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Semi-empirical Parameters in π-Electron Systems

VIII. Sulphur-containing Heteroaromatic Systems

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A modification of the Pariser-Parr-Pople method has been extended to sulphur-containing heteroaromatic molecules. The semi-empirical parameters obtained have been applied in calculations of different observables for thiophene, for thionaphthene, and for three isomers of thienothiophene. The overall agreement between predicted values and experimental results is satisfactory.

In the first paper of the present series a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation was suggested and applied to pure hydrocarbons.[1] The method has also been extended to various kinds of substituted conjugated systems.[2–7] The purpose of the present investigation is to extend this scheme further to the inclusion of sulphur-containing molecules. The study is limited to a treatment of thiophene and other polynuclear ring systems containing the thiophene unit.

The new features introduced by this particular scheme are: 1) the one-electron, "one-center", parameter W_μ is made dependent on the surroundings to atom μ, and 2) the two-electron Coulomb repulsion integrals between nearest neighbours are treated as semi-empirical parameters in the same way as the core resonance integrals.

A central point in the discussion of the electronic structure of sulphur-containing heterocyclics is the question of whether the 3*d* orbitals on the S atom have to be introduced in order to obtain a satisfactory description of the molecular properties. We have in the present study made the tacit assumption that the sulphur atom takes part in conjugation through its $3p\pi$ orbital only.

The semi-empirical parameters pertinent to the molecular systems described here were determined by adjustment to observed quantities for the molecules thiophene (I), thieno(3,2b)thiophene (II), and thieno(2,3b)thiophene (III).

DETERMINATION OF SEMI-EMPIRICAL PARAMETERS

The scheme applied for the evaluation of the semi-empirical parameters has been outlined in the first paper of this series.[1] Only the new parameters pertaining to the sulphur atom as a heteroatom in a conjugated ring system will be determined and discussed. The remaining parameters, appropriate to pure hydrocarbons, have been taken from Ref. 2 where corrected values from the first paper of this series are given.

One of the characteristic features of the method applied in this particular scheme is the assumed dependence of the one-electron integral W_μ on the surroundings to atom μ. This dependence was introduced by the linear expression:

$$W_\mu = W^0 + \sum_{\nu=1}^{3} [\Delta W_\mu{}^0(\nu) + \delta_{\mu\nu}{}^W(R_{\mu\nu} - R_0)] \quad (1)$$

where W^0 denotes the first ionization potential (IP) of the methyl radical, $\Delta W_\mu{}^0(\nu)$ is a constant correction to W^0 due to the replacement of a hydrogen atom by a different atom ν, and where the last term yields an additional correction in cases where the internuclear distance $R_{\mu\nu}$ differs from a standard reference distance R_0 for one particular bond. The gradient $\delta_{\mu\nu}{}^W$ is to be determined empirically.

The resonance integral, $\beta_{\mu\nu}$, and the Coulomb integral, $\gamma_{\mu\nu}$, between nearest neighbours are also assumed to obey linear relations:

$$\beta_{\mu\nu} = \beta_0 + \delta_{\mu\nu}{}^\beta(R_{\mu\nu} - R_0) \quad (2)$$

and

$$\gamma_{\mu\nu} = \gamma_0 + \delta_{\mu\nu}{}^\gamma(R_{\mu\nu} - R_0) \quad (3)$$

where R_0 is the standard distance referred to above, and where the δ's are treated as empirical parameters.

Special attention has been paid to the evaluation of the one-center two-electron Coulomb integral for the sulphur atom. In previous semi-empirical studies of sulphur-containing π-electron systems, integral values ranging from 9 eV to 12 eV have been applied.[8-11] For the sake of consistency we found it necessary to use a value for this atom which is evaluated along the same lines as for the other atoms treated in this series of papers. Furthermore, preliminary calculations clearly demonstrated that the relative order of some of the predicted spectral transitions in thiophene was sensitive to minor changes in the value of this integral.

Fischer-Hjalmars has previously drawn the conclusion that due to electronic correlation the theoretical value for the two-electron one-center integral over $2p$-orbitals should be lowered by a certain amount which is deducible from atomic correlation energy data.[12] Furthermore she was able to show that this correlation-energy correction was nearly constant for the L-shell.

If we extend this assumption to be valid also for $3p$-orbitals, and apply the appropriate atomic correlation energy data,[13] we estimate a lowering of the theoretical integral value by around 4.35 eV. By assuming a theoretical

value of 13.84 eV, given by ordinary Slater-type orbitals, we arrive at an appropriate value for this integral which is equal to 9.49 eV.

By estimating experimental values for the appropriate Slater-Condon parameters, and applying the well-known formula

$$\gamma_0(3p,3p) = F_0(3p,3p) + 4F_2(3p,3p) \quad (4)$$

Fischer-Hjalmars has suggested the value 9.58 eV for this integral.[14]

In fact these two methods give values which are in nice agreement for the whole series of atoms from Si to Cl.

Due to the comparatively large uncertainty inherent in the estimated correlation-energy correction, we have adopted the value 9.58 eV for the two-electron one-center integral appropriate to sulphur.

The two-electron two-center Coulomb integrals for non-neighbours were estimated by the uniformly charged sphere approximation. The diameter of the tangent spheres constituting a sulphur $3p$ orbital was assumed to be 0.84 Å, a value corresponding to the diameter of 1.47 Å introduced previously for the carbon atom.[2]

The parameters to be estimated empirically for the systems considered here are W_{S^+}, $\Delta W_C^0(S)$, δ_{CS}^W, β_{CS}, δ_{CS}^β, γ_{CS}^0 and δ_{CS}^γ. In view of the uncertainties inherent in the experimental information available, we found it advantageous to assume all the δ-values to be equal to their counterparts for a C—C bond. Due to this assumption the number of parameters to be determined is reduced to four. These parameters were estimated by requiring

Table 1. Semi-empirical parameters for heteroatomic systems containing one sulphur atom in the ring. For notation see text.

Carbon [a]		Sulphur	
R_{CC}^0 = 1.397 Å		R_{CS}^0 = 1.714 Å [b]	
$\gamma_{\pi\pi}$ = 11.97 eV		$\gamma_{\pi\pi}$ = 9.58 eV	
γ_{CC}^0 = 6.91 eV		γ_{CS}^0 = 7.28 eV	
δ_{CC}^γ = −3.99 eV/Å		δ_{CS}^γ = δ_{CC}^γ (ass.)	
β_{CC}^0 = −2.42 eV		β_{CS}^0 = −1.37 eV	
δ_{CC}^β = 3.05 eV/Å		δ_{CS}^β = δ_{CC}^β (ass.)	
W_C^0 = −9.84 eV		W_{S^+} = −20.20 eV [c]	
ΔW_C^0 = 0.07 eV		$\Delta W_C^0(S)$ = −0.70 eV	
δ_{CC}^W = 9.22 eV/Å		δ_{CS}^W = δ_{CC}^W (ass.)	

[a] Ref. 2.
[b] The experimentally determined distance in thiophene. Ref. 18.
[c] The value for a doubly charged core of the S atom in thiophene. The formal contributions $\Delta W_{S^+}^0(C)$ are included.

the predicted values to reproduce the measured values for: 1) the lowest π-electron ionization potential (IP) of thiophene,[15] 2) the lowest singlet-singlet transition energies for thiophene,[16] thieno(3.2b) thiophene,[17] and thieno(2.3b)-thiophene.[17] The parameter set obtained is presented in Table 1. For the sake of completeness, we have also included the parameters for pure hydrocarbons in the table.

Table 2. Comparison between calculated and experimental data applied in the evaluation of semi-empirical parameters. All values in eV. The calculated (IP)-values for (II) and (III) are included.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$	$\Delta E_{calc.}$	$\Delta E_{obs.}$
I	8.91	8.91 [a]	5.33	5.39 [b]
II	7.88	—	4.63	4.57 [c]
III	8.54	—	4.70	4.51 [c]

Observed values: [a] Ref. 15; [b] Ref. 16; [c] Ref. 17.

In Table 2 we present the calculated and the corresponding observed values of the quantities used for the determination of the parameters. As the number of parameters equals the number of constraints, all the experimental values should be reproduced exactly.

The small discrepancies revealed by the table are due to the fact that the positions of some higher electronic transitions also were taken into consideration by the adjustment of the parameters. Due to the rather large uncertainties in these data, emphasis was put on the agreement with the observables mentioned above.

The only experimental IP value found is the one reported for thiophene by Turner.[15] For the remaining molecules studied here no such values seem to be available.

The electronic transitions in thiophene have been extensively discussed in the literature. Rather strong evidences are given for assigning the medium intensity band observed in solution at 231 mμ to the lowest singlet-singlet transition. We have preferred to use the vacuum UV data presented by Price and Walsh.[16] Using their intensity estimates we adopt the value 5.39 eV for the lowest transition in thiophene.

For molecules (II) and (III) both vapour and solution spectra exist.[17] From the reported intensities of the vapour spectra we have estimated the values 4.51 eV and 4.57 eV for the lowest transitions. See Table 6.

RESULTS AND DISCUSSION

The parameter values obtained and presented in Table 1 were used in a study of the electronic structure and electronic spectra of thieno(3,4b)thiophene (IV) and thionaphthene (V) in addition to the reference molecules mentioned above.

1. Ground state properties. The carbon-carbon bond distances were calculated from bond orders using the equation

$$R_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu} \quad (5)$$

where $p_{\mu\nu}$ is the mobile bond order between carbon atoms. Arguments for using this particular formula have been given in a previous paper by one of us.[20]

The C—S bond lengths are calculated from a similar equation

$$R_{\mu\nu} = R_{\mu\nu}^{0} - 0.18 p_{\mu\nu} \quad (6)$$

where $R_{\mu\nu}^{0}$ is obtained from the thiophene data. The calculated value for the C—S bond order of this molecule is 0.326. The experimental bond length is 1.714 Å.[18] This gives:

$$R_{\mu\nu} = 1.773 - 0.18 p_{\mu\nu} \quad (7)$$

The calculated bond lengths are presented in Table 3 where also existing experimental values with given standard deviations are included for the purpose of comparison. Labelling of the molecules and notation of the atoms are given in Fig. 1.

Table 3. Calculated and observed bond distances. In Å units.

Molecule	Bond	$R_{calc.}$	$R_{obs.}$ (e.s.d.)	Molecule	Bond	$R_{calc.}$
I	1—2	1.714	1.7140 (0.0014) [a]	IV	1—2	1.718
	2—3	1.362	1.3696 (0.0017)		2—3	1.365
	3—4	1.434	1.4232 (0.0023)		3—4	1.734
					4—5	1.733
					5—6	1.351
II	1—2	1.361	1.36 (0.03) [b]		6—7	1.441
	2—3	1.439	1.41 (0.03)		3—7	1.441
	3—4	1.723	1.74 (0.02)		7—8	1.369
	4—5	1.719	1.72 (0.02)		1—8	1.714
	3—7	1.378	1.36 (0.04)			
				V	1—2	1.391
					2—3	1.408
III	1—2	1.720			3—4	1.452
	2—3	1.720			4—5	1.354
	3—7	1.379			5—6	1.726
	7—8	1.441			6—7	1.728
	1—8	1.360			3—7	1.404
					7—8	1.404
					8—9	1.393
					1—9	1.402

[a] Ref. 18; [b] Ref. 19.

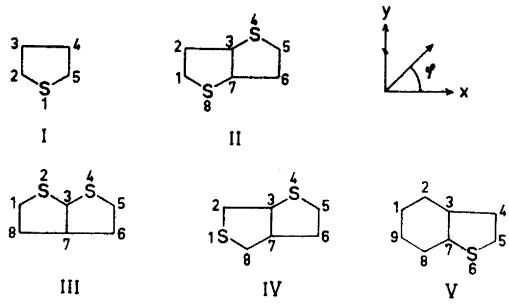

Fig. 1. Notation of atoms and labelling of molecules.

For thiophene, the experimental bond lengths have been determined with a high degree of precision in a microwave investigation.[18] In comparing with calculated values, it must be born in mind that the C—S bond distance in this molecule has been used for determining the constant term in eqn. (6).

The agreement between predicted and measured C—C distances is, however, satisfactory.

For (II) molecular structure data based on an X-ray crystallographic investigation are available.[19] In view of the large standard deviations reported, the agreement between calculated and observed values has to be considered as very good. Although there is some discrepancy between predicted and observed C—S bond lengths, it may be worth pointing out that bond 3—4 is found to be slightly longer than bond 4—5 in both sets of values.

For the three remaining molecules, no experimental structure determination has been carried out to the authors' knowledge. The distances calculated for (III) are strikingly close to the corresponding distances in (II). For (IV), the predicted C—S distances 3—4 and 4—5 are slightly longer than those in

Table 4. π-Electron charges on the different atoms. The numbering of the atoms is given in Fig. 1.

Atom	Molecule				
	I	II	III	IV	V
1	1.835	1.120	1.119	1.844	1.014
2	1.088	1.006	1.857	1.146	1.005
3	0.995	1.011	1.130	0.993	0.981
4		1.864		1.912	0.991
5				1.094	1.082
6				0.975	1.887
7			0.953	0.968	1.011
8			0.983	1.068	1.023
9					1.005

(II) and (III). The ring-connecting bond 3—7 is, however, found to be considerably longer in this molecule than in the other isomers. This is to be expected since in contrast to the other isomers it is impossible to draw a Kekulé diagram which contains this particular bond as a "double bond" in this isomer.

For (V), all distances in the benzene ring, including distance 3—7, are almost identical to the C—C distances of benzene itself, and the remaining distances are close to their counterparts in (I) and (II).

In Table 4 we present the values found for the atomic charges. The π-electron dipole moments are listed in Table 5. For thiophene, the calculated

Table 5. Calculated π-electron dipole moments. In Debye units.

Molecule	I	II	III	IV	V
μ_π	0.87	0	1.37	0.66	0.48

value is 0.873 D. The σ-electron contribution has been estimated to -1.49 D.[10] This gives $\mu_{total} = -0.62$ D as compared to an observed value of 0.53 D.[21]

The predicted first π-electron (IP)-values for (IV) and (V) are 8.35 eV and 7.86 eV, respectively. The corresponding values for the remaining mole-

Table 6. Conversion from solution to vapour spectra. Transition energies in eV.

Molecule	$\Delta E_{solution}$	ΔE_{vapour}	Correction term	Assumed vapour values
II	4.06 [a]			
	4.46	4.57 [a]	0.11	4.57
	4.62			
	4.79			
III	4.16 [a]			
	4.45	4.51 [a]	0.06	4.51
	4.61	4.67	0.06	4.67
	5.51			5.57
IV	4.18 [b]			
	4.51		0.08 [c]	4.59
	4.67		0.08	4.75
	4.84			4.92
	5.28		0.08	5.36
V	4.30 [d]	4.31 [e]		4.31
	4.82		0.08	4.90
	5.46		0.08	5.54

[a] Ref. 17. [b] Ref. 24. [c] Correction term taken as the average term of II and III. [d] Ref. 25. [e] Ref. 26.

cules are included in Table 2. The predicted values are estimated by Koopmans' theorem.

2. Electronic spectra. In principle the excitation energies predicted by our method should be compared to vapour phase spectra. For (II), (III), and (V) both solution and vapour phase values are available for certain electronic transitions. For the remaining transitions for these molecules and for (IV) we have worked out assumed vapour-values by adding a correction term as shown in Table 6.

Table 7. Calculated and observed electronic spectra. Transition energies in eV.

Molecule	$\Delta E_{calc.}$	$\Delta E_{obs.}$[a]	$f_{calc.}$	pol.[b]
I	5.33	5.39	0.15	A_1
	5.53	5.41—5.54	0.40	B_1
	7.42		0.32	A_1
II	4.63	4.57	0.57	201°
	5.06		0.36	265°
	5.50		forb.	—
	6.07		forb.	—
	7.46		0.45	326°
III	4.70	4.51	0.03	A_1
	4.75	4.67	0.11	B_2
	5.72	5.57	0.27	B_2
	5.73		0.97	A_1
IV	4.80	4.59	0.37	250°
	4.94	4.75; 4.92	0.06	152°
	5.81	5.36	0.48	20°
V	4.51	4.31	0.02	16°
	5.34	4.90	0.61	143°
	5.86	5.54	0.06	295°
	6.07		1.12	237°

[a] For references, see Table 6.
[b] For definition of angle, see Fig. 1.

In Table 7 we present the calculated values for the lowest singlet-singlet transitions. The electronically excited states have been described by a limited configurational mixing including all the singly excited configurations.

For comparison, the available observed spectral transitions are included in the table.

For thiophene, which has been extensively investigated, Price and Walsh [16] have recorded a vapour phase spectrum which is resolved into a series of progressions in the region 2400—2100 Å. From the reported intensities we have assumed the lowest excitation energy to be between 5.37 eV and 5.51 eV. Arbitrarily, one might adopt the average value of 5.44 eV for the lowest transition energy. There are, however, rather strong evidences for two close-lying electronic transitions in this region.

Milazzo [22] has reported a vapour spectrum with a transition at 5.33 eV, and recent measurements in solution [23] give a value of 5.37 eV. It is interesting to notice that Milazzo's value measured in vapour is lower than the reported solution value. This might be explained by interpreting the broad band in solution as containing two close-lying transitions.

By the adjustment of the semi-empirical parameters we have adopted the compromise value of 5.39 eV for the lowest singlet-singlet $\pi \rightarrow \pi^*$ transition in thiophene.

The data of Price and Walsh indicate a possible electronic transition in the region 5.41—5.54 eV. This compares favourably with our calculated value of 5.53 eV. The predicted value of 7.42 eV has not been observed explicitly, but a region of very strong absorption starting at around 6.6 eV has been reported.[16]

For (II) both solution and vapour spectra are available.[17] Absorption at 4.06 eV corresponding to the extremely weak longest wavelength band in solution has not been recorded in vapour. We therefore exclude this band from our further discussion. The solution spectrum of this isomer further reveals three absorption maxima corresponding to transition energies of 4.46 eV, 4.62 eV, and 4.72 eV, respectively. No assignment of these transitions are given, and it is not clear whether they represent one or more electronic transitions. A tentative vibrational analysis given of the vapour spectrum does indicate just one band in the same spectral region. The 0—0 transition which has the highest recorded intensity occurs at 4.57 eV. This transition has to be related to the solution value of 4.46 eV referred to above. Another transition absorbing in the neighbourhood of 5 eV cannot, however, be excluded.

Also for the isomer (III) spectra both in solution and vapour are available.[17] The gross features of the solution spectrum is strongly related to the corresponding one for the isomer (II) with recorded transitions at 4.16 eV, 4.45 eV, 4.61 eV, and 5.51 eV, the first one being extremely weak, and not observed in the vapour phase. A tentative vibrational analysis of the vapour spectrum does indicate one electronic transition in this region. The 0—0 band lies at 4.51 eV, but another band at 4.67 eV has an intensity comparable to the 0—0 band, and could be interpreted as the vertical transition in the Franck-Condon sense. However, our calculations predict two rather close-lying transitions in this region, so the vibrational assignment should not be considered as conclusive. The rather strong B_2-band observed at 5.51 eV is nicely reproduced by our calculations.

For the recently synthesized isomer (IV) no vapour spectrum is available to the authors' knowledge. The solution spectrum [24] shows a lowest energy transition at 4.18 eV, *i.e.* in the same region as the other isomers. The shape of the absorption peak does, however, indicate a higher intensity in this case. As the applied solvent, ethanol, is a polar substance, it is impossible to discuss the sensitivity of this particular transition to solvent effects.

If we, supported by the predicted transitions, make the tentative assumption that this peak is of the same nature as the corresponding ones for the other isomers, we are left with a spectral interpretation that parallels the one for (II) and (III).

By a study of the available experimental spectra for (II) and (III), we have found that the blue shift by changing from ethanol as a solvent to vapour,

was around 0.08 eV for each of the transitions studied here. By assuming the same shift also for the isomer (IV), we obtain an estimated experimental vapour phase spectrum with transitions at 4.59 eV, 4.75 eV, 4.92 eV, and 5.36 eV, see Table 6. These values are to be compared to the predicted ones given in Table 7.

Comparing with results from the other isomers, it is reasonable to relate the experimental value of 4.59 eV to the calculated one at 4.80 eV. Furthermore, the experimental value at 5.36 eV must correspond to the calculated value at 5.81 eV. Either of the two experimental values at 4.75 eV and 4.92 eV could be fitted to the calculated value at 4.94 eV. It may be that one of these experimental values is due to a vibrational transition.

For (V), both vapour [25] and solution spectra [26] exist. From the given intensities of the vapour spectrum, the vertical transition is taken to be at 4.31 eV. The solution spectrum shows three well defined absorption bands, at 4.30 eV, 4.82 eV and 5.46 eV. By adding the correction term of 0.08 eV to the two latter values the assumed vapour values are obtained and listed in Table 6.

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