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Theoretical Studies on the Electronic Spectra of Substituted Aromatic Molecules

IV. PPP-SCF Parameters for Polysubstituted Benzenes and Five-Membered Ring Heterocyclics Containing Nitrogen, Oxygen and Sulfur

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A simple Pariser-Parr-Pople π-electron SCF method (i.e. one in which parameter variation with charge densities and bond orders is neglected) is used to predict the first three electronic transitions and the ionization potentials of polysubstituted benzenes and five-membered ring heterocyclics containing nitrogen, oxygen, and sulfur. The parameters were chosen to fit results for the monosubstituted benzenes and then tested on the polysubstituted compounds, using charge transfer data and oxidation potentials to estimate the ionization potentials. No serious deviations other than those which could be ascribed to steric effects for the ortho disubstituted compounds were found, indicating that penetration integrals and non-nearest-neighbor effects can be absorbed into the semi-empirical parameters. For the five-membered ring heterocyclics it is shown that it is unsatisfactory to use the simple parent compounds, pyrrole, furan, and thiophene as reference molecules in choosing parameters, since satisfactory choices for these molecules often give quite unrealistic results for the corresponding benzo and dibenzo derivatives. Sets of parameters which give consistent results for the parent and the benzo and dibenzo derivatives are given for the nitrogen, oxygen and sulfur heterocyclics.

Mittels eines PPP-SCF-Verfahrens (mit von der Dichtematrix unabhängigen Parametern) werden die drei ersten Elektronenübergänge und Ionisationspotentiale von mehrfach-substituierten Benzolen sowie von heterocyclischen Fünfringen mit N, O und S berechnet. Die Parameter wurden an den einfach-substituierten Benzolen adjustiert. Bei Übertragung auf polysubstituierte Verbindungen ergaben sich nur bei den ortho-disubstituierten Abweichungen, die auf den spezifischen sterischen Verhältnissen beruhen dürften. Daraus wird der Schluß gezogen, daß Durchdringungsintegrale und Effekte übernächster Nachbarn in die Parameter eingeschlossen werden können. Im Fall der Fünfringe zeigt sich, daß man besser nicht die einfachen und unsubstituierten Ringe für die Parameterwahl benützt, weil man sonst oft für Benzo- und Dibenzoabkömmlinge unrealistische Resultate erhält. Dagegen lassen sich Parametersätze finden, die für alle drei Typen befriedigende Ergebnisse liefern.

Une méthode SCF Pariser-Parr-Pople pour électrons π, sans variation des paramètres avec les charges et les indices de liaison, est utilisée pour prédire les trois premières transitions électroniques et les potentiels d'ionisation des benzènes polysubstitués et des hétérocycles pentagonaux contenant de l'azote de l'oxygène et du soufre. Les paramètres ont été ajustés sur les benzènes mono-substitués et testés sur les composés polysubstitués, en utilisant les données du transfert de charge et les potentiels d'oxydation pour évaluer les potentiels d'ionisation. Peu d'écarts importants ont été obtenus, en dehors de ceux que l'on peut attribuer à des effets stériques dans les composés di substitués en ortho; ceci indique que les intégrales de pénétration et les effets des voisins lointains peuvent être introduits dans les paramètres semi-empiriques. En ce qui concerne les hétérocycles à cinq atomes, on montre qu'il n'est pas satisfaisant d'utiliser les composés parents simples: pyrrole, furane et thiophène, comme molécules de référence pour le choix des paramètres, car on obtient ainsi des résultats souvent non réalistes pour les dérivés benzo et di benzo correspondants. On donne des paramètres permettant d'obtenir des résultats satisfaisants dans ces cas.

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Introduction

In a previous paper [1] we showed that it was possible, by a Pariser-Parr-Pople (PPP) π-electron SCF treatment, to obtain good agreement between experiment and theory for the first three ultraviolet transitions for different classes of hydrocarbons (polycyclic alternants and nonalternants, and conjugated polyenes). In the present paper we describe an attempt to predict, using one set of parameters, and also restricting ourselves to the simplest type of PPP theory (i.e. without penetration integrals or inclusion of doubly excited states in the configuration interaction), both excited states and ionization potentials of mono- and poly-substituted benzenes and five-membered ring heterocyclics containing nitrogen, oxygen, and sulfur.

There have been many previous PPP SCF studies[1] on substituted benzenes, particularly monosubstituted compounds [2–7], and on the simplest five-membered ring compounds [8–10]. We could not, however, find any previous reports of systematic attempt to investigate the reliability of parameters, chosen for simple substituted compounds, for predicting the properties of the polysubstituted compounds (especially mixed) within the framework of the PPP SCF MO method. There is, however, a very thorough piece of work on the use of the Hückel method for this purpose [12]. Also, there seems to be no previous report on how parameters, chosen specifically for the simple five-membered ring compounds, can be used successfully for both the corresponding benzo and dibenzo derivatives, with the exception of the very recent study of Fischer-Hjalmars and Sundbom on nitrogen compounds [11]. This latter task is not trivial because many of the parameters sets previously reported as being satisfactory for the simple compounds [8–10] give quite unreasonable results for the benzo and dibenzo heterocyclic compounds because, whereas the simple compounds are fairly insensitive to parameter choice, the dibenzo derivatives are very sensitive as is shown by our results in Table 3.

Choice of Parameters

In the initial stages of the work, it was hoped that a set of parameters could be found that would apply equally well to both five-membered heterocyclics and substituted benzenes. However, although it was possible to get mutually satisfactory parameters for the nitrogen and oxygen compounds, we ran into great difficulties with the sulfur compounds.

As the starting point in our parameter evaluation, we adopted (a) the Nishimoto-Mataga [16] method of calculating the two center integrals from the one center integrals, and (b) the usual I–A approximation for the one center integrals [17]. The latter approximation gives rise to two different one center integrals for the heteroatoms depending on whether we consider the heteroatom to have a core charge of 2 (γ_{X^+}) [2, 5–10] or, as has often been used recently, a core charge of only 1 [3, 7, 18] giving γ_X.

Corresponding to these two ways of choosing γ_X values are two ways of choosing W_X [as defined by Eq. (1)] values from valence state ionization potentials [i.e. for W_X, the energy for the process X (trtrtrπ^2)$\rightarrow$X$^+$ (trtrtrπ), is used while for W_{X^+}, the energy for the process, X$^+$ (trtrtrπ)$\rightarrow$X^{++} (trtrtr) is used]. An alternative

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[1] Because of the vast number of published papers describing work on semi-empirical π-electron methods, we have made no attempt to compile a complete bibliography.

procedure also often used is the relationship $W_X = -I_{RX} - \gamma_X$, where I_{RX} is the observed ionization potential of either HX or CH_3X [3, 19].

None of these methods were found to be completely satisfactory for all the heteroatoms under consideration, and the only consistent method of getting good results appeared to be to use the one center repulsion integrals calculated for γ_{X^+} and to adjust W_{X^+} empirically arriving at the values listed in Table 1.

Table 1. *Parameter summary*

Substituent	γ_{X^+} (eV)	W_{X^+} (eV)	β_{C-X} (eV)	r_{C-X} (Å)
C	11.13	11.16	−2.32	1.397
NH_2	16.76	26.40	−2.30	1.360
$NH(CH_3)$	16.76	24.80	−2.30	1.360
$N(CH_3)_2$	16.76	24.30	−2.30	1.360
NH (pyrrole type)	16.76	24.80	−1.80	1.380
OCH_3	21.53	33.00	−2.11	1.360
O (furan type)	21.53	33.00	−1.80	1.370
SCH_3	13.05	22.20	−1.00	1.700
S (thiophene type set 1)	13.05	22.20	−1.00	1.720
S (thiophene type set 2)	13.05	22.20	−1.50	1.720

During our investigation on the monosubstituted benzenes, it was noticed that the values of γ_X and W_X were not completely independent, since the difference between them was the major influencing variable. This interdependence has also been noticed by Kwiatkowski for aniline [3], and was rationalized by him as being due to the quite small amount of charge transfer in the ground state. If this is the case, then the value of the π bond order of the amino nitrogen, P_{NN}, remains close to 2 so that the main factor influencing the diagonal of the F matrix in Eq. (1) is the difference $(-W_X + \gamma_X)$.

$$F_{XX} = -W_X + P_{XX}\gamma_X + \sum_{P \neq Q} (P_{PQ} - Z_Q)\gamma_{XQ} . \qquad (1)$$

This appears to be a general phenomenon for the monosubstituted benzenes as can be seen by our data for aniline and anisole in Table 2, and the data on thiophenol shown graphically by Fabian *et al.* [20]. Thus, by considering monosubstituted benzenes alone, it is not possible to arrive at a unique set of parameters. In particular it is not possible to decide on a choice between using γ_{X^+} or γ_X values for the one center repulsion integrals.

On the other hand, we found for carbazole, that this interdependence of γ_X and W_X, although operative for the excited states did not hold for the energy of the highest occupied molecular orbital (E(HO)) values (Table 2). A good fit between experiment and theory for the latter was found only when γ_{X^+} values rather than γ_X values were used.

The resonance integrals for the carbon-carbon bonds were calculated using a linear relation between β_{CC} and the bond distance, assuming $\beta_{CC} = -2.3194$ eV for a bond distance of 1.397 Å (benzene) [21], and $\beta_{CC} = -2.473$ eV for a bond distance of 1.335 Å (ethylene) [1].

As starting points for the resonance integrals in the substituted benzenes, the values of β_{CN} [21] and β_{CO} [5] were taken from the literature and found to be

Table 2. *Interdependence of* W_X *and* γ_X

	Aniline[a]		Anisole[a]		Carbazole[a]	
W_X (eV)	26.40	21.98	33.00	26.70	24.80	20.38
γ_X (eV)	16.76	12.34	21.53	15.23	16.76	12.34
E(HO) (eV)	−8.94	−8.82	−9.53	−9.48	−8.81[b]	−8.56[b]
E_1 (*kK.*)	35.25	35.14	36.92	36.94	31.61	30.80
	(0.05)[c]	(0.05)	(0.02)	(0.02)	(0.06)	(0.07)
E_2 (*kK.*)	43.18	42.16	46.08	45.71	35.98	35.08
	(0.34)	(0.38)	(0.15)	(0.18)	(0.10)	(0.13)
E_3 (*kK.*)	51.19	50.84	53.41	53.32	37.88	37.71
	(0.55)	(0.50)	(1.1)	(0.90)	(0.11)	(0.11)

[a] β_{C-X} values as in Table 1.

[b] E(HO) value estimated from Fig. 2 = −8.88 eV.

[c] Oscillator strength values given in parentheses.

satisfactory for aniline and anisole. For β_{CS} a wide range of values were considered, but consistent agreement between experiment and theory for substituted benzenes was reached only when values much lower than the values for the other resonance integrals were used. The final value of $\beta_{CS} = -1.0$ eV is consistent with other work on similar sulfur compounds [20].

Slightly different parameters were used for the five-membered heterocyclic compounds because the W_X of a given atom is influenced to some extent by the type of atoms that surround it. Thus on passing from aniline to N-methylaniline and N,N-dimethylaniline, the resonance integral was kept constant and W_X varied to take into account the effect of the addition of methyl groups to the nitrogen in accordance with the usual practice [3]. In going to carbazole, the same W_X as for N-methylaniline was used since the environment of the nitrogen (two carbon atoms and one hydrogen atom) is the same in both cases. Then the value of β_{CN} was varied empirically to fit the spectra and E(HO) of carbazole. The same parameters were then applied to indole and pyrrole with surprisingly good results (Table 4 and Fig. 4). A similar argument was used with the oxygen and sulfur compounds.The final parameters for all three types of compounds are listed in Table 1. This contains two sets of sulfur parameters because we were unable to find a completely unique set which was completely satisfactory.

In calculating the geometries of the molecules, the benzene ring in the substituted benzenes was assumed to be a regular hexagon with sides of 1.397 Å. The results of microwave studies were used for the geometries of pyrrole [22], furan [23], and thiophene [24], and used to construct thegeometrics for the benzo and dibenzo derivatives, for which no experimental geometries were available. The carbon-heteroatom distances used in the different compounds are listed in Table 1.

In our configuration interaction (CI) calculations, all the singly excited states were included except for the calculation on carbazole using the method of Ref. [10] which was made for purposes of comparison and includes only the limited configuration interaction suggested by the authors. It was evident that further CI would not significantly improve the results in this case.

Results and Discussion

Substituted Benzenes

Direct measurements of ionization potentials have been carried out on only a few substituted benzenes [25]. A much easier measurement, and one which has been found to give results in agreement with direct measurements for polycyclic hydrocarbons [26], is to use the first maximum in the spectra of the charge transfer complex produced by adding tetracyanoethylene (TCNE) to the donor hydrocarbon. Consequently, in out initial studies, we used a linear relationship between the charge transfer maximum and the energy of the highest occupied molecular orbital (E(HO)) to find the best W_X, using the extensive data of Zweig *et al.*for $N(CH_3)_2$, OCH_3, and SCH_3 compounds [12–15] and the data of Ref. [27] for NH_2 and $NHCH_3$ compounds. Calculations on polycyclic hydrocarbons were taken as a reference. It was found that it was not possible to obtain satisfactory agreement for the excited states using parameters obtained in this way. The use of a plot between oxidation potential values in acetonitrile and E(HO)'s yielded much better results wherever the necessary oxidation potentials were available [12–15, 28]. A plot of oxidation potentials versus TCNE charge transfer maxima (ν_{CT}) revealed some scatter (Fig. 1) and also a definite fall off from linearity at the lower frequencies, especially for the polysubstituted compounds. This could be attributed, either to a considerable perturbation in energy levels on complex formation for very strong donor molecules, or to difficulties in getting a true charge transfer peak because of chemical reaction. In order to make full use of Zweig *et al.*'s extensive experimental data [12–15], we evaluated effective charge transfer

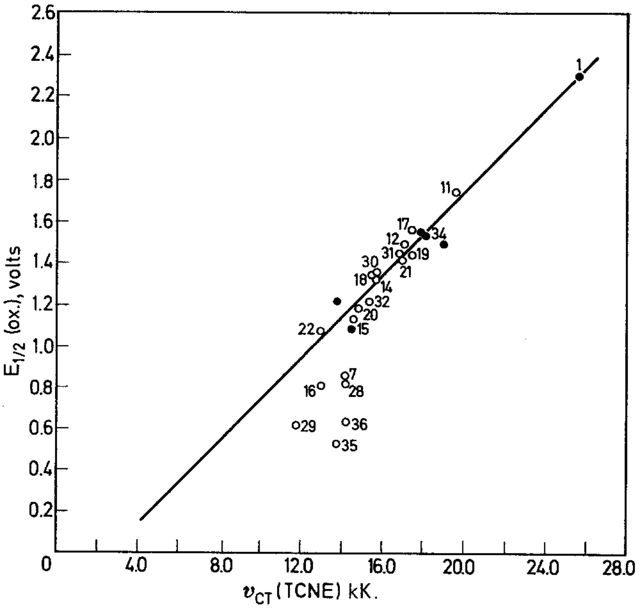

Fig. 1. $E_{1/2}$ (ox.) values versus $\tilde{\nu}_{CT}$ (TCNE) values. ● Hydrocarbons. ○ Substituted compounds. For numbering system see Tables 7 and 8. Experimental data taken from References [12–15, 26–28]

maxima, ν_{CT}(est.), from the oxidation potential versus ν_{CT} graph, using the hydrocarbons and weaker donors as a reference. These values are plotted against the calculated E(HO) values in Fig. 2. The agreement between experiment and theory was good. It was especially gratifying to find that for 1,2,4,5-tetramethoxy- and 1,2,4,5-tetramethylthiobenzene there was good agreement between experiment and theory. This demonstrates the applicability of the simple PPP SCF MO method to polysubstituted compounds, and appears to justify the assumption, which is implicit in our simple model, that penetration integral effects and sigma core polarizations can be absorbed into an empirically chosen W_X value.

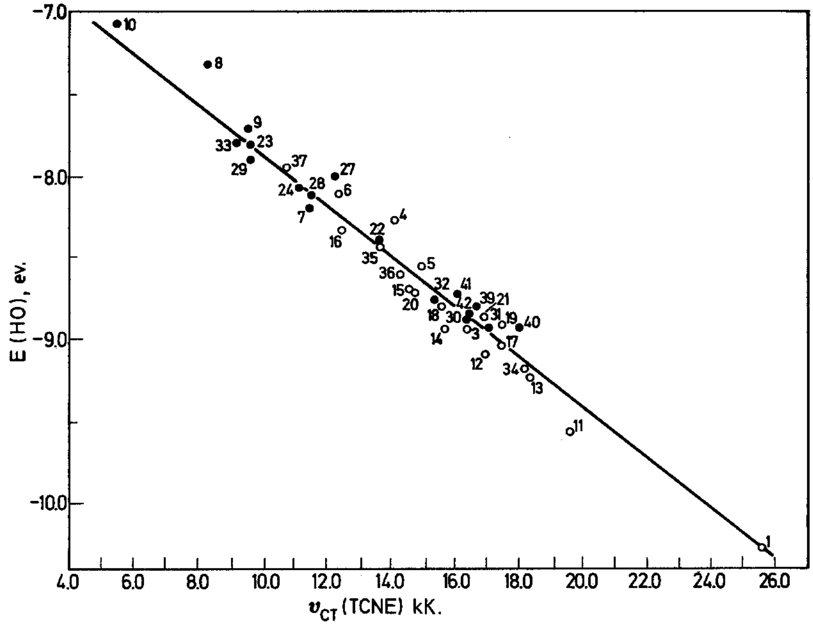

Fig. 2. Calculated E(HO) values versus $\tilde{\nu}_{CT}$ (TCNE) values. ○ Compounds using TCNE data taken from literature [12–15, 27]. ● Compounds using effective TCNE values estimated from oxidation potentials in Fig. 1. For numbering system see Tables 7 and 8

In the case of the ortho-disubstituted compounds where one of the substituents was $N(CH_3)_2$, the calculated E(HO) values were consistently too low, in accordance with the view that in the actual molecules there is sufficient steric repulsion to cause the lone pair of the $N(CH_3)_2$ group to be forced out of conjugation with the benzene ring. Agreement with experiment would necessitate lowering the β_{CN} value for these compounds, as was done, within the framework of Hückel calculations, by Zweig [12].

The assignments for the excited states of substituted benzenes are now fairly well understood [3, 29], so it is an easy task to correlate calculated excited states with experimental values for the first two excited states, and where available, the third (Fig. 3 and Table 7). The results for benzene, naphthalene, and also some monosubstituted naphthalenes (Table 8) are also included in Fig. 3. It can be seen that the overall agreement is satisfactory.

A trend was observed for the lowest transition (corresponding to the ^1L_b band of benzene). This band was predicted to be low by up to 2.0 *kK*. However, it is well known for this transition that doubly excited states and inductive effects (sigma core polarizations) are particularly important [29].

For o-dimethoxybenzene we find that the calculated frequencies for the first two absorptions are in good agreement with experiment, indicating the absence of any special ortho effect as was postulated by Petruska [30], when using a perturbation theory of substituent effects on benzene. For N,N,N′,N′-tetramethyl-o-phenylenediamine, the lowest transition is predicted to be at much lower frequencies (by 4.0 *kK*.) than the observed values. Again, as in the case of the *E*(HO) for this type of compound, we ascribe the discrepancy to steric hinderance.

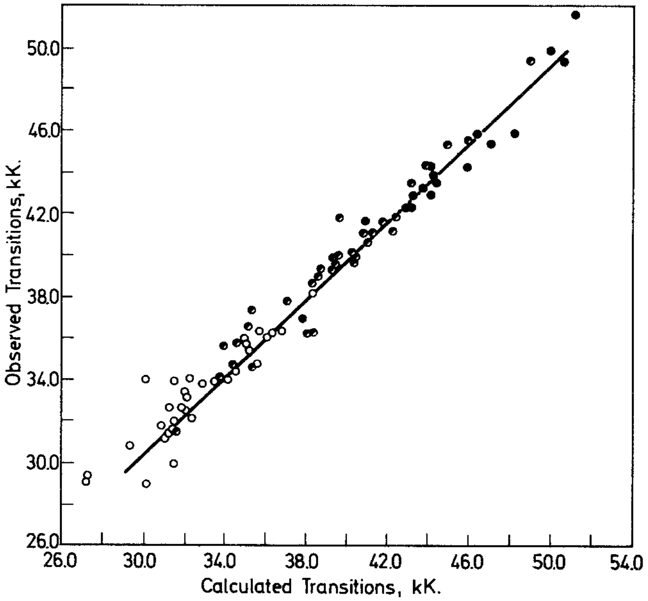

Fig. 3. Comparison between observed and calculated spectral transitions for substituted benzenes and naphthalenes. ○ First transition. ◐ Second transition. ● Third transition. Actual data in Tables 7 and 8

Five-Membered Heterocyclics

Although there have been many previous of PPP SCF calculations on the parent five membered ring compounds; pyrrole, furan, and thiophene [8–10], and some on benzo derivatives [31], the only full report of an SCF calculation on a dibenzo derivative is the very recent one of Fisher-Hjalmars and Sundbom on carbazole [11].

In carrying out our calculations, it was found that the dibenzo derivatives were far more sensitive to parameter variation than the parent compounds, and therefore most of our studies on the variation of parameters were made for the dibenzo derivatives. A calculation was judged to be successful if it predicted correctly, within reasonable limits, the *E*(HO) (±0.2 eV) as estimated from the

ν_{CT} graph in Fig. 2., and the transition energies of the first three *UV* transitions (±1.0 *kK*.). As a secondary criterion, we looked at the intensities of the transitions, but since these are most difficult to calculate correctly using a simple PPP SCF model which includes only a limited number of singly excited states in the configuration interaction, not too much importance was given to them [32].

The relative advantage of considering a series of compounds rather than just the parent molecule in choosing parameters is shown by the results on carbazole reported in Table 3. Calculation 1 was carried out using the parameters suggested by Solony and Birss [8] in their study of pyrrole. Calculation 2 utilized parameters suggested by Flurry *et al.* [10] from a similar study, but one which included non-nearest-neighbor resonance integrals. It can be seen that these parameters are completely unsatisfactory for carbazole. Calculation 3 is that reported in Ref. [11] using parameters calculated for a small number of standard molecules including aniline and pyrrole. These results are much better than either Calculation 1 or 2, although they still tend to give high results (by 4.0 *kK*.) for the first two transitions. Calculation 4 is the final result of our parameter study and is in good agreement with experiment. We have also not lost agreement for pyrrole and indole (Table 4) in contrast to the previous work in which pyrrole was chosen as the reference molecule.

Table 3. *Transferability of parameters from pyrrole to carbazole*

Calculation	E_1[a]	E_2	E_3	E_4	E_5	E_6	E_7
1[b]	19.99 (0.38)	21.90 (0.19)	30.84 (0.002)	34.12 (0.06)	38.73 (0.26)	44.85 (0.06)	46.62 (0.06)
2[c]	37.00 (0.02)	39.34 (0.48)	43.47 (0.10)	47.20 (0.71)	46.06 (1.5)	51.60 (0.48)	51.65 (0.020)
3[d]	34.00 (0.03)	38.10 (0.24)	40.50 (0.002)	45.70 (0.20)	45.80 (1.8)	47.60 (0.27)	50.80 (0.02)
4[e]	31.61 (0.06)	35.98 (0.10)	37.88 (0.11)	41.79 (0.13)	41.67 (1.5)	46.73 (0.38)	47.61 (0.16)
Experimental	30.00 (3.6)	34.50 (4.2)	38.80 (4.3)		42.70 (4.6)		48.00 (4.3)

[a] Transition energies are in *kK*. with the oscillator strengths in parentheses. For experimental, the values in parentheses are log ε.

[b] Parameters of Ref. [8].

[c] Parameters of Ref. [10].

[d] Parameters of Ref. [11].

[e] Parameters of Table 1.

Nitrogen Compounds. In varying our parameters for carbazole, it was found that both the frequency and intensity of the second transition, and the *E*(HO) were particularly sensitive to W_N. As we have already mentioned, the requirement of fitting both the *E*(HO) and the spectral transitions narrowed down the range of satisfactory parameters considerably (i.e. it required the use of γ_{N^+} rather than γ_N). On the other hand, we found that β_{CN} was a fairly insensitive parameter that also had to be varied to get a thoroughly satisfactory calculation. The parameters for carbazole were then found to be transferable to indole and pyrrole, although the *E*(HO) values for these two compounds turned out rather poor. In the case of

Table 4. *Summary of results (nitrogen and oxygen heterocyclics)*

Compound	E(HO)[a]		Transitions[c]		
	Calc.	Est.[b]	Calculated	Experimental	Ref.
Pyrrole	−9.63	−9.26	46.07 (0.23)	47.40 (0.12)	[42]
			47.68 (0.08)		
			58.85 (0.39)	58.50 (0.60)	
Indole	−8.91	−9.19	35.03 (0.07)	34.50 (3.6)	[43]
			37.26 (0.10)	38.00 (3.8)	
			45.55 (1.1)	46.70 (4.4)	
			48.70 (0.07)		
			52.09 (0.48)	52.00	
			53.45 (0.11)		
Carbazole	−8.81	−8.88	31.61 (0.06)	30.00 (3.6)	[44]
			35.98 (0.10)	34.50 (4.2)	
			37.88 (0.11)	38.80 (4.2)	
			41.79 (0.13)		
			41.66 (1.5)	42.70 (4.6)	
			46.73 (0.38)		
			47.61 (0.16)	48.00 (4.3)	
Furan	−9.73	−9.77	46.31 (0.31)	46.41 (3.7)	[38]
			48.09 (0.02)		
Benzofuran	−9.41	−9.66	36.29 (0.006)	35.59 (3.5)	[45]
			41.14 (0.39)	40.90 (4.0)	
			47.39 (0.72)	48.54 (4.4)	
			50.39 (0.09)		
			52.42 (0.52)		
Dibenzofuran	−9.49	−9.45	34.69 (0.01)	35.71 (4.2)	[44]
			37.94 (0.06)		
			39.93 (0.45)	40.16 (4.2)	
			45.56 (1.3)	45.87 (4.5)	
			46.65 (0.40)		
			49.68 (0.32)		
			52.55 (0.15)		

[a] Values listed are in eV.

[b] Values estimated from reference line of Fig. 2.

[c] Transition energies are in kK. with oscillator strengths in parentheses. For experimental data, values in parentheses are log ε.

pyrrole, the highest occupied MO (HOMO) is of a_2 symmetry in agreement with all valence shell electron calculation [33, 34]; however, it does not involve the substituent so that any improvement would have to come from changing the carbon parameters (i.e. by calibrating the calculations to fit cis-butadiene). Our final results are summarized in Table 4 and Fig. 4.

Oxygen Compounds. Fairly good agreement was found for the excited states of all three oxygen heterocyclic compounds (Table 4 and Fig. 4). We interpret the observed increased intensity of the first transition in dibenzofuran relative to carbazole as being due to the superposition of two transitions. The possibility of deciding whether this assignment is correct or not is by a study of substituent effects at different positions. This is at present underway, but is somewhat hampered by lack of experimental data. For the E(HO)s, the results are good for dibenzofuran and furan, for which the HOMOs are ones with modes at the substituent position (a_2 type). The HOMO for benzofuran involves considerable mixing of the heteroatom, and its value is predicted to be much too high, indicating that perhaps our calculation predicts too much delocalization in the ground state.

Sulfur Compounds. The spectrum of dibenzothiophene and the effect of substituents on it is very similar to that of carbazole [35], but the *E*(HO) estimated from TCNE CT spectra [36] is more negative for the sulfur compound. Similarly, the spectrum of thiophenol is similar to that of N-methylaniline [37] but the *E*(HO) is more negative for the sulfur compound than the nitrogen compound.

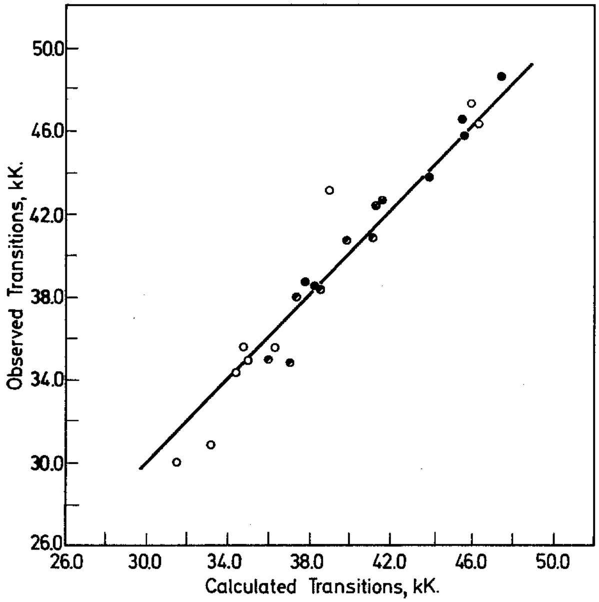

Fig. 4. Comparison between observed and calculated spectral transitions for heterocyclics. ○ First transition. ◐ Second transition. ● Third transition. ⊗ Fourth transition. Actual data in Tables 4 and 5

By contrast, the spectrum of thiophene is different from that of pyrrole and furan in having an absorption band below 45.0 *kK*. as is shown conclusively by Kiss in a study of the spectra of especially purified pyrrole, furan, and thiophene [38].

The *E*(HO) for thiophene is predicted from its TCNE CT spectrum to be quite close to that of benzene, which is in agreement with the direct measurement of the ionization potentials [25]. After many unsuccessful attempts to procedure a satisfactory match between experiment and theory for thiophene and dibenzothiophene, we arrived at two sets of compromise parameters (Table 1), the results of which are reported in Table 5. For comparison, also included in Table 5 and Fig. 4, we have carried out calculations using parameters recommended by Fabian *et. al.* [20], who suggested, on the basis of unpublished work, that a much lower value of β_{CS} (-1.6 eV) was necessary for the sulfur heterocyclics than for the thio substituted benzenes. Although all his parameters except β_{CS} ($\gamma_{SS} = \gamma_{CC} = 10.84$ eV, $\beta_{CS} = 0{,}7\,\beta_{CC}$, $W_S = 20.0$ eV, and $W_C = 11.42$ eV) are quite different from ours, it should be

Table 5. *Summary of results (sulfur heterocyclics)*

Calculation	E(HO)[a]	E_1[b]	E_2	E_3	E_4
Thiophene					
1[c]	−9.74	43.69 (0.20)	46.45 (0.33)		
2[d]	−9.54	38.94 (0.16)	43.96 (0.33)		
3[e]	−9.45	44.40 (0.17)	46.29 (0.35)		
Exp. [38]	−10.20[f]	43.30 (3.8)			
Benzothiophene					
1	−9.23	35.06 (0.09)	38.04 (0.12)	44.33 (0.85)	
2	−9.16	34.50 (0.08)	38.53 (0.18)	43.81 (0.70)	
3	−9.05	35.53 (0.05)	39.15 (0.21)	45.32 (0.85)	
Exp. [45]	−9.24[f]	34.42 (3.3)	38.84 (3.7)	43.86 (4.4)	
Dibenzothiophene					
1	−9.16	32.40 (0.07)	37.50 (0.05)	37.70 (0.06)	41.59 (1.4)
2	−9.14	33.20 (0.05)	37.10 (0.02)	38.40 (0.25)	41.40 (1.0)
3	−9.04	33.30 (0.05)	37.60 (0.08)	38.70 (0.08)	42.30 (1.4)
Exp. [44]	−9.14[f]	30.80 (3.5)	35.00 (4.1)	38.50 (str)	42.50 (4.8)

[a] Values are in eV.

[b] Transition energies are in *kK*. with the oscillator strengths in parentheses. For experimental, values in parentheses are log ε.

[c] Parameters of Ref. [20].

[d] Parameters of Table 1, set 1.

[e] Parameters of Table 1, set 2.

[f] E(HO) values estimated from Fig. 2.

noticed that the difference $W_S - \gamma_{SS}$ is the same in both cases, again emphasizing its importance in narrowing down the search for satisfactory parameters.

The value of $\beta_{CS} = -1.5$ eV is only introduced in our case as being necessary to fit the longwavelength transition of thiophene. This, however, could possibly be due to a transition not involving π-electrons at all, but could be due to n or σ-electrons. The low β_{CS} value was also necessary to increase the oscillator strength of the second transition in dibenzothiophene to bring it to a value of the same order of magnitude as the first transition. These pieces of evidence are not compelling by any means, so we are not prepared on the basis of our work to strongly favor this value of β_{CS}.

We conclude for the sulfur heterocyclics, that the results we report are about as good as one can get within the framework of the simple model. There is obviously room for improvement, perhaps through inclusion of d orbitals [9], doubly excited states, or sigma core polarizations.

Electron Densities

In comparing π-electron calculations with experimental data, the π-electron densities are often related to estimates of the π-electron dipole moment [2, 11, 20], and to proton chemical shifts [39]. In our recent work [33, 40] on calculations including all the valence shell electrons (the CNDO/2 SCF method [41]), we were able to calculate accurately (if agreement with experiment may be interpreted in this way) the total dipole moment and also the different contributions to this moment (i.e. the π-electron dipole, μ^{π}, the σ-electron dipole, μ^{σ}, and the atomic dipole, $\mu^{\text{at.}}$). The separation of the μ^{π} value from the total μ value enables us to make a direct comparison with μ^{π} values calculated by π-electron only methods. This comparison is given in Table 6. It is seen that there is a fairly strong parallel between the two sets, particularly since, as can be seen from the values for aniline, N-methylaniline, and N,N-dimethylaniline, the μ^{π} values are extremely sensitive to small changes in W_N. Our μ^{π} values are also very similar to those of Ref. [11]. It seems reasonable then to propose that we could use our parameters and those of Ref. [11] to calculate values for molecules too large to economically carry out CNDO/2 calculations.

Table 6. *π-electron dipole moments (μ^{π})*

Compound	this Work	CNDO/2	Ref. [11]
Aniline	1.87[a]	2.41	1.60
N-Methylaniline	2.61		
N,N-Dimethylaniline	2.90		
Pyrrole	2.54	2.62	2.55
Indole	2.43	2.47	2.27
Carbazole	1.96		1.72
Furan	1.42	1.83	
Benzofuran	1.28		
Dibenzofuran	0.97		
Thiophene	1.27		
Benzothiophene	1.11		
Dibenzothiophene	0.87		

[a] All values listed in debye units.

In view of our previous conclusions [33, 40] that NMR chemical shifts are more closely related to total electron densities rather than to π-electron densities only, and that there can be considerable sigma core polarization even at the para position, we have not attempted to relate our π-electron densities to chemical shifts. However, the values are similar in trend to those we obtained in our CNDO/2 calculations.

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Table 7. *Summary of results (substituted benzenes)*

No.	Compound	E(HO)[a]		Transitions[c]		
		Calc.	Est.[b]	Calculated	Experimental	Ref.[d]
1	Benzene	−10.28	−10.28	38.44 (0.0)	38.40	
				48.91 (0.0)	49.50	
				55.56 (1.2)	55.87	
				55.57 (1.2)		
2	N-Methylaniline	−8.38		32.97 (0.07)	33.90 (3.4)	[47]
				40.94 (0.46)	41.15 (4.1)	
				48.98 (0.27)		
				52.37 (0.76)		
3	Aniline	−8.94	−8.96	35.25 (0.05)	35.50 (0.03)*	[37]
				43.18 (0.34)	43.50 (0.14)	
				51.20 (0.55)	51.60 (0.51)	
				52.80 (0.87)	55.50 (0.57)	
4	o-Phenylenediamine	−8.26	−8.50	33.58 (0.07)	34.00 (0.04)*	[48]
				39.58 (0.22)	41.90 (0.11)	
				48.23 (1.0)	45.90	
				48.86 (0.45)		
5	m-Phenylenediamine	−8.53	−8.64	34.26 (0.04)	34.00 (0.02)*	[48]
				42.12 (0.11)	41.90 (0.19)	
				46.99 (0.50)	45.40	
				47.01 (1.1)		
6	p-Phenylenediamine	−8.09	−8.24	32.08 (0.11)	32.70 (0.04)*	[48]
				40.51 (0.53)	41.00 (0.17)	
				50.72 (0.0)	49.50	
				52.98 (0.94)		
7	N,N-Dimethylaniline	−8.19	−8.10	32.10 (0.08)	33.56 (3.4)	[47]
				40.40 (0.50)	39.84 (4.2)	
				48.44 (0.22)		
				52.26 (0.74)		
8	N,N,N′,N′-Tetramethyl-o-phenylenediamine	−7.29	−7.60	30.15 (0.12)	34.01 (3.3)	
				35.25 (0.32)	37.45 (3.8)	
				44.30 (0.24)	42.92 (4.1)	
				45.97 (1.0)		
				52.78 (0.002)		
9	N,N,N′,N′-Tetramethyl-m-phenylenediamine	−7.71	−7.80	31.38 (0.05)	32.70 (3.6)	[49]
				39.43 (0.05)	39.53 (4.2)	
				41.07 (0.40)		
				43.25 (1.2)	42.45 (4.5)	
10	N,N,N′,N′-Tetramethyl-p-phenylenediamine	−7.07	−7.14	27.17 (0.13)	29.00 (3.4)	[49]
				37.09 (0.74)	37.80 (4.3)	
				42.36 (0.0)		
				49.47 (0.0)		
				52.16 (0.0)		
				52.69 (0.89)		
				52.94 (0.62)		
11	Methoxybenzene	−9.53	−9.38	36.92 (0.02)	36.36 (3.2)	
				46.08 (0.15)	45.66 (3.8)	
				53.41 (1.1)		
				53.73 (0.92)		

Table 7 (continued)

No.	Compound	E(HO)		Transitions		
		Calc.	Est.	Calculated	Experimental	Ref.
12	1,2-Dimethoxy-benzene	−9.10	−8.96	35.81 (0.03)	36.36 (3.4)	
				43.82 (0.13)	44.44 (3.9)	
				51.26 (1.1)		
				51.68 (0.83)		
13	1,3-Dimethoxy-benzene	−9.23	−9.18	36.10 (0.02)	36.04 (3.3)	
				44.91 (0.06)	45.45 (3.9)	
				51.15 (1.2)		
				51.32 (0.83)		
14	1,4-Dimethoxy-benzene	−8.95	−8.78	35.17 (0.30)	34.90 (3.5)	
				44.21 (1.1)	44.25 (3.9)	
				53.50 (0.0)		
				53.53 (0.95)		
15	1,2,4-Trimethoxy-benzene	−8.69	−8.59	34.55 (0.06)	34.48 (3.6)	
				42.93 (0.18)		
				50.36 (1.2)		
				50.83 (0.82)		
16	1,2,4,5-Tetra-methoxybenzene	−8.34	−8.26	33.65 (0.07)		
				41.77 (0.18)		
				49.99 (0.81)		
				50.04 (1.4)		
				54.72 (0.0)		
17	Thioanisole	−9.03	−9.04	36.43 (0.01)	36.36 (3.2)	
				38.82 (0.20)	39.37 (4.0)	
				44.72 (0.06)		
				50.04 (0.09)	50.00	
18	o-Bis(methyl-thio)benzene	−8.79	−8.74	35.31 (0.02)		
				37.83 (0.10)		
				40.78 (0.35)		
				43.21 (0.06)		
				46.88 (0.0)		
				51.17 (0.06)		
19	m-Bis(methyl-thio)benzene	−8.90	−9.04	35.51 (0.01)		
				38.80 (0.09)		
				39.34 (0.33)		
				42.59 (0.09)		
				47.07 (0.03)		
				51.32 (0.09)		
20	p-Bis(methyl-thio)benzene	−8.71	−8.62	35.03 (0.03)	36.00 (4.3)	
				37.76 (0.33)		
				41.21 (0.0)	41.00	
				43.05 (0.0)		
				45.84 (0.11)		
				50.70 (0.23)		
21	s-Tris(methyl-thio)benzene	−8.85	−8.95	36.89 (0.0)		
				38.85 (0.0)		
				40.36 (0.44)		
				43.57 (0.18)		
				43.58 (0.18)		

Table 7 (continued)

No.	Compound	E(HO)		Transitions		
		Calc.	Est.	Calculated	Experimental	Ref.
22	1,2,4,5-Tetra-(methylthio)-benzene	−8.41	−8.42	35.59 (0.06)		
				37.16 (0.18)		
				41.30 (0.0)		
				41.86 (0.81)		
				42.49 (0.0)		
				43.42 (0.28)		
23	N,N-Dimethyl-p-anisidine	−7.81	−7.80	30.50 (0.10)	31.85 (3.4)	[49]
				39.59 (0.57)	40.00 (4.1)	
				48.21 (0.07)		
				52.13 (0.63)		
				54.97 (0.75)		
24	N,N-Dimethyl-m-anisidine	−8.06	−8.06	32.42 (0.06)	34.13 (3.5)	[49]
				40.45 (0.45)	39.84 (4.1)	
				46.36 (0.32)	45.87 (4.3)	
				48.96 (0.91)		
25	N,N-Dimethyl-amino-p-aniline	−7.52		29.34 (0.12)	30.96 (3.3)	
				38.55 (0.65)	39.06 (4.1)	
				46.38 (0.003)		
				51.62 (0.19)		
				53.24 (0.70)		
				53.27 (0.71)		
				54.65 (0.03)		
26	N,N-Dimethyl-amino-m-aniline	−7.95		32.30 (0.26)	33.33 (3.3)	[49]
				40.30 (0.25)	40.00 (3.9)	
				44.09 (0.37)	44.44 (4.4)	
				45.80 (1.0)		
27	o-(Methylthio)-N,N-dimethyl-aniline	−8.00	−8.20	31.58 (0.09)	33.90 (3.3)	[50]
				38.46 (0.23)	38.91 (3.9)	
				43.33 (0.51)	43.10 (4.2)	
				45.39 (0.20)		
				51.41 (0.04)		
				53.32 (0.47)		
28	m-(Methylthio)-N,N-dimethyl-aniline	−8.11	−8.10	32.04 (0.07)		
				39.45 (0.08)		
				41.05 (0.68)		
				44.01 (0.17)		
				51.31 (0.10)		
				53.65 (0.57)		
29	p-(Methylthio)-N,N-dimethyl-aniline	−7.91	−7.82	31.07 (0.09)	31.25 (3.4)	[50]
				38.49 (0.54)	36.37 (4.3)	
				43.08 (0.0)		
				44.80 (0.02)		
				48.95 (0.24)		
				52.26 (0.75)		
30	o-(Methylthio)-anisole	−8.88	−8.86	35.57 (0.03)	34.84 (3.5)	[50]
				39.47 (0.14)	40.00 (3.8)	
				44.75 (0.20)		
				47.80 (0.28)		
				54.76 (0.90)		

Table 7 (continued)

No.	Compound	*E*(HO)		Transitions		
		Calc.	Est.	Calculated	Experimental	Ref.
31	m-(Methylthio)-anisole	−8.92	−8.98	35.82 (0.03)		
				39.20 (0.17)		
				44.91 (0.14)		
				46.80 (0.30)		
				54.50 (0.81)		
				54.93 (0.78)		
32	p-(Methylthio)-anisole	−8.75	−8.72	35.09 (0.04)	35.72 (3.0)	[50]
				39.48 (0.27)	39.91 (4.0)	
				44.43 (0.02)	43.48	
				48.11 (0.004)		
				53.71 (0.85)		
				53.96 (1.0)		
33	3-Methoxy-4-(methylthio)-N,N-dimethylaniline	−7.80	−7.76	31.45 (0.07)		
				38.69 (0.46)		
				43.92 (0.02)		
				45.65 (0.08)		
				47.17 (0.30)		
				48.99 (0.87)		

[a] Values listed are in eV.

[b] Values estimated from Fig. 2.

[c] Transition energies in *kK*. with oscillator strengths in parentheses. For experimental spectra, values in parentheses are logε, except those marked by (*) which are oscillator strengths.

[d] Experimental spectra taken from Ref. [46] unless otherwise indicated.

Table 8. *Summary of results (monosubstituted naphthalenes)*

No.	Compound	*E*(HO)[a]		Transitions[c]		
		Calc.	Est.[b]	Calculated	Experimental	Ref.[d]
34	Naphthalene	−9.18	−9.18	32.53 (0.0)	32.10 (0.0)*	[51]
				35.45 (0.24)	34.70 (0.18)	
				45.90 (2.0)	44.30 (2.0)	
				50.88	50.88	
35	1-Napthylamine	−8.43	−8.44	31.48 (0.05)	30.09 (0.13)*	[52]
				31.82 (0.29)	31.46 (0.13)	
				42.33 (0.64)	41.23 (0.34)	
				43.73 (0.07)		
				44.79 (0.08)		
				47.21 (0.98)	47.44 (0.82)	
				51.21 (0.58)		
				52.79 (0.17)		
36	2-Naphthylamine	−8.61	−8.54	30.14 (0.08)	28.72 (0.03)*	[52]
				34.72 (0.14)	35.83 (0.10)	
				42.33 (1.0)		
				42.97 (0.64)	42.36 (0.86)	
				45.16 (0.13)		
				48.16 (0.69)	47.12	
				49.45 (0.06)		
				52.50 (0.18)		

Table 8 (continued)

No.	Compound	E(HO)		Transitions		
		Calc.	Est.	Calculated	Experimental	Ref.
37	1-N,N-Dimethylaminonaphthalene	−7.94	−7.98	29.27 (0.28)	32.26 (3.7)	
				29.99 (0.11)		
				40.43 (0.39)		
				41.65 (0.23)	41.67 (4.2)	
				43.45 (0.0)		
				47.23 (0.77)		
				50.28 (0.55)		
				51.45 (0.59)		
38	2-N,N-Dimethylaminonaphthalene	−8.07	−7.86	27.38 (0.12)	29.41 (3.4)	
				33.96 (0.16)	35.71 (3.8)	
				40.00 (0.03)		
				40.99 (1.5)	41.67 (4.7)	
				43.04 (0.03)		
				47.93 (0.65)		
				49.38 (0.07)		
				50.90 (0.35)		
				52.52 (0.01)		
39	1-Methoxynaphthalene	−8.77	−8.90	32.10 (0.02)	32.68 (3.5)	
				33.83 (0.27)	34.13 (3.8)	
				43.88 (0.77)	43.29 (4.5)	
				44.83 (0.03)		
				46.66 (0.90)	46.29 (4.5)	
				47.07 (0.23)		
				51.06 (0.57)		
				54.72 (0.05)		
40	2-Methoxynaphthalene	−8.91	−9.10	31.56 (0.04)	31.95 (3.2)	
				35.17 (0.18)	36.76 (3.6)	
				44.17 (1.0)	44.05 (4.8)	
				46.12 (0.37)		
				48.89 (0.41)		
				49.57 (0.26)		
				54.36 (0.05)		
41	1-(Methylthio)naphthalene	−8.71	−8.81	31.52 (0.24)	31.75 (2.6)	
				32.50 (0.02)		
				38.20 (0.04)	36.35 (3.7)	
				42.17 (0.40)		
				44.52 (0.04)		
				46.85 (1.3)		
				48.97 (0.25)		
				51.07 (0.43)		
				53.54 (0.32)		
42	2-(Methylthio)naphthalene	−8.83	−8.88	31.28 (0.04)	31.45 (2.2)	
				34.43 (0.14)	34.48 (3.5)	
				37.92 (0.40)	37.04 (3.7)	
				41.48 (0.26)		
				46.98 (1.4)		
				47.73 (0.22)		
				52.28 (0.40)		

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[a] Values listed are in eV.

[b] Values estimated from Fig. 2.

[c] Transition energies in *kK*. with oscillator strengths in parentheses. For experimental data, values in parentheses are $\log\varepsilon$, except those marked by (*) which are oscillator strengths.

[d] Experimental spectra taken from Ref. [46] unless otherwise indicated.

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