2 Solvent and substituents effect on the oscillator strength

Presented in Tables 2-4 are 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 electronic transitions for compounds in a given solvent increases with increasing solvent polarity [26]. This is particularly true for most electronic transitions for these compounds. 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 [27].

For the excited states observed for the absorption spectra of the compounds studied, transition intensities (*f*) are small in conformity with the degree of forbiddance of the transitions (Tables 2-4). These decrease with decreasing solvent polarity except in few cases. For these compounds, 2, 5-diphenyl-3, 4-dicarboxylicthiophene recorded the highest oscillator strength associated with its excited states in the three solvents. This indicates greater charge distribution associated with the excitation of its electrons. The common excited level with highest oscillator strength occurred at the excited state 1 for 2, 5-diphenyl-3, 4-dicarboxylicthiophene; 6 for 3, 4-diphenylthiophene; 4 in n-heptane and 6 in both methanol and dichloromethane for benzo[b]thiophene.

3.3 Substituents effect on the spectra properties

The different perturbation effects of substituents on the electronic absorption spectra of these compounds indicate great changes in their band positions and intensities. The excited states of 3, 4-diphenylthiophene compared with those of benzo[b]thiophene are red shifted due to the extended conjugation from the phenyl rings. The principal effect of this contributes to the π-electron of the molecule and increases the packing density due to the elongated molecular sizes [28, 25], as indicated in Table 1. Thus, the overall electronic transitions increase slightly towards longer wavelength and higher intensity (bathochromic and hyperchromic effects) in both polar and non-polar solvent relative to benzothiophene. The additional substituents (electron withdrawing) on the diphenylthiophene ring (as in 3, 4-dicarboxylic-2, 5-diphenyl thiophene) also have profound influence on the spectra parameters. The results recorded bathochromic shift associated with decreasing vertical excitation energies (EE) for all the transitions except the excited states 2 and 5 when compare with the recorded transitions observed for 2 ,3-diphenylthiophene and benzo[b]thiophene This indicated greater charge distribution and increasing delocalization of electrons as a result of extension of conjugation, increasing activity and greater charge transfer phenomena in this compound relative to other thiophene derivatives studied. The most interesting effect of changing solvent polarity is that, 3, 4-

dicarboxylic-2, 5- diphenyl thiophene, although possesses the electron donating phenyl ring systems as substituents; does not exhibit the similar trend in its absorption spectra with 3, 4-diphenyl thiophene. There are modifications in the band gaps (EE), band position and intensity. This could be as a result of the probability of intra-molecular charge transfer (ICT) characteristic from the phenyl rings (donors) moieties to the carboxylic (acceptors) moieties [19]. The π-π* nature (as a results of bathochromic shift) of the excited states 2 and 5 is an indication of the stability of the polar excited states of the molecules relative to the ground states as the polarity of the solvent medium increases i.e lower excitation energy is required in methanol than in n-heptane. Although, dichloromethane is characterized by smallest ε and ΔP (Table 1), the charge transfer bands show a small red shift in the absorption maximum of the compound in it than in methanol. This shift can be explained on the basis of the amphiprotic character of methanol (i.e the alcohol can behave as proton donor or acceptor) towards the lone pair of electron on the sulphur-group on thiophene ring through hydrogen bonding. These two types of bonding will compensate each other, indicating that the small blue shift observed in methanol is the net effect of increasing solvent polarity. The effect of extension of π-conjugation is evident from the absorption spectra of the compound relative to other thiophene molecules as reported by [21].

3.4 Electronic transition dipole moments and polarizabilities.

The calculated transition dipole moment values (Δμ) for the different transitions (Table 8) are functions of the oscillator strength (*f*) values. The higher the *f*, the larger the dipole moment for each compound as confirmed by [21] and supported by the approximate theory [26, 12]. 3,4-dicarboxylic-2,5 diphenylthiophene recorded the highest μ* and α* (which increases with a decrease in optical gap) among the studied thiophene derivatives. This is attributed to the increase in size and planarity of the molecules as substituent on the conjugated system increases. In comparison with experimental estimation [21], the calculated increase in μ shows the strong activity of these thiophene compounds with 3, 4-dicarboxylic-2, 5 diphenylthiophene being the highest. The presence of ICT character of the singlet state is also reflected by the increase in the dipole moment and lower values of optical gap and excitation energy of 3,4-dicarboxylic-2,5 diphenylthiophene. Overall, the results show that 3,4-dicarboxylic-2,5 diphenylthiophene is the most active specie of the studied hetero-aromatic molecules, with tendency to exhibit highest electro-optic responses on the basis of its largest size, highest planarity, least energy gap and largest polarizability followed by benzo[b]thiophene and 3,4-diphenylthiophene.

3.5 HOMO-LUMO energy gaps and related molecular properties.

The calculated HOMO-LUMO using TD-DFT possesses solid state packing effect and the aqueous state has been taken into consideration. Figure 2 shows the HOMO and LUMO structures for the studied compounds. Their HOMO and LUMO are both localized on the thiophene and phenyl rings as well as fused benzene in DPT and BT. Similar trend was observed for DCDPT but LUMO being more localized on both acceptor and donor moieties while HOMO was slightly less localized on the carbonyl carbon of one of the carboxylic groups. All electronic properties are hence governed by these orbitals.

The HOMO-LUMO energy gap reflects the chemical activity of the molecules [22, 29]. The LUMO is an electron acceptor and represents the ability of any molecule to obtain an electron (or electrons) whereas the HUMO represents the ability to donate an electron [30] since it is the outermost molecular orbital with electrons. Consequently, a HOMO→LUMO interaction implies the movement of electrons to or from the aromatic parts of the molecules, the substituents on the ring system of molecules and the lone pairs of electrons on the S-atom of the thiophene moieties. Associated within the frame work of self-consistent field molecular orbital (SCF-MO) theory, other molecular properties can be expressed through the E_{HOMO} and E_{LUMO} (optical gaps) [29, 13, and 30]. The larger the optical band gaps, the harder the molecules and electron charge transfer is most when the optical band gap is low. Thus, the calculated values of ϗ, EA, IE, ɳ, χ, ω and S expressed through HOMO and LUMO energy values for the molecules are as presented in Table 9.

For all the molecules, the HOMO, LUMO and the optical band gaps has been found to be closer in methanol and dichloromethane, but differ on changing to n-heptane. This shows that these properties are greatly influenced by solvent polarity, and are higher in polar solvent relative to non-polar solvent. This indicates that electron distribution, conductivity, reactivities or activities of these compounds are greatly reduced in polar solvents. The decrease in optical band gaps observed for 3, 4-dicarboxylic-2, 5-diphenylthiophene relative to 3, 4-diphenythiophene and benzo[b]thiophene shows its high conductivity, and further attests to greater charge distribution associated with this molecule. This is because, with the extended conjugation of 3, 4-dicarboxylic-2, 5 diphenylthiophene and its largest size (Table 1), the HOMO-LUMO orbitals are closer; and the energy gaps decreases. This is in excellent agreement with the experimental findings [21]. Moreover, the values of the calculated molecular descriptors/ structure-activity relationship properties are dependent on the substituents attached to the parent ring of the molecules. These slightly depend on the ΔP. The electrotronegativity index (χ) values for these molecules in the representative solvents follow the trend $\chi_{\text{n-heptane}} < \chi_{\text{DCM}} < \chi_{\text{methanol}}$ (i.e increases with increasing solvent polarity). In all the solvents, χ values are relatively higher in 3, 4-dicarboxylic-2, 5 diphenylthiophene compare with the other studied thiophene derivatives, attesting to its strong affinity for electrons. This is also indicated by its relatively high electron affinity values; high chemical potential and ionization energy when compare with other thiophene molecules studied. However, for the three thiophene derivatives, the global handness (ɳ) increases with increasing solvent polarity but these are lowest in 3, 4-dicarboxylic-2, 5 diphenylthiophene in all the solvents. And, associated with these are the relatively higher global softness (*S*) which is an indicator of the high succeptibility or unstability of the molecule to UV–light, i.e, high reactivity. This indicate that 3, 4-dicarboxylic -2, 5-diphenylthiophene will probably be a better candidate for the development of organic photovoltaic cell than the reported 3, 4-diphenylthiophene [31, 32].

Also, the calculated Self Consistent Field (SCF) solvation energy (E_s) of these molecules slightly decreases with decrease in solvent polarities. Thus, the selected TD-DFT based molecular descriptors vary systematically with the solvent polarity, number and position of substituents.

CONCLUSION

It follows from the analysis of the calculated quantum chemical descriptors (ϗ A, I, η, χ ω and S) that the polar solvents stabilized the observed transition bands of the studied compounds relative to non-polar solvents. 3, 4-dicarboxylic-2, 5 diphenylthiophene will probably have more photovoltaic application than the reported 3, 4-diphenylthiophene as affirmed from their global softness and chemical potential values.

Density functional theory with TD-DFT B3LYP/6-31G* levels has also been found to provide support for the earlier experimentally observed electronic properties of the studied systems in this research when the experimental errors, solvent interactions and various assumptions and simplifications made experimentally are considered.

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