Studies on the Electronic Absorption Spectra of 2,2′-Bithienyl and Some of Its Derivatives. A Molecular Orbital Treatment

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The electronic absorption spectra of 2,2′-bithienyl and a number of its derivatives have been investigated. The predominant conformer as well as the polarity of the molecule were predicted from the spectrum. Molecular orbital calculations were performed on different conformers of 5-formyl-2,2′-bithienyl and the s-*trans* geometry proved to be the predominant conformer of the molecule. A good agreement is observed between calculated and observed transition energy and intensity.

Bithienyls and their derivatives are important compounds from the biological, pharmaceutical and analytical point of view. Compounds with strong nematocidal activity are derivatives of 2,2′-bithienyl.[1] The absorption spectra of bithienyl[2-4] and substituted bithienyls have been investigated. The transitions observed in the spectra of 5- and 5,5′-substituted 2,2′-bithienyls have been assigned to intramolecular c.t., locally excited and $n\rightarrow\sigma^*$ transitions.

Molecular refraction and dipole moment measurements (in benzene at 25 °C) have shown that the s-*cis*-conformer of 2,2-bithienyl predominates.[6] On the other hand, the apparent polarization and molar Kerr constant[7] and electron diffraction[8] studies indicated that the preferred conformation is defined by an angle of twist ϕ, about the central C–C bond, of 34° from the crystal state.

The investigation of the spectra[9] of the three possible isomeric thienothiophenes as well as the CNDO/2 computations indicated that contribution of the 3d and higher orbitals of sulfur atom has negligible effect on the electronic spectra of sulfur containing composite molecules as was concluded for thiophene. Molecular orbital calculations, using the SCF–MO method, of the UV spectra of thiophene, 3,3′-, 2,3′-, and 2,2′-bithienyls have been described.[10-12] The PPP-approximation has been applied in an SCF study to investigate the barrier to internal rotation of the two isomers of bithienyl.[13] For 3,3′-bithienyl, energy minima were found at about 20° and 150° from the planar form. For the 2,2′-isomer no distinct minima were found.

In this work the electronic absorption spectra of 2,2′-bithienyl and some of its derivatives were investigated. The effect of solvent polarity and refractive index on band maxima and intensity helped in assigning the predominant conformer of the molecule. Molecular orbital calculations were carried out on 5-formyl-2,2′-bithienyl. Results obtained for the transition energies and band intensities agree satisfactorily with experimental results.

Experimental

All the solvents used were BDH-special for spectrocopy grade regents and used without further purifications.

2,2′-Bithienyl was prepared by refluxing a mixture of 2-iodothiophene, copper bronze and *N,N*-dimethylformamide for 22 h.[14] The product was recovered by steam distillation and purified by vacuum distillation (mp 34 °C).

5-Formyl-2,2′-bithienyl was prepared by stirring a mixture of bithienyl, *N,N*-dimethylformamide, dry toluene and phosphoryl chloride. The residue was recrystallized from ethanol (mp 59 °C).[15]

5,5′-Diacetyl-2,2′-bithienyl was prepared by refluxing a mixture of 85% phosphoric acid and 2,2′-bithienyl in acetic anhydride for 1 h. The mixture was cooled while stirring. The separated product was recrystallized from 1,4-dioxane, mp 235 °C (lit,[14] 233—234 °C).

5-Nitro-2,2′-bithienyl: To a solution of bithienyl and acetic anhydride at 0—5 °C fuming nitric acid in acetic anhydride was added. The nitro product was isolated by steam distillation and recrystallized from ethanol as yellow needles (mp 109 °C as reported).[16]

5,5′-Dimethyl-2,2′-bithienyl was prepared by heating a mixture of 2-iodo-5-methylthiophene and copper powder at 200—210 °C for half an hour. The mixture was colled and the product was extracted with boiling chloroform and steam-distilled. The dimethylbithienyl was recrystallized from methanol (mp 67—68 °C as reported 15—17).

5,5′-Dichloro- and 4,5,5′-Trichloro-2,2′-bithienyl: Sulfuryl chloride was added with stirring to a mixture of 2,2′-bithienyl, acetic acid, and aluminium chloride at 40 °C. The mixture was cooled and the separated solid was filtered and crystallized from chloroform (measured mp of the dichloro derivative was 109 °C, that of the trichloro was 103 °C).[18]

The absorption spectra were measured with a Pye Unicam Sp 500 spectrophotometer using 1.0 cm fused silica cells.

Results and Discussion

A. Electronic Absorption Spectra. (i) 2,2′-Bithienyl: The molecule, bithienyl (*R*-S), can be treated as a composite molecule consisting of two subsystems, each of which (*R* and *S*) is a thiophene nucleus and both are joined, apparently, by a single bond. The MO's of the composite molecule are built up from those of its subsystems and the excited states result from mutual interaction of the excited states of the subsystems. This interaction is predominant in the planar conformer of bithienyl. As the planarity is distorted, the spectrum of bithienyl will approach that of thiophene.

The calculations of the electronic spectra of sulfur

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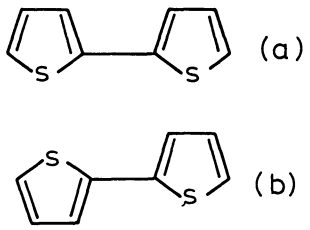
containing molecules have shown trivial dependence on the inclusion of the 3d or higher atomic orbitals of sulfur atom.[19-21] Microwave spectroscopic, electron and X-ray diffraction data[22-25] on five-membered heterocycles containing sulfur have shown that the bond angle on the sulfure atom is close to 90°, indicating that the σ-bonds result from overlap of the P_x and P_y orbitals of sulfure. Using Slater exponents for sulfur and carbon atomic orbitals, the calculated overlap integral between carbon $2P_z$ and sulfur $3P_z$ is 0.492 while that between carbon $2P_z$ and sulfur $3d_{xz,yz}$ is only 0.109.[26] Figures 1a and 1b show the electronic absorption spectra of bithienyl and that of thiophene. Thiophene spectrum consists of a singlet $\pi \rightarrow \pi^*$ transition with λ_{max} at 235 nm (log ε=4.22) in addition to a long wavelength shoulder in the region of 268 (log ε<1) nm. No discrete absorption band is observed for $n \rightarrow \pi^*$ transition and singlet→triplet transitions were assigned to very weak bands at about 5.63 eV and in the range of 3.90—3.96 eV.[27] On the other hand, the spectrum of bithienyl shows three well defined electronic transitions in the accessible UV region, none of which can be identified as the thiophene electronic transition. This result is an experimental evidence that bithienyl is a "coplanar," "rigid" or "quasi-rigid" molecule. If it were a "freerotator" the probability of getting a perpendicular conformer should be the same as that of getting a planar conformer. The electronic spectrum of the perpendicular conformer would be merely that of thiophene. As Fig. 1 shows the spectrum of bithienyl differs completely from that of thiophene. The planer conformer of bithienyl may be either the s-*cis* (a) or the s-*trans* (b)



one. The former follows the C_{2v} whereas the latter follows the C_{2h} symmetry point group. Transition probability would be different for the two conformers. The s-*cis* conformer is of much higher dipole moment than the s-*trans* conformer, consequently the electronic transitions of the former should be more affected with solvent polarity than those of the latter. Figure 1 shows a slight shift of λ_{max} with solvent polarity indicating a low polarity of both the ground and excited states.

Many physical studies concerned with the determination of the preferred conformation of 2,2′-bithienyl have been reported. In the solid state, planar *trans* configuration is favored.[28] In gaseous[29] state the angle of twist about the central C–C bond varies between 34—85° from the *cis*-conformer. In solution, the angle of twist is found to be similar to that in gaseous state.[30] However, theoretical consideration favors a near planar structure.[31,32] A molecular orbit-

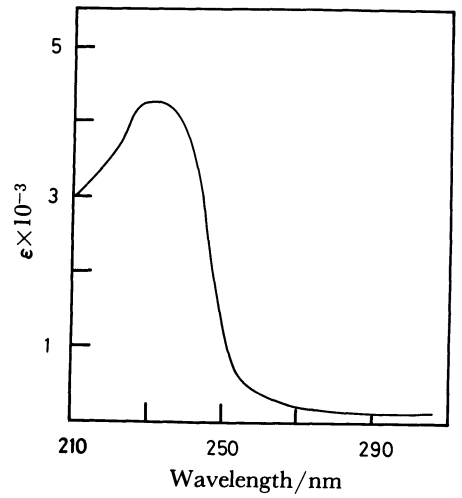


Fig. 1a. Electronic absorption spectrum of thiophene in ethanol.

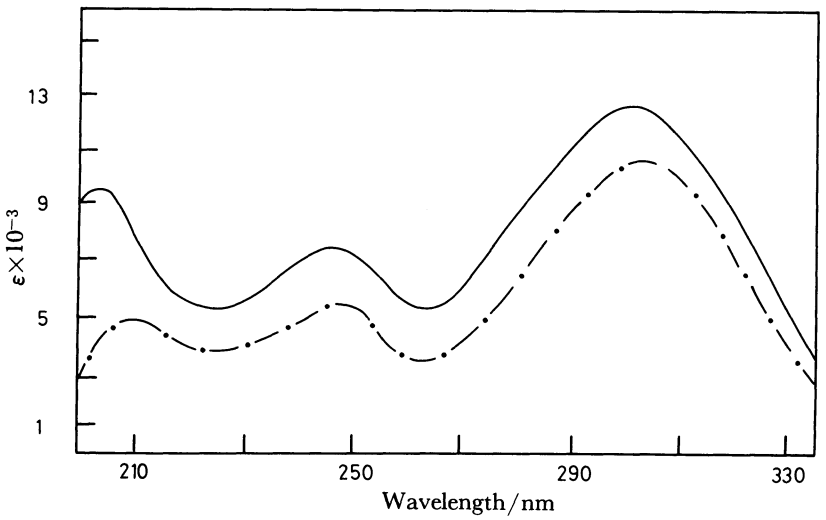


Fig. 1b. Electronic absorption spectra of bithienyl: in cyclohexane (——), in methanol (-·-·-).

Table 1. Numerical values of band maxima and band intensity of 2,2′-bithienyl in different solvents

Solvent	λ_{max}/nm	ε/M^{-1}†cm^{-1}	f
Methanol	303	13440	0.35
	247	7030	0.21
	209	6110	0.11
-2-Butane-01	303	10290	0.26
	248	5360	0.17
N,*N*-Dimethylformamide	305	12480	0.31
Glycerol	305	5820	0.17
	249	3230	0.11
Ethylene glycol	305	12520	0.32
	248	7720	0.23
Cyclohexane	301	13240	0.36
	248	5660	0.22
Hexane	301	13810	0.40
	249	7540	0.25
Heptane	302	13280	0.34
	248	6990	0.22
Decane	304	13320	0.33
	248	6730	0.21
Dodecane	303	10990	0.28
	248	4980	0.11

† 1 M = 1 mol dm^{-3}.

al study of the barrier to internal rotation in bithienyl has shown no distinct energy minima on varying the angle of twist from 0—180°.

The observed three electronic transitions of bithienyl, Fig 1b are $\pi \rightarrow \pi^*$, none of them is localized on a subsystem of the composite molecule. The broad feature of band 1 (lowest energy) as well as the relative blurring of its vibrational components is an evidence that, in solution, bithienyl exists in a number of nearly planar conformers of comparable energy. A statistical distribution is expected to exist between the different conformers. The spectra of 2,2′-bithietyl were investigated in a wide variety of polar and nonpolar solvents (Table 1). In polar solvents, band intensity decreased with the increase of dipole moment and in non-polar solvents band intensity also decreased with the increase of refractive index. On the other hand band maxima slightly increased with the increase of both refractive index and dipole moment.

(ii) Substituted 2,2′-Bithienyl: Figure 2 shows the electronic absorption spectra of 5,5′-dimethyl-, 5,5′-dichloro-, and 4,5,5′-trichloro-2,2′- bithienyls using cyclohexane as a solvent. The features of the spectra are similar to those of the unsubstituted compound. An important observation is the broadness of the lowest energy band in addition to the blurring nature of its vibrational components.

The spectra of 5-formyl- and 5,5′-diacetyl-2,2′-bithienyl are shown in Fig. 3. A significant red shift is observed for the lowest energy transition compared to the unsubstituted compound or to the methyl or halo-substituted bithienyl. This is the result of the strong perturbing effect of the >C=O group which also incrcases the polarity of both the ground and the excited states. The lowest energy transition is apparently red shifted in polar solvent which is an indication of a large

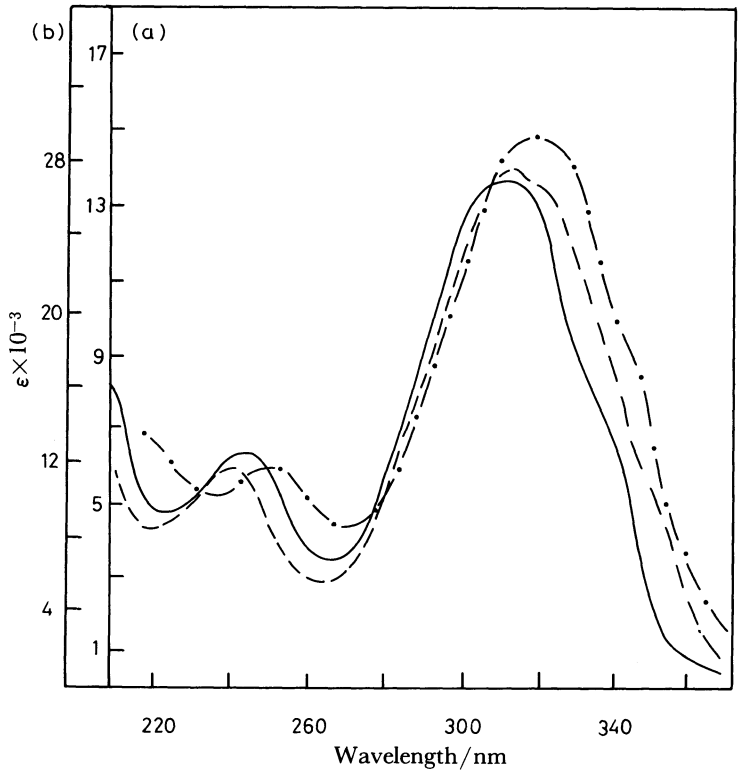


Fig. 2. Electronic absorption spectra of substituted bithienyls in cyclohexane.
5,5′-Dimethyl-2,2′-bithienyl (——); 5,5′-dichloro-2,2′-bithienyl (---) (both on scale a). 4,4,5′-Trichloro-2,2′-bithienyl (-·-·-) (on scale b).

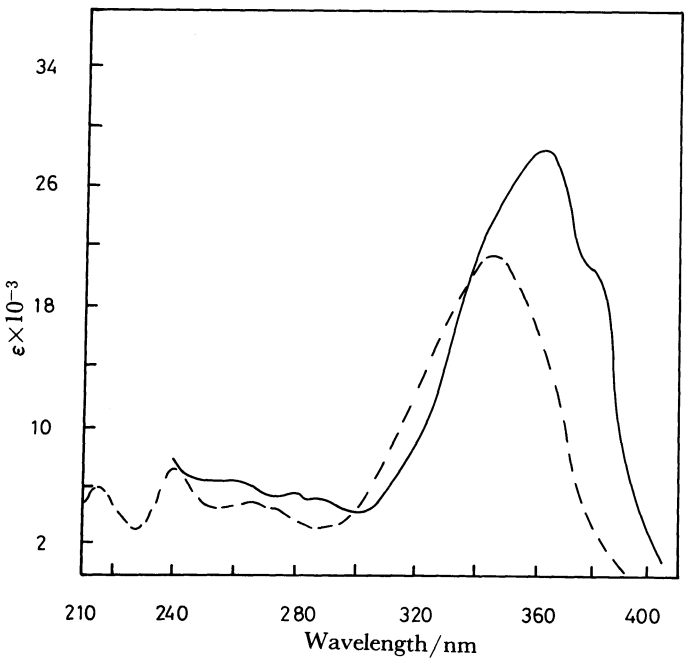


Fig. 3. Electronic absorption spectra of: 5,5′-diacetyl-2,2′-bithienyl in 1,4-dioxane (——); 5-formyl-2,2′-bithienyl in cyclohexane (---).

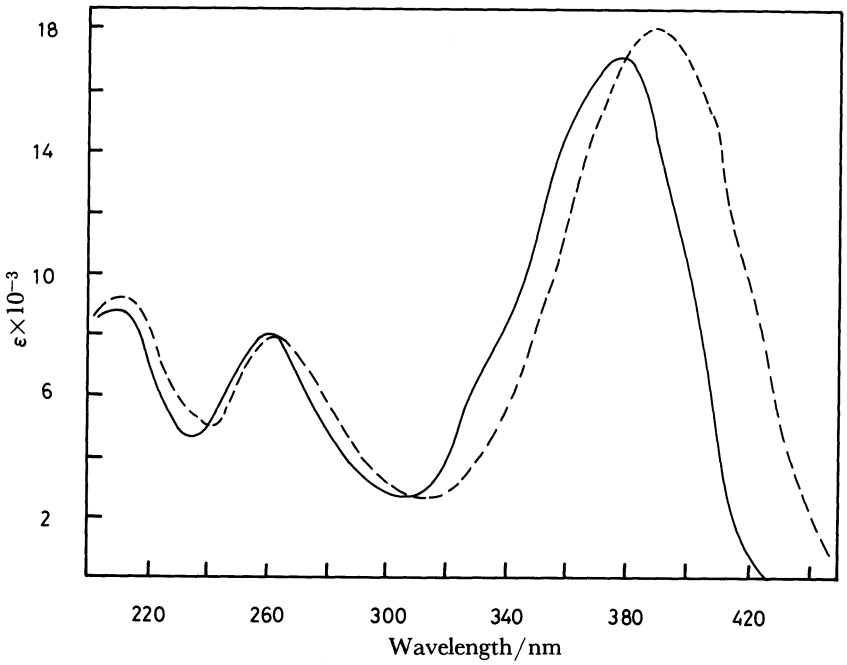
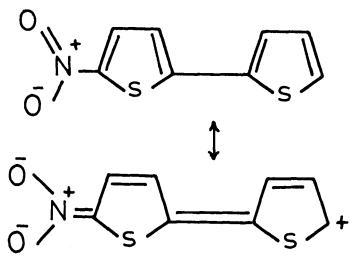


Fig. 4. Electronic absorption spectra of 5-nitro-2,2′-bithienyl: in cyclohexane (——), in methanol (---).

contribution of a polar configuration to the excited state.

Substitution by a nitro group in the 5-position of bithienyl will not affect the coplanarity of the molecule but will reduce its symmetry. Forms as (a) will mainly contribute to the excited states. The interaction between the nitro group and bithienyl nucleus is substantial and is reflected in the spectrum (Fig. 4). Four electronic transitions ($\pi \rightarrow \pi^*$) are observed in the 200—500 nm region. The lowest energy band is substantially red shifted in polar solvent, a characteristic of



(a)

charge transfer transitions. The highest energy band was not observed in the spectra of any of the studied

Table 2. Numerical values of band maxima and band intensities of some 2,2′-bithienyls

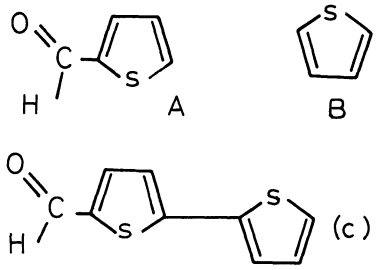
Compound	λ_{max}/nm[a]	ε/$M^{-1}cm^{-1}$	f
5,5′-Dichloro-	315(317)	13830(17110)	0.38(0.43)
2,2′-Bithienyl	242(241)	5930(5880)	0.20(0.19)
5,5′-Dimethyl-	314(315)	13370(14890)	0.35(0.38)
2,2′-Bithienyl	245(244)	6335(6380)	0.21(0.19)
5-Formyl-	345(354)	21630(20900)	0.47(0.47)
2,2′-Bithienyl	265(268)	5570(4340)	0.21(0.15)
	245(246)	7480(6440)	0.18(0.12)
5-Nitro-	380(391)	17130(18120)	0.36(0.40)
2,2′-Bithienyl	275(264)	6329(7870)	0.16(0.29)
	260	8075	0.28
	212(212)	8730(8910)	—
4,5,5′-Trichloro-	316(320)	29120(18860)	0.76(0.48)
2,2′-Bithienyl	252(252)	11650(6600)	0.54(0.32)
5,5′-Diacetyl-	363(367)	28760(36950)	0.63(0.85)
2,2′-Bithienyl[b]			

a) Values in parentheses are those when methanol was used as a solvent. b) Dioxane is the solvent.

bithienyls except the diacetyl derivative. Table 2 gives the numerical values of band maxima and oscillator strength of the studied compounds.

B. Molecular Orbital Calculations. The method of molecule-in-molecule[34] has been accurately adobted to MO calculations on composite systems such as phenylthiophenes,[35] bithienyls,[32] phenylfurans,[36] and *N*-(2-furylmethylene)aniline.[37] In this work the method is applied for calculations on the different conformers of 5-formyl-2,2′-bithienyl.

The two subsystems of the composite molecule, 5-formyl-2,2′-bithienyl, are 2-thiophenecarbaldehyde (A) and thiophene (B). The molecule-in-molecule method



is based on calculating the interaction between the electronic states of subsystems (A) and (B). The SCF-CI[38] state functions were calculated for the two subsystems, results are given in Table 3. The electronic states of 5-formyl-2,2′-bithienyl were calculated for many conformers of the molecule by considering the following interactions between (i) the CI state functions of the subsystems (A) and (B); (ii) the CI state functions of the subsystems and charge-transfer configurations where an electron transfers from (A) to (B) or from (B) to (A) ; (iii) the ground state and the charge-transfer configurations. For the perpendicular conformer the resonance integral $\beta_{22'}$ is zero and interaction of the type (i) are only considered. The state functions and the corresponding energies of the s-*trans* conformer (C) and the perpendicular conformer (planes of thiophene and formylthiophene are perpendicular) are given in Table 4. The variation of transition energies with the angle of rotation around the C_2–$C_{2'}$ bond is given in Table 5.

Table 3. Configuration interaction state functions and the corresponding energies (eV) of 2-thiophenecarbaldehyde and of thiophene

2-Thiophenecarbaldehyde	eV
$\theta_1=0.4306\theta_4^{-1}\theta_5$[a]$+0.3691\theta_4^{-1}\theta_6-0.1119\theta_4^{-1}\theta_7$ $-0.6282\theta_3^{-1}\theta_5+0.5121\theta_3^{-1}\theta_6$	4.22
$\theta_2=0.5196\theta_3^{-1}\theta_5-0.1130\theta_3^{-1}\theta_6-0.7617\theta_4^{-1}\theta_5$ $-0.3214\theta_4^{-1}\theta_7$	4.50
$\theta_3=0.3737\theta_4^{-1}\theta_5+0.5369\theta_4^{-1}\theta_6+0.5122\theta_3^{-1}\theta_5$ $+0.4906\theta_3^{-1}\theta_6$	5.70
$\theta_4=0.1620\theta_4^{-1}\theta_5+0.2459\theta_4^{-1}\theta_6+0.4627\theta_4^{-1}\theta_7$ $+0.8308\theta_3^{-1}\theta_7$	7.16
Thiophene	**eV**
$Y_1=0.9999y_3^{-1}y_4$[b]$-0.0092y_2^{-1}y_5$	5.64
$Y_2=0.8933y_2^{-1}y_4-0.4495y_3^{-1}y_5$	5.93
$Y_3=0.4495y_2^{-1}y_4+0.8933y_3^{-1}y_5$	7.74
$Y_4=0.0092y_3^{-1}y_4+0.9999y_2^{-1}y_5$	8.03

a) $\theta_4^{-1}\theta_5$=Electronic configuration in which an electron transfers from the fourth MO(θ_4) to the fifth MO(θ_5). b) $y_3^{-1}y_4$=Electronic configuration in which an electron transfers from the third MO(y_3) to the fourth MO(y_4).

Table 4. State functions and the corresponding energies (eV) of 5-formyl-2,2′-bithienyl

s-*trans* Conformer	eV
$\Psi_0=0.9821\Gamma-0.0213CR_I+0.1862CR_{II}$	−0.19
$\Psi_{EX,I}=0.4121\theta_2-0.1013\theta_3-0.2819Y_1$ $-0.6042CR_I-0.1743CR_{II}$.	3.53
$\Psi_{EX,II}=0.7052\theta_1+0.6422\theta_2-0.1689Y_3$ $-0.1352CR_I-0.2563CR_{II}$	4.53
$\Psi_{EX,III}=0.4513Y_1-0.2992\theta_1+0.1764\theta_2$ $+0.4172\theta_3+0.2981CR_I-0.6163CR_{II}$	5.01
Perpendicular conformer	**eV**
$\Psi_{EX,I}=0.1292Y_1+0.0293Y_3+0.9893\theta_1-0.0662\theta_2$ $+0.0124\theta_3-0.1203\theta_6$	4.19
$\Psi_{EX,II}=0.1762Y_1-0.0871\theta_1-0.9803\theta_2-0.0412\theta_6$	4.56
$\Psi_{EX,III}=0.7363Y_1-0.0942\theta_1+0.1573\theta_2+0.6421\theta_3$ $-0.0924\theta_4-0.0512\theta_6$	5.53

Γ=Ground configuration, θ_1—θ_6 excited states on subsystem A, Y_1—Y_4 excited states on subsystem B, CR's charge resonance functions.

The oscillator strength was calculated from the equation

$$f = 2.085 \times 10^{-5} M^2 \bar{\nu}$$

where M is the transition moment and $\bar{\nu}$ (cm^{-1}) is the wave number of the electronic transition. M was calculated from

$$\vec{M} = \langle \Psi_0 | \hat{M} | \Psi_E \rangle,$$

where Ψ_0 and Ψ_E are the ground and excited state wave functions, respectively. In the molecule-in-molecule procedure the wave functions have the forms:

$$\Psi_0 = {}_a\Gamma + \sum_n b_n T_n$$

$$\Psi_E = \sum_n c_n A_n + \sum_{n'} d_{n'} T_{n'} + {}_e\Gamma$$

Table 5. Variation of transition energy with the angle of rotation about the 2,2′-bond

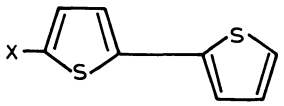
Rotation angle/deg	Transition energy/eV	Oscillator strength
30	3.72	1.00
	4.47	0.17
	5.16	0.24
60	4.06	0.51
	4.45	0.20
	5.01	0.05
90	4.19	0.39
	4.56	0.11
	5.53	0.07
120	4.15	0.28
	4.50	0.22
	4.80	0.02
180(s-*trans*)	3.72	0.85
	4.56	0.20
	5.20	0.23
Experimental	3.65	0.47
	4.68	0.22
	5.06	0.18

where A_n is the n-th excited state function and T is the charge-transfer state function. Applying the ZDO approximation

$$\langle \Psi_0|M|\Psi_E\rangle = a\sum_n \langle T|M|A\rangle + \sum_n\sum_{n'} b_n d_{n'} \langle T_n|M|T_{n'}\rangle$$

C. Comparison with Experimental Results: Table 5 gives the values of the transition energy and the oscillator strength computed as a function of the angle of rotation about the C_2–$C_{2'}$ bond together with the experimental values. The results show a good correspondence between the experimental values and the theoretical ones computed for the s-*trans* conformer. An angle of 30° between the planes of the subsystems did not lead to better results than those of the planar conformer. The electronic absorption spectra of 2,2′-bithienyl and some of its derivatives have been investigated in a wide variety of solvents. The important observation is the persistance of the features of the first band (lowest energy) in the spectra of all the studied derivatives. This band is broad, though it corresponds to one electronic transtion, intense and includes a number of blurred vibrational components, though coplanarity of the molecules is not distorted.

A simple way[5] that has been followed in interpreting the spectra of 2,2′- bithienyls is to attribute the observed transitions to: (i) locally excited on a certain subsystem of the composite molecule, (ii) charge transfer from the substituent (X) to the parent molecule or in the opposite direction and (iii) n→π^* transitions.



The results of this work prove, on the contrary to what has been previously reported,[5] that the observed transitions are not localized. There is an extensive "mixing" of the state of the subsystems (Table 4) to produce the states of the composite molecule. Also, the slight shift of band maxima with solvent polarity is a proof that none of the observed transitions is a "pure" charge transfer one. The intensity and position for the observed bands indicate that none of them corresponds to n→π^* transitions.

Computations on 5-formyl-2,2′-bithienyl indicated that coplanarity of the molecule is not apparently distorted and the interaction between the states of the subsystems, thiophenecarbaldehyde and thiophene, is predominant. The contribution of the charge-transfer configurations (from one subsystem to the other) is significant. The calculated parameters, transition energy and band intensity, as a function of the angle between the planes of the subsystems indicate that the s-*trans* conformer is a good representative of the geometry of the molecule in solutions. It is also evident that the height of the barrier of internal rotation is small since transition energies did not show a wide variation with the angle of rotation.

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