Semi-empirical Parameters in π-Electron Systems

I. Method and Application to Pure Hydrocarbons

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A simple scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation is suggested and applied to a series of unsaturated pure hydrocarbons. The parameter $W\mu$, usually assumed to be exclusively an atomic property, is made dependent on the type of surrounding. This gives a considerable improvement of the results as compared to previous work.

In the past years a vast number of calculations on π-electron systems based on the semi-empirical molecular orbital theory has been made. Several methods for the determination of the semi-empirical parameters have been proposed. In most of these methods some of the parameters are determined from experiments while others are given a theoretical interpretation.

In the present study limited to pure hydrocarbons all parameters occurring in the zero differential overlap (ZDO) approximation have been chosen empirically. It has been found that the number of parameters necessary to determine all atomic integrals can be reduced to eight by the introduction of appropriate interpolation formulae.

In most previous studies of hydrocarbons the parameter W_μ is given the same value for all carbon atoms μ. As has been discussed by Fischer-Hjalmars,[4] this is, however, not consistent with the general features of the ZDO-approximation. Accordingly, in this paper different values of W_μ for different types of carbon atoms are used. A method for the determination of W_μ in the different cases is proposed. The obtained results show a considerable improvement compared to previous works using the same W_μ for all carbon atoms.

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SEMI-EMPIRICAL PARAMETERS FOR UNSATURATED HYDROCARBONS

The Pariser-Parr-Pople (PPP) approximation [1-3] in the SCF-MO-LCAO theory is characterized by the following features:

The zero-differential overlap (ZDO) approximation is applied. The resonance integrals between non-neighbouring atoms are put equal to zero. The remaining integrals in the atomic orbital basis are chosen semi-empirically. Thus the following approximations are made:

$$(\mu|\nu) = S_{\mu\nu} = \delta_{\mu\nu} \tag{1a}$$

$$(\mu|H^{\mathrm{core}}|\mu) = \alpha_\mu \neq 0 \tag{1b}$$

$$(\mu|H^{\mathrm{core}}|\nu) = \beta_{\mu\nu} \neq 0 \qquad \mu \text{ and } \nu \text{ neighbours} \tag{1c}$$

$$(\mu|H^{\mathrm{core}}|\nu) = 0 \qquad \mu \text{ and } \nu \text{ non-neighbours} \tag{1d}$$

$$(\mu\alpha|\nu\beta) = \gamma_{\mu\nu}\, \delta_{\mu\alpha}\, \delta_{\nu\beta} \tag{1e}$$

The approximations introduced in the PPP-method have been critically examined by Fischer-Hjalmars.[4] It was shown that they are equivalent with a formal transformation of the atomic orbital (AO) basis to an orthogonalized atomic orbital (OAO) basis. The interesting question arises, whether the integrals (1b), (1c) and (1e) have local character in the formal OAO basis, and thus are transferable from one molecule to another. It was concluded that the integrals (1c) and (1e) are local to the second order in the overlap integral between nearest neighbours. Thus the parts of $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ that include contributions from other centres than μ and ν are of third order in $S_{\mu\nu}$. The situation for the diagonal elements α_μ of the core operator is, however, more complicated. This integral may according to Goeppert-Mayer and Sklar [5] be rewritten in the following way:

$$\alpha_\mu = W_\mu - \sum_{\nu \neq \mu} \gamma_{\mu\nu} \tag{2}$$

Eqn. (2) represents the special case where each atom contributes only one electron to the π-electron system. It should be emphasized that (2) at this stage may be considered merely as a formal way of rewriting (1b) without introducing any further approximation. The new semi-empirical parameter W_μ contains the one-centre part of the core Hamiltonian and the penetration to formally neutral neighbouring atoms. It was shown by Fischer-Hjalmars [4] that this integral is local to the first order in the overlap integral. The terms of second order contain contributions from the nearest neighbours of atom μ, as well as from μ itself. Thus W_μ in a second order theory should be made dependent on the types of neighbours to atom μ. For a closer study of these terms and the other results briefly discussed above, we refer to the paper by Fischer-Hjalmars.

The present study deals with an attempt to choose the semi-empirical parameters (1b), (1c) and (1e) on the basis of the analysis mentioned above. By choosing the parameters according to this scheme the same degree of approximation is used for all parameters, thus making the method consistent. It is not meaningful to go beyond this approximation only for some of the

parameters, *e.g.* to choose $\beta_{\mu\nu}$ different from zero for non-neighbouring atoms, which is occasionally done.

The purpose has been to choose all parameters empirically from experimental information on a set of model molecules. In order to limit the number of parameters some sort of R-dependence has to be introduced, where R is an internuclear distance. For parameters depending only on the nearest neighbour distances a linear relationship between the parameters and $R_{\mu\nu}$ is used. This choice is based on the fact that the distance $R_{\mu\nu}$ between neighbouring carbon atoms in unsaturated hydrocarbons varies only within a range of around 0.2 Å. Accordingly, $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ for nearest neighbours are given by

$$\beta_{\mu\nu} = \beta_0 + \delta_\beta(R_{\mu\nu} - R_0) \tag{3}$$

$$\gamma_{\mu\nu} = \gamma_0 + \delta_\gamma(R_{\mu\nu} - R_0) \tag{4}$$

Here benzene has been chosen as a reference molecule. Thus R_0 is the nearest neighbour distance in the benzene molecule (1.397 Å), and β_0 and γ_0 the corresponding resonance and repulsion integrals. The very high number of Coulomb repulsion integrals between non-neighbouring atoms prevents them from being determined by the present method. The inter-nuclear distances are here in most cases larger than 2.4 Å. Because of this $\gamma_{\mu\nu}$ should not be very different from $1/R_{\mu\nu}$, and the results should not be very sensitive to the method used for the calculation of these integrals. Here we have used an expression for $\gamma_{\mu\nu}$ introduced by one of us in a previous work,[6] where

$$\gamma_{\mu\nu} = \gamma_{\mu\mu} \; f(z_{\mu\nu}) \tag{5a}$$

where

$$z_{\mu\nu} = \gamma_{\mu\mu} \; R_{\mu\nu} \tag{5b}$$

and

$$f(z) = 1/(z + e^{-z}) \tag{5c}$$

For a discussion of this method we refer to the previous paper.[6] The choice of the function $f(z)$ is to a certain extent arbitrary. However, (5c) seems to give values of the repulsion integrals, which are in agreement with values obtained by more elaborate methods. Pariser has determined the four parameters β, γ_{11}, γ_{12}, and γ_{13} in the benzene molecule by fitting three singlet-singlet and one singlet-triplet transition to the observed absorption spectrum.[7] He thereby obtained the value 5.79 eV for the integral γ_{13}, while (5a)—(5c) gives 5.77 eV for the same integral.

The one-center integral $\gamma_{\mu\mu}$ has been given the value 11.97 eV obtained from atomic spectral data.[6,8]

According to the discussion above the parameter W_μ should in the second order approximation be made dependent on the type of nearest neighbours to the atom μ. As a basis for the determination of W_μ we have used the ionization potential (IP) for the π-orbital in the planar CH_3 radical, 9.843 eV, which has been determined spectroscopically.[9] In this case the carbon atom is surrounded by three hydrogen atoms. By substituting one of these by an $sp^2\pi$-hybridized carbon atom there is a change ΔW_μ in W_μ. Thus W_μ is given by

$$W_\mu = W_0 + \sum_\nu q_\nu \; \Delta W_\mu(R_{\mu\nu}) \tag{6a}$$

where W_0 is the IP of the methyl radical. The constant q_ν is zero if the neighbour ν is a hydrogen atom and unity if it is an $sp^2\pi$-hybridized carbon atom. Following the argumentation made for $\beta_{\mu\nu}$ and nearest neighbour $\gamma_{\mu\nu}$ we have approximated $\Delta W_\mu(R_{\mu\nu})$ by a linear function of the carbon-carbon distance $R_{\mu\nu}$.

$$\Delta W_\mu(R_{\mu\nu}) = \Delta W_0 + \delta(R_{\mu\nu} - R_0) \qquad (6b)$$

where as before R_0 is the bond lenght in the benzene molecule and ΔW_0 the value of ΔW_μ in this molecule. Thus we have, e.g., for W_1 in benzene,

$$W_1(C_6H_6) = W_0 + 2\Delta W_0 \qquad (6c)$$

while in the ethylene molecule,

$$W_1(C_2H_4) = W_0 + \Delta W_0 + \delta(R_{12} - R_0) \qquad (6d)$$

where R_{12} is the C—C bond lenght in this molecule.

By the method discussed above the number of parameters to be determined from experiments has been reduced to eight, namely $\gamma_{\mu\mu}$, γ_0, δ_γ, β_0, $\delta\beta$, W_0, ΔW_0, and δ. Of these $\gamma_{\mu\mu}$ and W_0 have been determined as mentioned above. The parameters β_0 and γ_0 have been determined through a least squares fit to the three transitions $^1A_{1g} \rightarrow {}^1B_{2u}$, $^1A_{1g} \rightarrow {}^1B_{1u}$ and $^1A_{1g} \rightarrow {}^1E_{1u}$ in the benzene molecule. The IP of the same molecule has been used to determine ΔW_0. This leaves three parameters $\delta\beta$, $\delta\gamma$, and δ to be determined from experimental information on other molecules. These molecules should contain C—C bonds with lengths appreciably different from R_0. We have therefore chosen the molecules ethylene and 1,3-butadiene. The parameters were obtained through a simultaneous fit to the IP's of C_2H_4 and C_4H_6, to the N $\rightarrow$ V transition in C_2H_4, and to the two lowest singlet-singlet transitions in C_4H_6. The parameter set thus obtained is summarized in Table 1.

Table 1. Semi-empirical parameters for unsaturated hydrocarbons.

$\gamma_{\mu\mu} =$	11.97 eV	$\beta_0 =$	−2.43 eV	$W_0 =$	−9.84 eV
$\gamma_0 =$	6.95 eV	$\delta_\beta =$	3.21 eV/Å	$\Delta W_0 =$	0.09 eV
$\delta_\gamma =$	−4.65 eV/Å			$\delta =$	8.63 eV/Å

As we have incorporated more conditions than there are parameters to be determined, we have the possibility of testing numerically the consistency in the computational scheme applied. The extent to which applied observed quantities are reproduced by the optimal parameter set, may be inferred from the data given in Table 2. It is gratifying to notice that the experimental values are reproduced rather accurately.

The experimental values quoted in Table 2 have been taken from different sources. The IP value for CH_3 is determined spectroscopically.[9] The remaining IP values are from the work of Turner.[10,32]

Table 2. Comparison between calculated and experimental data applied in the evaluation of the semi-empirical parameters. IP values in eV, and ν values in cm^{-1}.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$	$\nu_{calc.}$	$\nu_{obs.}$
CH_3	9.84	9.84[a]	—	—
C_2H_4	10.52	10.52[b]	61.460	61.460[c]
Benzene	9.25	9.25[d]	39.330	39.500[e]
			50.630	50.600[f]
			56.000	55.900[f]
I	9.07	9.08[d]	47.770	47.760[g]
			57.370	57.010[g]

[a] Ref. 9. [b] Ref. 10. [c] Ref. 11. [d] Ref. 32. [e] Ref. 33. [f] Ref. 12. [g] Ref. 13.

The experimental value for the N→V transition in ethylene is the one reported by Evans.[11] The quoted transitions in benzene are those given by Potts,[12] and by Sponer *et al.*,[33] and the values for butadiene (I) are from the work of Jones and Taylor.[13]

In the calculations of the excited states encountered in the determination of parameters, configurational mixing including all singly excited configurations was invoked.

RESULTS AND DISCUSSION

The approach outlined above was applied in a study of the electronic structure and electronic spectra of some conjugated hydrocarbons.

The discussion is divided into two main parts. In Part 1 an examination of some ground state properties will be carried through. Part 2 is concerned with predictions made for different electronically excited states of the molecules.

The calculations of the molecular ground states were based on a single determinant wave function, whereas configurational mixing, including all singly excited configurations, was introduced in the description of the excited states.

1. Ground state properties. We estimated the carbon-carbon bond distances from the calculated bond orders by means of the relation

$$R_{\mu\nu} = 1.517 - 0.18\, p_{\mu\nu} \tag{7}$$

where $p_{\mu\nu}$ is the mobile bond order between atoms μ and ν. This formula is a linear form of the well-known expression developed within the Hückel approximation by Coulson.[14] Arguments for applying (7) also in SCF calculations have been given previously.[15]

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

Table 3. Calculated and observed bond distances (Å).

	Bond	$R_{calc.}$		$R_{obs.}$	$\varDelta$	
I[a]	1—2	1.346		1.344	0.002	
	2—3	1.464		1.467	—0.003	
II	1—2	1.347		—	—	
	2—3	1.460		—	—	
III[a]	1—2	1.347		1.345 av.	0.002	
	2—3	1.461		1.450	0.011	
	3—4	1.354		1.345 av.	0.009	
IV[b]	1—2	1.424		1.422(0.004)	0.002	
	3—4	1.379		1.371(0.009)	0.008	
	4—5	1.417		1.412(0.014)	0.005	
	2—7	1.412		1.420(0.007)	—0.008	
V[c]	1—2	1.385		1.372(0.002)	0.013	
	2—3	1.485(1.500)		1.514(0.003)	—0.029(—0.014)	
	4—5	1.412		1.423(0.003)	—0.011	
	5—6	1.385		1.385(0.004)	0.000	
	3—8	1.418		1.426(0.003)	—0.008	
			R_X[d]	$R_{E.D.}$[e]	$\varDelta_X$	$\varDelta_{E.D.}$
VI	1—2	1.399	1.394	1.399(0.009)	0.005	0.000
	2—3	1.407	1.398	1.418(0.010)	0.009	—0.011
	3—4	1.403	1.391	1.383(0.008)	0.012	0.020
	4—5	1.403	1.400	1.406(0.016)	0.003	—0.003
	5—6	1.398	1.392	1.403(0.014)	0.006	—0.005
	3—9	1.473	1.498	1.501(0.005)	—0.025	—0.028

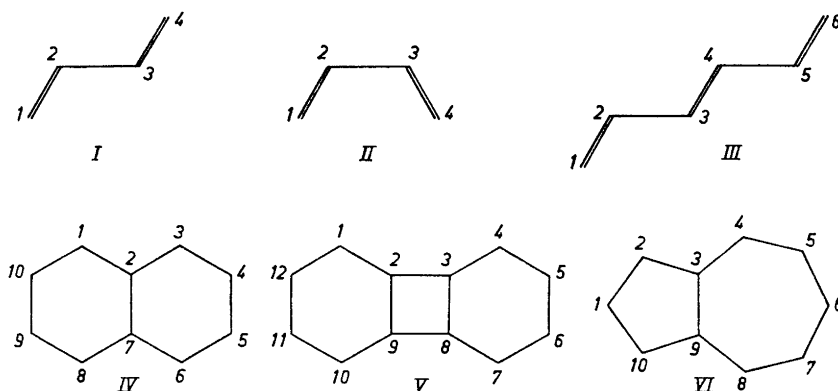Observed *R*-values: [a] Ref. 16; [b] Ref. 17; [c] Ref. 18; [d] Ref. 19; [e] Ref. 20.

Fig. 1. Notation of atoms.

In (I) we find a complete agreement with results obtained by a very recent electron diffraction investigation.[16]

For (II) no accurate experimental values seem to be available. As expected, the predicted bond lengths in (II) are almost identical with the corresponding values found in (I). The agreement with recent measurements made for (III) is also satisfactory.

The molecular structure of (IV) has been studied in detail with experimental methods, and rather precise information on the carbon-carbon bond distances in this molecule is available.[17] The disagreements between calculated and measured bond distances, given in the last column of the table, are all within the reported standard deviations. These are included in parentheses in the fourth column of the table.

The bond distances in (IV) were estimated previously by a similar calculation, but with a single fixed value of W_μ for all the carbon atoms.[15] The present calculation gives results that are in far better agreement with the experimental values. In particular there is an improvement in the predicted length for the central bond. This does indicate that the assumption of different values of W_μ for different carbon atoms is appropriate, and that the adopted linear variation given by eqn. (6b) is a proper one.

The predicted bond distances in (V) are in satisfactory agreement with experimental results recently obtained.[18] For the long bond 2−3 two calculated values are given. The value in parenthesis is obtained by a correction for internal strain discussed previously.[15]

The bond distances in (VI) have been measured rather accurately. In the table two sets of experimental values are quoted, one obtained by X-ray analysis,[19] and one by electron diffraction in the vapour phase.[20] The values are called R_X and $R_{E.D.}$, respectively. Both sets of values are to a good approximation reproduced by the calculation.

The vertical molecular IP as approximated by Koopmans' theorem is very sensitive to variations in the parameter W_μ. Hence a comparison between calculated and observed IP values is a rather sharp test on the goodness of the adopted W_μ values. In Table 4 we have quoted values obtained by different experimental methods.

For the molecules (II), (III), (IV), and (VI) the agreement between calculated and experimental values is satisfactory. This is gratifying as it lends strong support to the assumptions imbedded in eqns. (6a) and (6b). For (V) no experimental data seem to be available. IP values for (IV) and (V) have

Table 4. Calculated and observed ionization potentials. In eV.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$	Ref.
II	9.11	8.75	10
III	8.35	8.26	29
IV	8.17	8.26	30
V	7.61	—	
VI	7.03	7.43	31

been calculated previously by a similar method but with the assumption of a fixed common W_μ value for all the carbon atoms.[15] The present results deviate appreciably from those, especially in the case of (V), for which the IP value was lowered by around 1.2 eV.

Due to the different W_μ values for the different atoms, the Coulson-Rushbrooke theorem [21] according to which all atomic charges are equal to unity, breaks down. Consequently only chemically equivalent carbon atoms in the molecule will have the same π-electron charges. In Table 5 we present

Table 5. Pi-electron charges on the different atoms. In electron units.

Atom	I	II	III	IV	V	VI
1	−0.067	−0.060	−0.070	−0.015	−0.063	+0.001
2	+0.067	+0.060	+0.060	+0.053	+0.071	−0.126
3			+0.010			+0.078
4				−0.011		+0.029
5					−0.008	+0.003
6						+0.030

the values found for the atomic charges. For notation of molecules and atoms, see Fig. 1. The only molecules having a dipole moment are (II) and (VI). The calculated value for (VI), 2.4 D, is somewhat higher than the experimental [22] one of 0.80 D. However, the discrepancy has the expected sign, and may qualitatively be interpreted in terms of the π-electron approximation. The π-electron moment found for (II) was 0.7 D.

2. Electronic spectra. In Table 6 we present the results obtained for some of the electronic transitions in the molecules studied, and make a comparison with experimental values where such are available. The predicted values are based on a configurational interaction calculation where all the singly excited, but no doubly excited configurations were mixed in.

The overall agreement between calculated and observed values is satisfactory. The transition frequencies for the lowest singlet-singlet transitions are in accordance. The oscillator strengths, calculated from the standard formula of Mulliken and Rieke,[23] are on the whole higher than the measured ones.

For (II) no experimental spectrum is available.

The lowest transition frequency in (III) is in nice agreement with the observed vapour phase spectrum. No experimental *f*-value for this transition is reported, but the absorption is found to be very strong.[24,25]

The spectra of the isomers (IV) and (VI) have been investigated systematically. The experimental values quoted in the table are taken from the work of Mann, Platt and Klevens.[26] The component bands referred to are those which are expected to be relevant in a discussion of vertical transitions. The general features of the spectra are rather well accounted for, and the observed resemblances [26] in the five lowest absorption bands are fairly well reproduced.

Table 6. Calculated and observed electronic spectra. Transitions given in cm^{-1}. Singlet-singlet transitions.

Molecule	$\nu_{calc.}$	$\nu_{obs.}$	$f_{calc.}$	$f_{obs.}$	pol. calc.	pol. obs.
II	44.700	—	0.44			
	56.100	—	0.01			
III[a]	40.900	41.500	1.39	—		
	51.200		forb.			
	54.300		»			
	57.700	57.100	0.03	—		
IV[b]	34.100	32.800	0.03	0.002	x	x
	39.600	37.800	0.20	0.18	y	y
	46.900		forb.			
	48.300		»			
	49.600	48.000	2.07	1.68	x	x
	52.200	53.000	0.80	0.2	y	—
	67.400	~60.000	0.88	0.6?	y	—
V[c]	31.700	>25.400	forb.	—	forb.	forb.
	33.200	>28.200	0.10	—	x	x
	38.500	>40.300	forb.	—	forb.	—
	45.100		2.04		x	—
VI[b]	17.000	16.700	0.05	0.01	y	y
	28.900	28.800	0.04	0.08	x	x
	34.700	32.700?	0.30	—	y	y
	42.100	37.100	2.05	1.10	x	x
	42.700	42.300	0.07	0.38	y	—
	49.800	51.800	0.04	0.65	x	—
	51.200		0.02		y	

Observed values: [a] Refs. 24, 25; [b] Ref. 26; [c] Refs. 27, 28.

The electronic spectrum of (V) deviates substantially from that of the polyacenes. The lowest singlet-singlet transition has a 0—0 band at 25 400 cm^{-1} in the vapour.[27] The band corresponding to the vertical transition is hard to locate as it is submerged in the strong absorption system at around 3.500 Å. A vibrational analysis of the lowest band has led to the conclusion that the nuclear configuration is probably very different in the ground and excited state.[27] This would give a vertical transition absorbing at an appreciably higher frequency than that corresponding to the 0—0 band. The two subsequent observed bands also refer to 0—0 transitions [27,28] which absorb at lower frequencies than the vertical transitions. The assignments of the transitions agree with the observed ones where such are available.[27]

CONCLUSION

The simple scheme suggested for the parametrization in the semi-empirical SCF method for π-electron systems yields results that are in good agreement with observed quantities for the pure hydrocarbons studied. The refinement introduced by taking into account neighbouring effects on the parameter W_μ leads to predictions for ionization potentials and electronic spectra that represent a significant improvement of the results obtained by a previous calculation with a common fixed value of W_μ for all the carbon atoms.

This particular scheme may easily be extended to molecules containing hetero-atoms. Studies along this line are in progress.

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