The Electronic Spectra of Some Phenylthiophenes. A Molecular Orbital Treatment

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The electronic absorption spectra of the thiophene derivatives: mono, di-, and poly-phenylthiophenes are studied in both polar and non-polar solvents. The interaction between thienyl and phenyl chromophores is investigated both experimentally and theoretically. Assuming planar and perpendicular conformers, molecular orbital calculations are carried out on 2-phenylthiophene and on 3-phenylthiophene using the Localized-Orbital Model. The results show: (i) the planar conformer is more adquate than the perpendicular one, (ii) the near UV spectra of the two isomers are similar though their degree of conjugation is different, and (iii) excited states arise from substantial configuration interaction. There is a good agreement between the observed and calculated spectra of the two isomers.

The electronic structures of the studied compounds are of interest since though aryl thiophenes are of chemical and biological importance, yet their chemistry has made no remarkable progress. Substitution in the thiophene ring affects the spectrum in a way which depends on the type of the substituent and position of substitution. Ostman[1)] used the ω technique and the "p" and "d" models for the "π" orbitals and showed that α-position in thiophene is more active than the β-position. It is found that the position of the longest wavelength band of 2-substituted thiophenes is lineary related to the ^1L_a band of monosubstituted benzenes.[2)]

Many molecular orbital calculations have been reported on the π-electron system of thiophene and related compounds.[3—6)] The electronic spectra of some thiophene derivatives are interpreted *via* SCFMO calculations,[7—9)] and the results agree with the experiment. It has been shown that d-orbital participation is considered trivial in correlation with the spectra of thiophene[4—10)] as well as the spectra of composite molecules containing thiophene.[11,12)]

The spectra and theoretical treatment of arylthiophenes are not thoroughly studied in the literature. The extended Hückel theory has been applied to 2- and 3-phenylthiophenes and showed that the molecules have an equilibrium conformation twisted by 37° from the planar conformer.[13)] Elpern and Nachod[14)] reported the spectra of 2- and 3-phenylthiophenes and interpreted them on the basis of linear and cross conjugated systems.

In this work, the electronic spectra of some phenylthiophenes are investigated. Results (experimental and theoretical) show that differentiation of phenylthiophene to linear and cross conjugated systems cannot be done on the basis of their spectra. The LOM has been applied successfully to conjugated hydrocarbons made up of two unsaturated residues joined by a single bond.[15)]

Experimental

The studied phenylthiophenes were prepared by the methods reported in the literature,[16—18)] the products were purified by repeated crystallization and the melting points correspond well with the reported values. The compounds, 2,4- and 3,4-diphenylthiophenes, were kindly provided by Prof. El-Gindy.

Solvents were purified as given before[19)] and the spectra were scanned on a Beckman DK Spectrophotometer using 1.0 cm fused silica cells.

Results and Discussion

Interpretation of the Spectra. The electronic absorption spectra of 2-phenylthiophene are given in Fig. 1 using ethanol, 1- and 2-propanol as solvents. The shift in band maxima depends on both dipole moment and refractive index of the solvent as shown by Bayliss and McRae.[20)] The spectrum in the 330—200 nm region includes three electronic transitions identified as I, II, and III (starting from lowest energy). Two transitions (I and II) are overlapping and appear as a broad asymmetric band in the 300—240 nm region and the third transition appears as an intense shoulder in the region of 220 nm. That the broad asymmetric band consists of two overlapping transi-

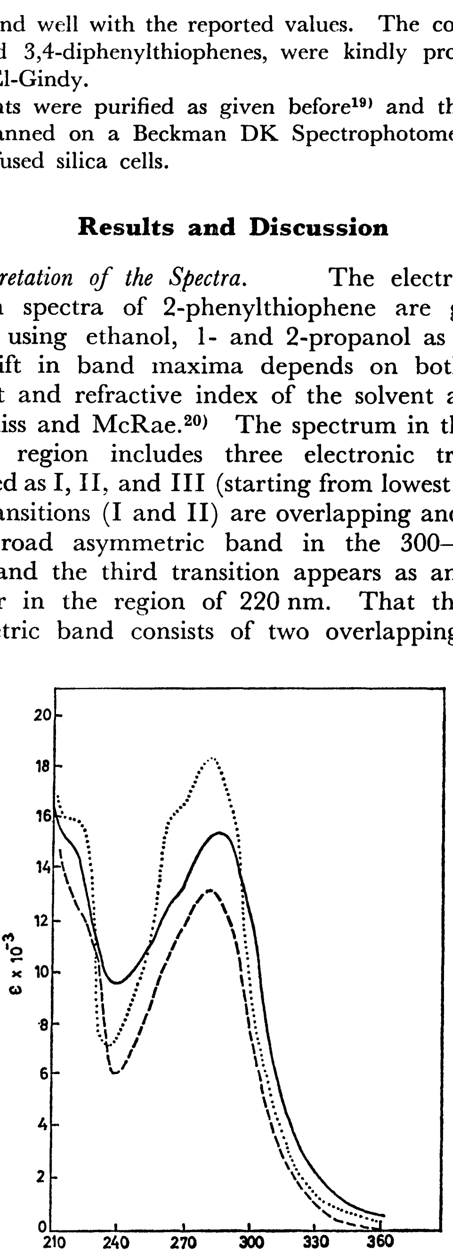

Fig. 1. Electronic absorption spectra of 2-phenylthiophene in 2-propanol (——), ethanol (----), and propanol (······).

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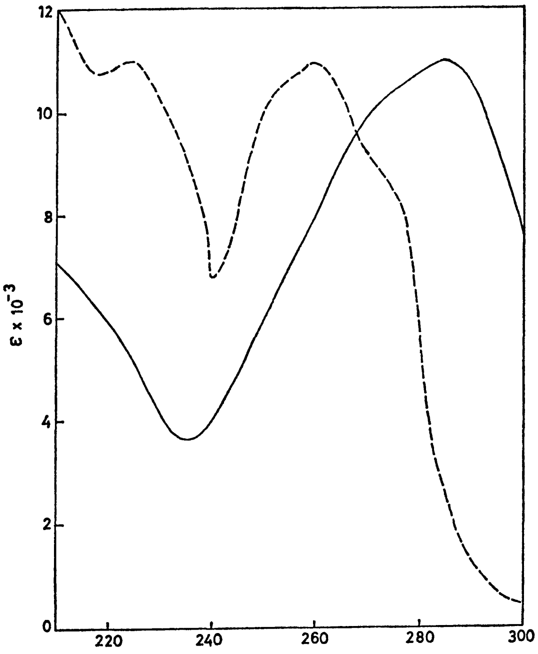


Fig. 2. Electronic absorption spectra of 2-phenylthiophene (——) and 3-phenylthiophene in ethanol (----).

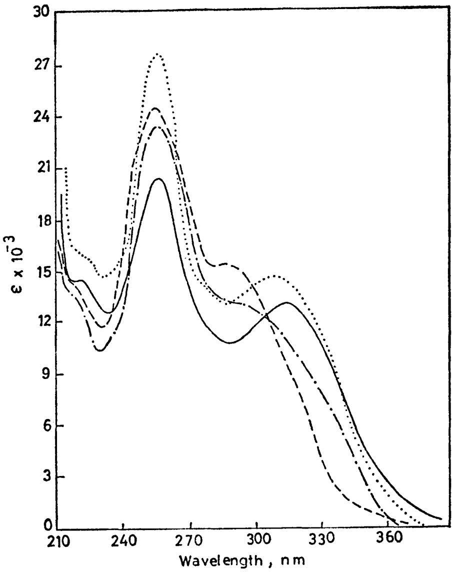


Fig. 3. Electronic absorption spectra of 2,4-diphenylthiophene in ethanol (——), 2,4-diphenylthiophene in cyclohexane (······), 2,5-diphenylthiophene in ethanol (—·—), and 2,5-diphenylthiophene in cyclohexane (----).

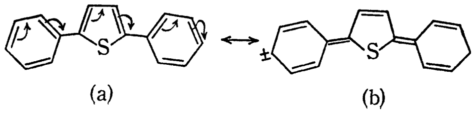
tions is seen when comparing the spectra in ethanol and 1-propanol (Fig. 1). In the latter, the extent of overlap is decreased and transition II is easily traced. In ethanol and 2-propanol the extent of overlap of the first two electronic transitions is appreciable, yet careful examination of the band indicates that it comprises two overlapping transitions. Confirmation of this conclusion will be obtained *via* MO calculations.

The composite molecule, 2-phenylthiophene, can be considered to consist of two subsystems: thiophene and benzene. Since the two subsystems are separated by one single bond, interaction between the excited states of the two subsystems will be extensive. As a result, the excited states of the composite molecule will differ appreciably from the excited states of the separate subsystems. Hence it is not adequate to assign the transitions in 2-phenylthiophene to ones localized over the thiophene nucleus and others localized over the benzene nucleus especially if coplanarity of the molecule is not significantly distorted.

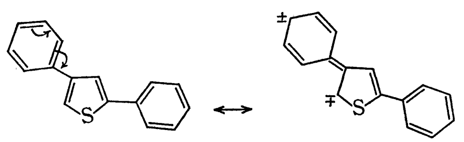
According to the resonance theory, the spectrum of 3-phenylthiophene should be different from that of the 2-phenyl derivative. However, this is not the case as Fig. 2 shows, and the two phenyl derivatives of thiophene have comparable spectra. The spectrum of the 3-phenyl derivative shows a broad band (300—240 nm) which also consists of two overlapping transitions (I and II) and the third transition appears as a shoulder. The dipole moments of 2- and 3-phenylthiophenes are 0.8 and 0.81 D respectively.[21] This shows that charge distribution in the two compounds are similar and consequently their spectra are expected to be similar. Substitution in the α-position of thiophene affects the spectrum but slightly and the resonance theory cannot adequately interpret the spectra of compounds as phenylthiophenes. The spectra of nitroanilines cannot be interpreted on the basis of the resonance theory. Contrary to the prediction of this theory, *ortho-* and *meta*-derivatives have similar spectra which differ from that of the *para*-derivative.[18,22]

Elpern and Nachod[14] reported the spectra of 2- and 3-phenylthiophene. They assigned the first transition of the two compounds to bands with $\lambda_{max}=280$ and 260 nm respectively and overlooked the fact that the first band in the spectra of the two compounds consists of two overlapping transitions. They attributed the difference in band maxima of the two compounds to the fact that the 3-phenyl isomer is cross conjugated. The results of this work indicate that 2-phenylthiophene has the first two electronic transitions at 282 and 264 nm whereas 3-phenylthiophene has the first two transitions at 275 and 260 nm which is quite comparable. The difference in transition energies of the two compounds is much less than that expected according to the resonance theory.

To confirm the above conclusion the spectra of 2,4-, 3,4-, and 2,5-diphenylthiophenes are investigated and shown in Figs. 3 and 4. The spectra of all diphenylthiophenes show three electronic transitions in the accessible ultraviolet region. In case of 2,5-diphenylthiophene the lowest energy transition (294 nm) appears as a shoulder at the long wavelength tail of the strong ~250 nm transition. The highest energy transition appears as a shoulder in the region of 220 nm. Band maxima are of the same value when the solvent is cyclohexane or ethanol, indicating that the bands are due to π–π* transitions and charge transfer character is not apparent in the observed transitions.

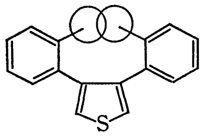


A comparison of the spectra of 2,5-diphenylthiophene and 2,4-diphenylthiophene is worthy. The extent of coplanarity is expected to be the same in the two compounds yet both have different sturctures (b) and (c).



(c)

Accordingly, the two compounds ought to have different spectra and that the 2,5-diphenylthiophene absorbs light at longer wavelength than the 2,4-diphenyl derivative due to contribution of forms as (b) to the excited state. Experimentally, the spectra of the two compounds are comparable and 2,4-diphenylthiophene absorbs light at wavelength longer than the 2,5-diphenyl derivative. The bands observed for the studied compounds are assigned to excited states of the composite molecule and not to excited states of any of the subsystems (benzene and thiophene).



In case of 3,4-diphenylthiophene steric hindrance is significant and the spectrum of the composite molecule will be the additive spectra of the subsystems. This is seen in Fig. 4. The two benzene rings are not in one plane and probably not in the plane of thiophene ring. If one benzene ring is coplanar with the thiophene ring the spectrum of 3,4-diphenylthiophene would be similar to that of 3-phenylthiophene, this is not the case.

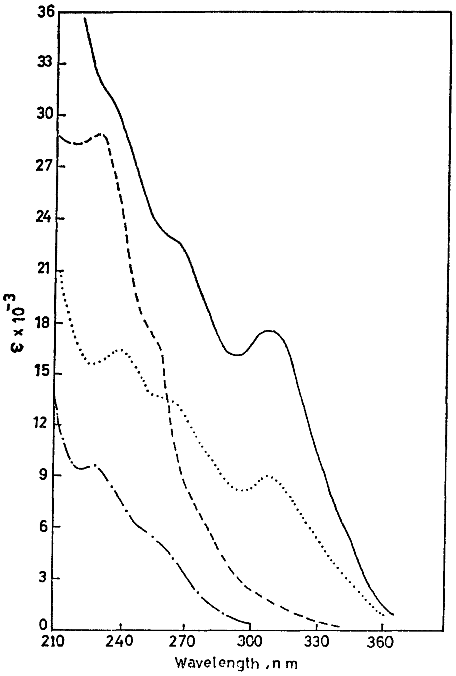


Fig. 4. Electronic absorption spectra of tetraphenylthiophene in ethanol (——), tetraphenylthiophene in cyclohexane (······), 3,4-diphenylthiophene in ethanol (—·—), and 3,4-diphenylthiophene in cyclohexane (----).

TABLE 1. BAND MAXIMA AND INTENSITIES OF THE STUDIED PHENYLTHIOPHENES IN ETHANOL

Compound	$\lambda_{\max}$, nm	ε M^{-1} cm^{-1}	f
2-Phenylthiophene	282	13 280	0.40
	264	6 500	0.19
	220	8 320	0.34
3-Phenylthiophene	275	6 350	0.07
	260	11 000	0.24
	222	11 000	0.22
2,5-Diphenylthiophene	294	13 265	0.32
	255	23 600	0.86
	220	14 189	—
2,4-Diphenylthiophene	312	13 147	0.44
	256	20 840	0.70
	222	14 430	0.59
3,4-Diphenylthiophene	255	5 200	0.13
	230	7 820	0.34
Tetraphenylthiophene	306	17 460	0.53
	258	23 280	1.05
	230	30 652	1.80

The spectrum of tetraphenylthiophene is shown in Fig. 4. If one considers unsymmetric twist of the phenyl groups, the spectrum of tetraphenylthiophene will be that of the 2,4- and 3,4-isomers.

Table 1 gives the numerical values of band maximum, molar absorptivity and oscillator strength.

Molecular Orbital Calculations. The self-consistent molecular orbitals of the composite molecule A–B are those of the separate constituents A and B. If the subsystems are joined through atom u in A and atom ν in B, then their extent of interaction is determined by the value of the resonance integral $\beta_{u\nu}$. If $\beta_{u\nu}=0$, the electronic excited states will be the locally excited ones A*, and B*, in addition to the charge transfer ones. The general expression for the interaction between two different singly excited configurations $^1\psi_{a-b}$ and $^1\psi_{c-d}$ is given by[23]:

$$\langle {}^1\psi_{a-b}|\hat{H}|{}^1\psi_{c-d}\rangle = 2(cd|ab) - (ca|bd)$$

where $\hat{H}$ is the Hamiltonian for the system for which $\beta_{u\nu}=0$

Application to Perpendicular Conformers. *2-Phenylthiophene*: The effect of steric hindrance in 2-phenylthiophene will cause the rings of the constituents to be non-coplanar. The value of β will be small and in the case the two rings are perpendicular will be zero. The self consistent orbitals of benzene (θ's) and of thiophene (y's) subsystems are shown in Fig. 5, and a schematic energy level diagram is shown in Fig. 6. In case of thiophene, the d-orbitals are not included since its participation is considered trivial when dealing with the UV spectrum. The singly excited states of benzene are:

$$\theta_{\beta'} = (1/2^{1/2})(\theta_3{}^{-1}\theta_4-\theta_2{}^{-1}\theta_5);\ \theta_\beta = (1/2^{1/2})(\theta_3{}^{-1}\theta_5+\theta_2{}^{-1}\theta_4)$$

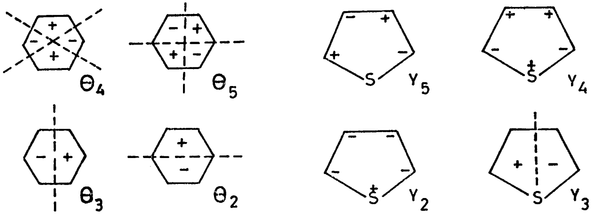


Fig. 5. The self consistent orbitals of benzene (θ) and thiophene (Y).

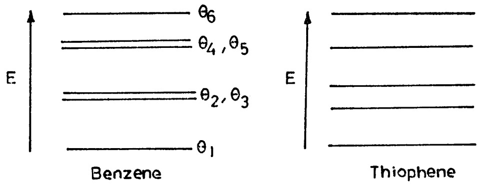


Fig. 6. A non scale energy level diagram for benzene and thiophene molecules.

$$\theta_p = (1/2^{1/2})(\theta_3{}^{-1}\theta_4+\theta_2{}^{-1}\theta_5);\ \theta_\alpha = (1/2^{1/2})(\theta_3{}^{-1}\theta_5-\theta_2{}^{-1}\theta_4)$$

The singly excited states of thiophene ring are constructed from the interaction between configurations of the same symmetry. The energy of the different configurations: $y_3{}^{-1}\,y_4$, $y_3{}^{-1}\,y_5$, $y_2{}^{-1}\,y_4$, $y_2{}^{-1}\,y_5$ are computed by the usual procedure,[24)] and the configuration interaction matrix of thiophene is solved. The form of the first four singly excited states of thiophene are:

$$Y_I = (0.999y_3{}^{-1}y_4-0.009y_2{}^{-1}y_5);$$
$$Y_{II} = (0.893y_2{}^{-1}y_4-0.449y_3{}^{-1}y_5);$$
$$Y_{III} = (0.449y_2{}^{-1}y_4+0.893y_3{}^{-1}y_5);$$
$$Y_{IV} = (0.009y_3{}^{-1}y_4+0.999y_2{}^{-1}y_4).$$

Since orbitals θ and y are self consistent, the ground state will not interact with any of the singly excited configurations. There will be, however, interaction between the locally excited states of the thiophene and benzene rings. The molecule, 2-phenylthiophene, is not symmetric and as a result we consider interaction between all the excited states of the two subsystems. The matrix elements of the Hamiltonian between the locally excited states Y's and θ's are computed as follows:

$$\langle Y_I|\hat{H}|\theta_\alpha\rangle = \langle(0.999y_3{}^{-1}y_4-0.009y_2{}^{-1}y_5)|\hat{H}| (1/2^{1/2})(\theta_3{}^{-1}\theta_5-\theta_2{}^{-1}\theta_4)\rangle \tag{1}$$

$$\langle y_3{}^{-1}y_4|\hat{H}|\theta_3{}^{-1}\theta_5\rangle = 2(\theta_3\theta_5|y_3y_4)-(\theta_3y_3|\theta_5y_5). \tag{2}$$

The second term in integral 2 is zero and to evaluate the first term of this integral, one expands[15)] the MO in terms of the AO functions and using the ZDO approximation,

$$2(\theta_3\theta_5|y_3y_4) = 2(\sum_{u,\nu} C_{\theta_{3u}}C_{\theta_{5u}}C_{y_4\nu}C_{y_3\nu}\gamma_{u\nu}).$$

For the perpendicular conformers, only, electron repulsion integrals are considered between atom (1) in benzene (u), and atom (2) of thiophene (ν), and the terms $\gamma_{u\nu}$ are evaluated using the Nishimoto-Mataga[25)] equation. Proceeding in this way the matrix elements of the Hamiltonian are computed between the eight states of 2-phenylthiophene. Solving this matrix, the energies and state wave finctions are obtained. The first three are:

(1) $0.765Y_I - 0.116Y_{II} + 0.182Y_{III} - 0.495\theta_\beta - 0.292\theta_p + 0.191\theta_\alpha$ ……4.78 eV

(2) $\theta_{\beta'}$ ……4.91 eV

(3) $0.184Y_I + 0.981Y_{II}-0.022Y_{III}+0.068\theta_p$ …5.92 eV.

Comparison with experiment is postponed till we consider the planar conformer.

3-Phenylthiophene: Before considering the effect of conjugation between benzene and thiophene nuclei in 2-phenylthiophene it would be interesting to consider the perpendicular conformer of 3-phenylthiophene, computations are analogous to those of the 2-isomer. The matrix elements of the Hamiltonian between the locally excited states of the two subsystems are calculated as is done with the 2-phenyl isomer. The numerical values of these elements are much less than the corresponding ones of the 2-phenyl isomer. To this reason we attribute the difference in transition energies of the two isomers. Solving the interaction matrix of 3-phenylthiophene one gets the state functions and energies, of which:

(1) $\theta_{\beta'}$ ……4.91 eV

(2) $0.726Y_I + 0.116Y_{II} + 0.229Y_{III} + 0.172\,Y_{IV} + 0.527\theta_\beta + 0.274\theta_p - 0.158\theta_\alpha$ ……5.19 eV

(3) $0.343Y_I - 0.914Y_{II} - 0.089Y_{III} - 0.064Y_{IV} - 0.177\theta_\beta - 0.052\theta_p$ ………………6.91 eV.

Application to Planar Conformers. When considering the perpendicular conformers, interaction between singly excited configurations arises from electron repulsion alone. When considering the planar structures, resonance integrals, $\beta_{u\nu}$, between the two subsystems will not be zero. The resonance integral will mix together configurations which differ by the position of just one electron. The integrals to be evaluated are:

$$\int\psi_0\hat{H}^{core}\psi_a{}^{-1}\psi_b d\tau = (2^{1/2})\int\psi_a(i)\hat{H}_i{}^{core}\psi_b(i)d\tau_i \tag{3}$$

$$\int\psi_c{}^{-1}\psi_a\hat{H}^{core}\psi_c{}^{-1}\psi_b d\tau = \int\psi_a(i)\hat{H}_i{}^{core}\psi_b(i)d\tau_i \tag{4}$$

$$\int\psi_a{}^{-1}\psi_c\hat{H}^{core}\psi_b{}^{-1}\psi_c d\tau = -\int\psi_a(i)\hat{H}_i{}^{core}\psi_b(i)d\tau_i. \tag{5}$$

The three integrals 3—5 will be zero unless ψ_a belongs to one subsystem and ψ_b to the other.

2-Phenylthiophene: Following the above rules one has to consider the interaction between: (1) Ground state ψ_0, and charge transfer states, (2) charge transfer states to produce "charge resonance" wave functions, (3) locally excited configurations and charge resonance, and (4) locally excited configurations of the two subsystems.

To begin with, the charge transfer states: $\theta_2{}^{-1}y_4$, $y_3{}^{-1}\,\theta_5$, $\theta_3{}^{-1}y_4$, $y_3{}^{-1}\,\theta_4$ are combined to produce the following charge resonance wave functions:

$$CR_I = (1/2^{1/2})(\theta_2{}^{-1}y_4+y_3{}^{-1}\theta_5)$$
$$CR_{II} = (1/2^{1/2})(\theta_2{}^{-1}y_4-y_3{}^{-1}\theta_5)$$

$$\mathrm{CR}_{\mathrm{III}} = (1/2^{1/2})(\theta_3{}^{-1}\mathrm{y}_4+\mathrm{y}_3{}^{-1}\theta_4)$$
$$\mathrm{CR}_{\mathrm{IV}} = (1/2^{1/2})(\theta_3{}^{-1}\mathrm{y}_4-\mathrm{y}_3{}^{-1}\theta_4).$$

Since, 2-phenylthiophene is not symmetric we computed the interaction terms between thirteen different states, namely, the ground state, four charge resonance states, and eight locally excited states of the two subsystems (θ and Y's). Interaction integrals between the ground state and the charge resonance wave functions reduce to terms including the resonance integral β_{12} (between atom 1 in benzene and atom 2 in thiophene). The same thing applies to interaction integrals between the locally excited configurations of each subsystem and the charge resonance wave functions. The energies of "CR" are computed as such:

$$\langle\theta_2{}^{-1}\mathrm{y}_4|\hat{\mathrm{H}}|\theta_2{}^{-1}\mathrm{y}_4\rangle = E_4 - E_2 - (\mathrm{y}_4\mathrm{y}_4|\theta_2\theta_2)$$

where E_4 is the ionization potential of the fourth MO of thiophene and is calculated by.[26]

$$E_4 = \sum_{\mathrm{u},\nu} C_{4\mathrm{u}}C_{4\nu}F_{\mathrm{u}\nu}$$

and

$$F_{\mathrm{u}\nu} = \beta_{\mathrm{u}\nu} - 1/2P_{\mathrm{u}\nu}\gamma_{\mathrm{u}\nu}.$$

The resonance integral, $\beta_{\mathrm{u}\nu}$, between carbon atoms, in the benzene ring, is taken as -2.4 eV whereas that between carbon and sulfur atoms, in the thiophene ring, is taken as -1.63 eV. Other values of $\beta_{\mathrm{u}\nu}$ are calculated using the relation[27]

$$\beta_{\mathrm{u}\nu} = [S_{\mathrm{u}\nu}/(1+S_{\mathrm{u}\nu})][(I_{\mathrm{u}}+I_{\nu})/2].$$

The computed value of E_4 is 1.406 eV. The values of $E_2(E_{\theta_2})$ is considered equal to $E_3(E_{\theta_3})$ *i.e.* the ionization potential of benzene (9.76 eV). Also, (E_{y_3}) is taken as the ionization potential of thiophene (9.1 eV). The electron repulsion integrals are considered between all atoms (p π atomic orbitals) of benzene and all atoms of thiophene and calculated using the ZDO approximation The energies computed for the charge resonance wave functions and interaction terms are (eV):

$\mathrm{CR}_{\mathrm{I}} = 5.93$; $\mathrm{CR}_{\mathrm{II}} = 5.03$; $\mathrm{CR}_{\mathrm{III}} = \mathrm{CR}_{\mathrm{IV}} = 5.92$;

and

$(\mathrm{CR}_{\mathrm{I}}|\mathrm{CR}_{\mathrm{II}}) = -0.360$; $(\mathrm{CR}_{\mathrm{III}}|\mathrm{CR}_{\mathrm{IV}}) = -0.263$

$(\mathrm{CR}_{\mathrm{I}}|\mathrm{CR}_{\mathrm{III}}) = (\mathrm{CR}_{\mathrm{I}}|\mathrm{CR}_{\mathrm{IV}}) = (\mathrm{CR}_{\mathrm{III}}|\mathrm{CR}_{\mathrm{IV}}) =$ Zero.

The elements of the interaction matrix for the planar conformer of 2-phenylthiophene are thus calculated. Solving this martix (13×13) the energies and state wave functions of the compound are obtained. Those of the ground state and of the first three excited states are:

(1) $0.984\psi_0-0.103\mathrm{CR}_{\mathrm{I}}-0.141\mathrm{CR}_{\mathrm{III}} \cdots\cdots\cdots\cdots -0.2$ eV

(2) $0.225\theta_{\beta'} + 0.341\theta_\beta + 0.162\theta_{\mathrm{p}} - 0.07\theta_\alpha$
$- 0.608\mathrm{Y}_{\mathrm{I}} + 0.081\mathrm{Y}_{\mathrm{II}} - 0.091\mathrm{Y}_{\mathrm{III}}$
$- 0.211\mathrm{CR}_{\mathrm{I}} - 0.352\mathrm{CR}_{\mathrm{II}} - 0.498\mathrm{CR}_{\mathrm{IV}} \cdots 4.46$ eV

(3) $0.107\theta_\beta - 0.852\theta_{\beta'} - 0.111\mathrm{Y}_{\mathrm{I}} - 0.167\mathrm{Y}_{\mathrm{III}}$
$- 0.391\mathrm{CR}_{\mathrm{II}} + 0.160\mathrm{CR}_{\mathrm{III}} + 0.179\mathrm{CR}_{\mathrm{IV}} \cdots 4.53$ eV

(4) $0.175\mathrm{Y}_{\mathrm{II}} - 0.086\,\mathrm{Y}_{\mathrm{I}}-0.293\theta_{\beta'} + 0.226\theta_{\mathrm{p}} + 0.324\theta_\alpha$
$+ 0.611\mathrm{CR}_{\mathrm{I}} + 0.109\mathrm{CR}_{\mathrm{II}} + -0.481\mathrm{CR}_{\mathrm{III}}$
$- 0.320\mathrm{CR}_{\mathrm{IV}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 5.52$ eV.

3-Phenylthiophene: Computations for this molecule are carried out similar to those of the 2-phenyl derivative. Interaction elements are of different values for the two isomers. On the other hand, β_{12} is taken equal to β_{13} (between atom 1 to benzene and atom 3 of thiophene). The following are the wave functions and the corresponding energies of the ground state and the first three excited states (covered by the spectrum in the 350—200 nm region):

(1) $0.993\psi_0 + 0.075\mathrm{CR}_{\mathrm{II}} + 0.094\mathrm{CR}_{\mathrm{IV}} \cdots\cdots -0.097$ eV

(2) $0.137\mathrm{Y}_{\mathrm{I}} - 0.138\mathrm{Y}_{\mathrm{III}} + 0.110\mathrm{Y}_{\mathrm{IV}} - 0.917\theta_{\beta'}$
$+ 0.076\theta_\beta+0.292\mathrm{CR}_{\mathrm{I}} - 0.080\mathrm{CR}_{\mathrm{II}} \cdots\cdots\cdots 4.695$ eV

(3) $0.141\theta_\alpha - 0.188\theta_{\mathrm{p}} - 0.189\theta_\beta-0.280\theta_{\beta'} - 0.424\mathrm{Y}_{\mathrm{II}}$
$- 0.475\mathrm{Y}_{\mathrm{I}} - 0.431\mathrm{CR}_{\mathrm{I}} - 0.388\mathrm{CR}_{\mathrm{II}}$
$- 0.291\mathrm{CR}_{\mathrm{III}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 4.87$ eV

(4) $0.742\mathrm{Y}_{\mathrm{I}} - 0.528\mathrm{Y}_{\mathrm{II}} - 0.209\theta_\beta-0.112\theta_{\mathrm{p}}$
$-0.300\mathrm{CR}_{\mathrm{II}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 5.61$ eV.

Band Intensity. The intensity of a band is calculated by the equation

$$f= 1.085\times10^{-5}\,M^2\nu$$

where M is the transition moment and ν (cm^{-1}) the frequency. In the LOM, the ground state is described by the wave function $\psi_0=a\Gamma+\sum_n b_n T_n$ and the excited state is described by:

$$\psi_{\mathrm{Ex}} = \sum_n C_n\Lambda_n + \sum_{n'} d_{n'}T_{n'} + e\Gamma$$

then the transition moment, whithin the limits of zero overlap approximation, is calculated from:

$$\langle\psi_0|\hat{\mathrm{M}}|\psi_{\mathrm{Ex}}\rangle = a\sum_n C_n\langle\Gamma|\hat{\mathrm{M}}|\Lambda_n\rangle +$$
$$\sum_n\sum_{n'} b_n d_{n'}\langle T_n|\hat{\mathrm{M}}|T_{n'}\rangle.$$

The first term reduces to the transition moment between two molecular orbitals and the second term is zero unless the charge transfer states (T_n and $T_{n'}$) are identical. It is calculated by expanding the wave function of the charge transfer state and considering integrals as $\langle\mathrm{y}_i|\mathrm{y}_j\rangle$, $\langle\theta_i|\theta_j\rangle$, and $\langle\mathrm{y}_i|\theta_j\rangle$ to be zero. Also, the operator $\hat{\mathrm{M}}$ is a one electron operator which does not depend on the electron spin.

Band intensities were calculated for the planar conformers. The origin of coordinates was assumed to be in midpoint of the bond joining the two subsystems. Results are given in Table 2.

Comparison with Experiment. A comparison of the experimental and computed transition energies and band intensity is given in Table 2.

Discussion and Conclusions

According to the resonance theory, 2-phenylthiophene is expected to possess a spectrum different from that of the 3-phenyl isomer. The two compounds have different resonating structures and different resonance energy. Consequently, Elpern[14] assigned the first band in the spectra of the two compounds to one electronic transition with λ_{max} at 282 nm for 2-phenylthiophene and at 260 nm for 3-phenylthiophene.

Table 2. Calculated and experimental transition energies of 2- and 3-phenylthiophenes

Compound	Transition energy, eV			*f*	
	Perpendicular	Planar	Expt	Expt	Calcd
2-Phenylthiophene	4.78	4.66	4.40	0.40	0.40
	4.91	4.73	4.63	0.19	0.06
	5.92	5.72	5.64	—	0.14
3-Phenylthiophene	4.91	4.79	4.51	0.07	0.02
	5.19	4.97	4.77	0.24	0.10
	5.91	5.71	5.54	—	0.16

However, careful examination of the spectra (Fig. 2) shows that the first band comprises two electronic transitions whose energies are not widely separated. Calculation of band intensity confirms this conclusion. The calculated "*f*" for bands II in 2-phenylthiophene and I in 3-phenylthiophene is not zero. The calculated values are less than the experimental ones since they borrow some of their intensity from the stronger transitions with which they overlap. The resonance theory could not correlate the spectra of nitroanilines.

The results of computation of this work verify the following:

(1) The long wavelength band in the spectra of 2- and 3-phenylthiophene consists of two electronic transitions.

(2) The numerical values of the elements of the interaction matrix of 3-phenylthiophene are less than the corresponding ones of the 2-phenyl isomer. Due to this, we attribute the difference in transition energies of the two isomers.

(3) Contribution of the charge transfer wave function to the excited states of 2-phenylthiophene is more pronounced than in case of the 3-phenyl isomer. That is, dipolar resonating structures contribute substantially to the excited states of the 2-phenylthiophene.

(4) Results of the LOM treatment are reliable and correspondence between them and the experiment is quite satisfactory (Table 2).

(5) Excited states of phenylthiophenes arise from extensive interaction between the states of benzene and thiophene.

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