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ULTRAVIOLET SPECTRA AND PARAMETERS IN SCF-MO CALCULATIONS ON SULPHUR CONTAINING HETERO-AROMATIC SYSTEMS

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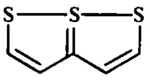
Abstract—Electronic transitions and ionization potentials of a number of heterocyclic compounds containing one, two, or three S atoms have been calculated by the Pariser–Parr–Pople semi-empirical SCF method and compared with experimental values. The coulomb and resonance integrals involving the S atom were varied to obtain a best fit to the UV spectra. It was possible to accommodate all the results, without the explicit inclusion of S d-orbitals by the use of a small range of these integrals rather than unique or best values.

INTRODUCTION

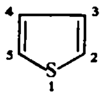
THE calculation of SCF MO's by the Pariser–Parr–Pople method has been applied successfully to the computation of those physical properties of aromatic hydrocarbons and heterocyclic compounds in which the sigma and pi-electron systems can be regarded as separable. The pi-electron transitions in such systems are a good test of the validity of the computations since UV spectra have been measured accurately for a wide variety of compounds and the calculations are relatively sensitive to changes in parameters.

At the start of our work, relatively few SCF calculations had appeared on sulphur heterocyclic compounds, and even these were concerned mainly with thiophen. The earlier work on thiophen using Hückel MO methods has been adequately summarised[3] but, subsequently, criticism of Longuet-Higgins' approach[4] involving 3d-orbitals has appeared.[5] Previous SCF calculations on thiophen[6-9] are summarized in Table 1 together with values used for the core integral parameters. Recently, calculations of electronic transitions in more complicated sulphur hetero-aromatic systems have appeared.[10-12] During our work on the bonding in 6a-thiathiophthens (I),[13] we attempted to calculate its pi-electron transitions using the empirical values adopted by Wachters and Davies[7] for the parameters used in an SCF calculation on thiophen. The results for the thiathiophthens (I) were in extremely poor agreement with the experimental UV spectrum, particularly as no long wavelength transition was predicted near 500mμ, a region in which thiathiophthens absorb strongly. Accordingly, we developed new values for the empirical parameters in the SCF equations for sulphur heterocyclics containing one, two, and three S atoms so that a consistent set of values could be applied to the thiathiophthens. Work which appeared recently[10-12] overlaps some of our results on the sulphur compounds (II–VII).

Initial difficulties in the choice of parameter values for sulphur heterocyclics lie firstly in the amount of 3d-orbital participation in bonding, and secondly in the amount of sp-hybridization of sulphur.



I



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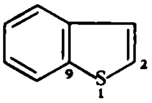

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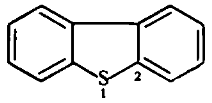

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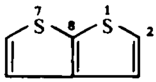

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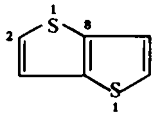

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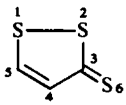

VII

Generally, approaches to 3d-orbital participation fall into three categories: (a) complete neglect of d-orbitals, (b) some allowance for d-orbital participation by changes in the one-centre integrals, and (c) explicit inclusion of d-orbitals in the basis set of atomic orbitals used in the SCF LCAO method. The approach in method (c) has been examined in some detail for thiophen[9] and it appears that inclusion of d-orbitals has only a small effect on the predicted pi-electron transitions. The pi-electron charge densities are modified sufficiently however to lead to a total dipole moment for thiophen close to the observed value. However, calculated dipole moments are known to be very sensitive to small changes in charge densities and the postulate that sigma and pi-electrons may be separated could be unsound. No account is normally taken of changes in the sigma dipole moment caused by polarization of the sigma bonds in a direction opposite to the polarization of the pi-bonds. Because of this sensitivity of the calculated dipole moment to changes in the parameter values and the estimated nature of the sigma dipoles, the use of the dipole moment for defining a set of parameters is questionable.

Similar to the question of d-orbital participation is the question of the amount of sp-hybridization in sulphur heterocyclic compounds. Usually, sulphur is assumed to bond exclusively through its 3p-electrons but consideration of bond angles shows there must be some hybridization. For example, the C-S-C bond angle in thiophen (II) is slightly greater than 90° implying that bonding to the adjacent C atoms is not purely a p-type. Since the electronegativity of an atom changes with the type of hybridization the value of the valence state ionisation potential (used to evaluate the coulomb integral) will change also.

As the PPP-SCF method is semi-empirical and as we did not expect to find a unique value for the core integrals, for the reasons discussed above, we have preferred to examine the size of the range of values necessary to predict the pi-electronic transitions observed in sulphur heterocyclics. We have retained both the core integral terms, ω_s and β_{cs}, as variable parameters.

A further difficulty is that of obtaining a consistent set of values for the core integrals in sulphur heterocyclics because of a general lack of data concerning their geometries, and concerning detailed vapour phase analyses of their UV spectra. The geometry of thiophen is well known,[14] but although many measurements have been made of the UV spectrum of thiophen and its simple alkyl derivatives[15-19] there appears to be some discordance in the results. The results of the major work on the UV spectrum of thiophen are shown in Fig. 1; for convenience all quoted transition energies have been converted to electron-volts. The intense band progression noted by Price and

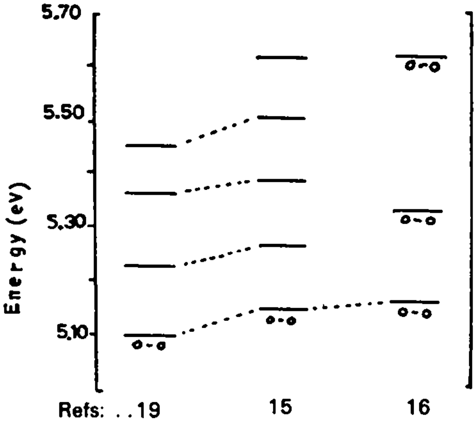

FIG. 1 Experimental UV transitions in thiophene.

Walsh[15] beginning at 5·15 eV is clearly reflected in the solution spectrum obtained by Mason[19] (allowing for a small solvent shift), and is supported by the work of Milazzo,[16] who reported a progression beginning at 5·16 eV. There seems little doubt therefore that a o—o, π → π* transition occurs near 5·15–5·16 eV. Milazzo reported a second progression having a o—o band at 5·33 eV and these bands are quoted by Price and Walsh at 5·30, 5·32 eV but it is not suggested in the latter work that this is a o—o, π → π* transition. Assuming Milazzo's interpretation of the spectrum to be correct, then both sets of workers report a second, fairly strong transition near 5·30–5·33 eV. An absorption band at 5·63 eV occurs in Milazzo's, and Price and Walsh's work but whereas the former ascribes it to an n → π* transition, the latter mention it only as part of the band progression beginning at 5·15 eV. Milazzo suggested that due to instrumental imperfections, Price and Walsh had missed the band progression beginning at 5·63 eV, but this weak progression could be due to impurity in the thiophen which could also explain why it was not observed by them. There is obviously need for a clarification of the UV spectrum of thiophen, but whichever explanation of the nature of the 5·63 band is correct, it clearly need not be considered in these calculations as a o—o, π → π* transition. A short wavelength transition is also observed at 6·56 eV.[15]

Method. The PPP adaptation of the Hartree-Fock SCF LCAO method is well documented elsewhere.[1, 2] Neglecting penetration integrals, the matrix elements are defined by:

$$F_{\mu\mu} = \omega_\mu + \tfrac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\mu} (P_{\nu\nu} - 1)\gamma_{\mu\nu}$$

$$F_{\mu\nu} = \beta_{\mu\nu}^{\text{core}} - \tfrac{1}{2} P_{\mu\nu}\gamma_{\mu\nu}\,(\mu \equiv \nu)$$

where $\omega_\mu = Wx - Wc$ and Wx, Wc are the valence state ionisation potentials for the heteroatom and carbon respectively. For the reasons given in the introduction, we retained $\omega_\mu(\mu \equiv S)$ and $\beta_{\mu\nu}$ $(\mu \equiv S;\ \nu \equiv C)$ as variable parameters in the calculations, which were carried out using simple Hückel MO's as the starting point, and a computer programme written by us. In molecules of up to ten atoms, full configuration interaction is included between all singly excited states, but for larger molecules,

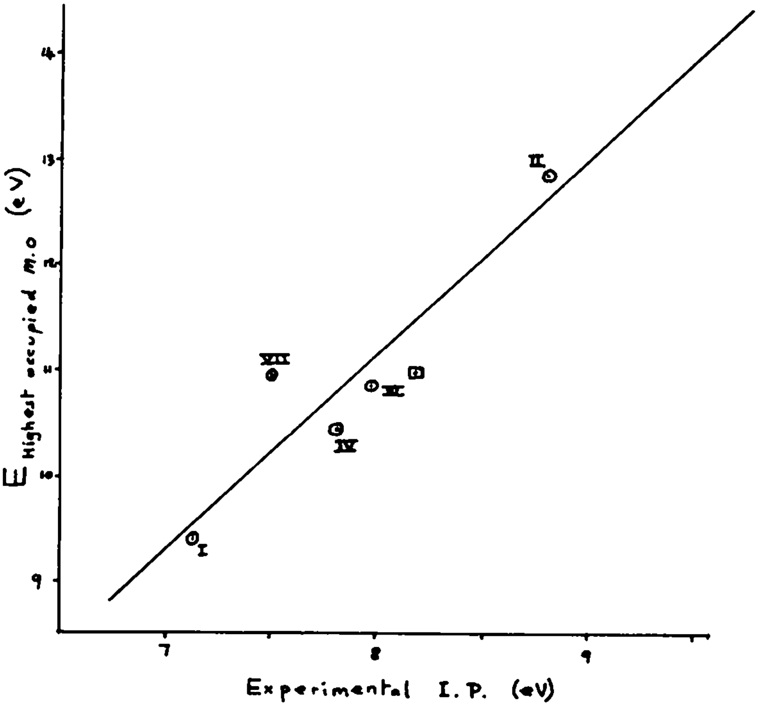

FIG. 2 Correlation of experimental Ionisation potentials and calculated energies of the highest occupied molecular orbitals in *l*ompounds I, II, III, IV, VII and naphthalene (⊡).

limited configuration interaction including at least the seventeen lowest states is allowed. In one or two cases, penetration integrals were included but changed the results only slightly. Based on overlap proportionality, β_{cs}^{core} has been varied around the HMO method value of 0·6 β^{core}.[13, 20] The values for β_{cc}^{core} were obtained from the relationship, $\beta_{cc} = 2524 \exp. (-5r)$.[21] The one-centre integrals, $\gamma_{\mu\mu}$, were obtained either from the I-A approximation[1] or from the empirical formula suggested by Paoloni.[22] It is interesting to note that the theoretical values of $\gamma_{\mu\mu}$ obtained by Saturno's method[23] agree very well with the empirical ones. Whereas Paoloni's formulae for $\gamma_{\mu\mu}$ are 3·294 $Z_{\mu\mu}$ and 1·794 $Z_{\mu\mu}$ for first and second row elements respectively in their p-state, Saturno's formulae are 3·024 $Z_{\mu\mu}$ and 2·016 $Z_{\mu\mu}$. The two-centre integrals, $\gamma_{\mu\nu}$, evaluated either from the Nishimoto-Mataga formula[24] or by the Pariser–Parr method[1] yielded substantially the same results.

Where data regarding bond-lengths and angles is not available, we have used typical values from compounds of similar structures.

RESULTS

(i) *Electronic transitions.* The $\pi \rightarrow \pi^*$ transitions for the molecules (II–VII) were calculated and the results are given in Tables 2–7; all calculated transition energies ($E_{calc.}$), observed transitions ($E_{obs.}$), and integrals are given in electron-volts.

The singlet transition energies calculated for thiophen are shown in Table 2 along with the values of the parameters ω_s and β_{cs}. In keeping with earlier work,[6, 8, 9]

TABLE 1. EARLIER WORK ON THIOPHEN (II)

ω_s	β_{cs}	Calculated π-Transition Energies ($E_{calc.}$)	Comments	Ref.
− 8·46	− 1·36	5·13 5·71 6·62	Penetration integrals included γ_{ss} = 9·79	6
− 18·00	− 2·51	5·50 6·85 7·19 8·18	γ_{ss} = 11·9	7
− 11·9	− 0·9	5·13 5·42 7·18	γ_{ss} = 11·9	8
− 11·66	− 1·4	5·23* 5·63* 7·02*	γ_{ss} = 12·14	9

* Estimated from published diagram.

reducing these parameters from those used by Wachters and Davies[7] leads to much improved results. The ranges $\omega_s = -9$ to -10 eV and $\beta_{cs} = -1{\cdot}2$ to $-1{\cdot}5$ eV yield good agreement with the observed transition energies. This range of parameter values is close to the values used in some earlier work[6, 9] and improves the predicted transitions slightly.

The calculations were next carried out for the monosulphur hetero-aromatic systems, benzothiophen (III) and dibenzothiophen (IV), the results being shown in Tables 3 and 4. The pi-electron transitions in benzothiophen (III) are successfully accommodated by the ranges of ω_s and β_{cs} used for thiophen, but the dibenzothiophen calculations required a smaller value of ω_s.

The di-sulphur containing thienothiophens (V, VI) gave the satisfactory agreement between predicted and observed electronic transitions shown in Tables 5, 6. We have assumed that the very weak absorption near 4·1 eV observed[25] in solution spectra of thienothiophens (V, VI) but not in its vapour phase spectrum,[25] is not a fundamental singlet–singlet, $\pi \rightarrow \pi^*$ transition and therefore not covered by this work. Again, β_{cs} values close to $-1{\cdot}2$ eV appeared to yield best results with ω_s set at $-8{\cdot}0$ eV. The value of β_{cs} used in Clark's work[10] was similar to this but his value for ω_s was larger.

Finally, in a test of these parameter values on the tri-sulphur compound, trithione (VII), the calculated transitions given in Table 7 were in good agreement with the observed values.[26]

In general, the results show that a small range of values of ω_s between -8 and -10 eV is necessary to predict the pi-electron transitions in a variety of sulphur containing hetero-aromatics. In fact, if thiophen itself is omitted from the analysis, the best values of ω_s lie close to -8 eV. The variation in β_{cs} is not so large, with generally a

TABLE 2. THIOPHEN (II)

$\gamma_{\mu\mu}, \gamma_{\mu\nu}$	ω_s	β_{12}	β_{23}	β_{34}	$E_{calc.}$	E_{obs}[15–19]
I–A	− 18	− 2·90	− 2·39	− 2·39	6·060	5·16
NM					6·301	5·33
					8·071	(5·63)*
					9·026	6·56
I–A	− 8	− 2·90	− 2·39	− 2·39	6·410	
NM					6·845	
					7·780	
					8·105	
					5·796	
I–A	− 11·75	− 1·00	− 2·66	− 2·07	5·842	
NM					7·271	
					8·135	
					6·234	
I–A	− 11·75	− 2·00	− 2·66	− 2·07	6·350	
NM					8·190	
					8·219	
					5·090	
P	− 9·00	− 1·50	− 2·66	− 2·07	5·547	
PP					6·977	
					7·656	
					5·168	
P	− 10·00	− 1·20	− 2·66	− 2·07	5·373	
PP					7·278	
					7·317	
					5·112	
P	− 9·5	− 1·36	− 2·66	− 2·07	5·465	
PP					7·099	
					7·599	

$\gamma_{\mu\mu}$: I–A approximation or Paoloni (P) method.
$\gamma_{\mu\nu}$: Nishimoto, Mataga (NM) or Pariser, Parr (PP) method.
* See text.

value near − 1·2 eV providing the better results. This value of β_{cs} is close to that suggested (− 1·4 eV) by taking β_{cs} (1·7) = 0·6 β_{cc}. Apart from thiophen, thienothiophen (VI),[27] and the methyl homologue of trithione (VII),[28] the accurate geometries of the compounds treated here are unknown and when these are available the range in ω_s values could well be reduced in future. The calculated second longest absorption bands generally lie a little below the measured positions, in keeping with earlier observations on this point for other compounds.[29]

(ii) *Ionization potentials.* It has frequently been observed that ionization potentials calculated by Koopmans' Theorem[30] are 1–2 eV too large and is also evident in our

TABLE 3. BENZOTHIOPHEN (III)

ω_s	β_{12}	β_{19}	E_{calc} (f)	E_{obs} (log ε)[33]
− 11·75	− 1·20	− 1·50	4·510 (0·006)	4·325 (3·31)
			4·753 (0·063)	4·850 (3·74)
			6·103 (0·985)	5·490 (4·45)
			6·434 (0·828)	6·200 (strong)
− 11·75	− 1·00	− 1·25	4·519 (0·004)	
			4·761 (0·068)	
			6·071 (0·919)	
			6·433 (0·845)	
− 10·00	− 1·20	− 1·50	4·458 (0·031)	
			4·690 (0·028)	
			5·806 (0·496)	
			6·076 (0·695)	
− 10·00	− 1·00	− 1·25	4·474 (0·025)	
			4·701 (0·029)	
			5·632 (0·357)	
			6·019 (0·662)	
− 9·00	− 1·36	− 1·36	4·357 (0·068)	
			4·575 (0·019)	
			5·345 (0·291)	
			5·643 (0·365)	

In obtaining results in this, and subsequent Tables, $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ were calculated by the Paoloni and Pariser–Parr methods respectively.

calculations. However there is a fair correlation ($\rho = 9{\cdot}3$) between experimental ionization potentials and calculated energies of the highest occupied MO's as shown in Fig. 2. Interestingly naphthalene also falls near the correlation line. Ionization potentials were determined by electron impact using a modification of Warren's method[31] to process the ionisation efficiency curves.

CONCLUSIONS

Employing a small range of empirical values for the parameters ω_s, β_{cs} in PPP SCF calculations on sulphur hetero-aromatic compounds, and keeping standard values for the other integrals, the $\pi \rightarrow \pi^*$ electronic transitions and ionization potentials in these compounds can be satisfactorily accounted for without specifically incorporating d-orbitals or specifically allowing for small changes in the hybridization of sulphur. It has been found[32] that these values of ω_s and β_{cs} will then account satisfactorily for the long wavelength absorption in thiathiophthens (I).

TABLE 4. DIBENZOTHIOPHEN (IV)

ω_s	β_{cs}	$E_{calc.}$ (f)	E_{obs} (log ε)[33]
− 9·00	− 1·00	4·433 (0·088)	3·81 (3·4)
		4·771 (0·069)	4·31 (4·04)
		4·875 (0·0001)	
		5·128 (0·028)	4·70 (3·94)
		5·54 (0·504)	5·30 (4·58)
− 9·00	− 1·36	4·370 (0·064)	
		4·709 (0·125)	
		4·976 (0·001)	
		5·000 (0·012)	
		5·609 (0·741)	
− 8·00	− 1·5	4·032 (0·087)	
		4·275 (0·206)	
		4·720 (0·011)	
		4·935 (0·001)	
		5·479 (0·483)	
− 8·00	− 1·20	3·989 (0·109)	
		4·238 (0·153)	
		4·508 (0·016)	
		4·999 (0·001)	
		5·409 (0·349)	

TABLE 5. THIENO[2.3*b*]THIOPHEN (V)

ω_s	β_{12}	β_{18}	E_{calc} (f)	E_{obs} (log ε)[25]
− 9·00	− 1·25	− 1·00	4·426 (0·166)	4·18* (1·43)
			5·118 (0·267)	4·48 (2·99)
			5·180 (0·0004)	5·03 (3·28)
			6·305 (0·685)	5·54 (4·38)
− 8·00	− 1·50	− 1·50	4·49 (0·192)	
			5·18 ($\cong$ 0)	
			5·50 (0·543)	
			6·336 (0·943)	
− 8·00	− 1·50	− 1·25	4·274 (0·251)	
			5·187 (0·106)	
			5·376 (0·392)	
− 8·00	− 1·05	− 1·00	4·255 (0·117)	
			4·754 (0·229)	
			5·160 (0·014)	
			6·190 (0·854)	

* Weak band in solution spectrum; see text.

TABLE 6. THIENO[3.2*b*]THIOPHEN (VI)

ω_S	β_{12}	β_{18}	E_{calc}(f)	E_{obs} (log ε)[25]
− 11·75	− 1·50	− 1·25	4·970 (0·541)	4·08 (1·12)*
			6·169 (0·233)	4·47 (4·04)
			6·429 (0·00)	4·99 (4·09)
			6·772 (0·00)	
− 9·00	− 1·50	− 1·25	4·620 (0·502)	
			5·262 (0·00)	
			5·376 (0·308)	
			6·492 (0·00)	
− 9·00	− 1·25	− 1·00	4·338 (0·417)	
			4·801 (0·00)	
			5·195 (0·353)	
			6·358 (0·00)	

* Weak band in solution spectrum; see text.

TABLE 7. TRITHIONE (VII)

ω_S	ω_s	β_{12}	β_{15}	β_{23}	β_{36}	$E_{calc.}$ (f)	E_{obs} (log ε)[26]
− 9·00	− 1·00	− 1·00	− 1·30	− 1·00	− 1·60	3·301 (0·479)	3·0 (3·83)
						4·488 (0·317)	3·71 (3·81)
						4·872 (0·172)	4·90 (3.92)
						5·551 (0·034)	5·42 (3·87)
− 8·00	− 1·00	− 0·70	− 1·50	− 1·20	− 1·80	3·418 (0·524)	
						4·059 (0·192)	
						5·226 (0·382)	
						5·356 (0·003)	
− 8·00	− 1·50	− 0·70	− 1·50	− 1·20	− 1·80	3·434 (0·509)	
						4·019 (0·198)	
						5·224 (0·353)	
						5·452 (0·017)	
− 8·00	0·00	− 1·50	− 1·30	− 1·00	− 1·60	2.911 (0·513)	
						4·292 (0·037)	
						4·724 (0·491)	
						5·222 (0·092)	

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