Tetrahedron Letters No. 21, pp.1785-1788, 1971. Pergamon Press. Printed in Great Britain.

THE CNDO/2 STUDIES ON THE ELECTRONIC SPECTRA OF THE ISOMIRIC THIENOTHIOPHENES

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(Received in Japan 15 March 1971: received in UK for publication 16 April 1971)

Only recently has been completed the synthesis of the series of the three possible isomeric thienothiophenes, thieno[4,5-b]thiophene II, thieno[2,3-b]-thiophene III and thieno[3,4-b]thiophene IV (Fig.1), with an appearance of the report on the isolation of the most unstable isomer of the above three, IV, by Wynberg and Zwanenburg(1).

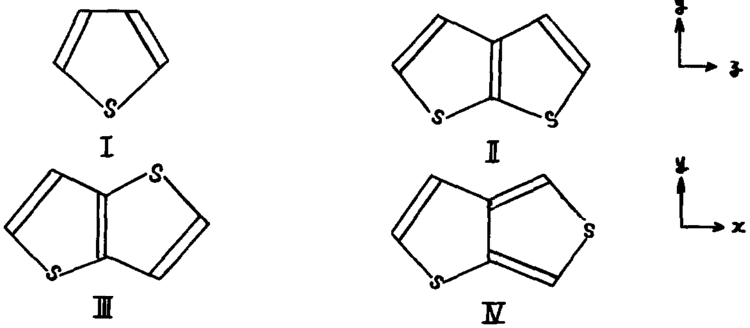

Figure 1. Nuclear Arrangement and Choice of Axes of Thiophene and Three Isomeric Thienothiophenes.

Since they exhibit quite interesting electronic spectra(1-3) and chemical reactivities(4), many authors have tried to elucidate their chemical and physical properties by means of the π-electron approximation MO method(5-11). From the observed spectra of II and III, there is a good reason to believe that the longest wavelength absorption includes the lone pair electrons on sulfur atoms because of their enormously low intensities as compared with the other absorption bands and, in accordance with these facts, of their absence in the vapour phase spectra(2).

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We here report the calculations of the excitation energies of the isomers by means of the semi-empirical LCAO MO SCF CNDO/2 method including all valence electrons, but not 3d AO's(12). As is well known, the original CNDO/2 method is not a good approximation for the prediction of the excited state electronic properties, such as the transition energies, of the molecule(13). In this calculation, therefore, we introduce a parameter κ which correlates with the core resonance integral $\beta_{\mu\nu}$ for π-bond according to the following relations(14),

$$\beta_{\mu\nu} = \frac{\kappa}{2}(\beta_A^\circ + \beta_B^\circ) S_{\mu\nu}$$

The value of κ which is unity in the original CNDO/2 method was so determined as to well reproduce the electronic spectra of methane, ethylene and benzene. This required the values of 0.75, -15.0eV and -8.0eV for κ, β_C° and β_H°, respectively. Using thiophene I as a reference molecule, we obtained -13.9eV as a value of β_S°. It is assumed that the molecular geometry of thiophene(15) is retained in each thienothiophene except the central bond of IV, which was varied between 1.40Å and 1.65Å. Our results are shown in Tab.1 along with the experimental data.

For II and III the longest wavelength absorption arising from $\pi-\sigma^*$ electronic transitions are predicted to be 4.20eV and 4.25eV(forbidden), respectively. It is found that σ^*-orbitals pertaining to these transitions are mainly localized on the hetero atoms and could be said to be the lone pair orbitals of the sulfur atoms. In the usual PPP SCF CI calculations of Clark these longest wavelength transitions are unfortunately lost(11). The higher allowed $\pi-\pi^*$ transitions are predicted to be 4.44eV and 5.36eV for III. They are both polarized in the molecular plane. As for II the long axis polarized $\pi-\pi^*$ transition is predicted at 4.87eV followed by two other short axis polarized transitions, B_2 at 5.00eV and B_2 at 5.49eV. These results are in quite good agreement with the experimental values.

On the other hand, there is no $\pi-\pi^*$ type transitions predicted in the long wavelength region until 280 mμ, when the shorter central bondlength other than 1.65Å is adopted for IV. The predicted values shown in Tab.1 all correspond to those which were calculated using the geometry having a longer central bondlength of 1.65Å. The spectral features are the same as the above

Table 1. Singlet-Singlet Transition Energies ΔE and the Oscillator Strengths $\underline{f}$.

Molecule	Symmetry	$\Delta E_{calc.}$(eV)	$\underline{f}_{calc.}$(cgs)	$\Delta E_{obs.}$(eV)
I	B_1	4.71	0.000	——
	B_2	5.39	0.24	5.37(log ε=3.77)*
	A_1	5.88	0.037	——
	B_1	5.92	0.000	——
II	B_1	4.20	0.000	4.19(1.44)**
	A_1	4.87	0.083	4.49(3.00)†
				4.65(3.28)
	B_2	5.00	0.024	5.00(?)
	B_2	5.49	0.55	5.56(4.38)
	B_1	5.74	0.000	——
III	B_g	4.25	forb.	4.10(1.11)**
	B_u	4.44	0.44	4.50(4.04)†
				4.66(4.08)
				4.83(4.09)
	A_u	4.54	0.000	——
	B_u	5.36	0.11	5.00(?)
	A_u	5.91	0.000	——
IV	A''	3.27	0.000	——
	A'	4.01	0.43	4.18(ε = 5330)
	A'	4.91	0.006	4.50(3650)††
				4.66(3650)
				4.81(3370)
	A'	5.17	0.14	5.28(16800)
	A'	5.66	0.11	——

* G.Horvath and A.I.Kiss, Spectrochim. Acta, 23A, 921 (1967)

** See Reference 2.

† In the vapour phase spectra these bands show the vibrational progressions with a main frequency 1238cm^{-1} for II and 1250cm^{-1} for III, respectively.

†† See Reference 1.

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two isomers, but the longest wavelength transition containing the dominant contribution of $\pi-\sigma^*$ transition is markedly shifted toward the longer wavelength as compared with the above two transitions in interest of II and III. Unfortunately, however, as for IV there is no spectral data available for the comparison between the theory and experiment because of the lack of the measurement in the long wavelength region above 310 mμ. The longest wavelength $\pi-\pi^*$ transition energy is calculated to be 4.01eV which is assigned to a medium intensity band at about 297 mμ in the observed spectrum of IV. Next transition predicted at 4.91eV with a small oscillator strength corresponds to an absorption which exhibits a vibrational progression starting at 280 mμ. Thus according to the agreement of our calculated transition energies with the experimental data, we conclude that the 3d and the higher orbitals have little effect on the calculation of the electronic spectra of sulfur containing molecules as was concluded by Biefield and Fitts for thiophene(16).

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