Semi-empirical Parameters in π-Electron Systems

V. The Carbonyl Group

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In an extension of a modified Pariser-Parr-Pople approximation a set of semi-empirical parameters appropriate to the carbonyl group has been evaluated. The resulting parameter values have been applied in calculations of bond distances, ionization potentials, and electronic spectra of a series of molecules containing keto groups. The predicted values are in satisfactory agreement with experimental results.

In a series of previous papers [1-4] a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation has been introduced. In the first paper [1] (hereafter referred to as I) the method was developed and applied to pure unsaturated hydrocarbons. The subsequent papers have dealt with extensions of the scheme to account for the methyl group,[2] different kinds of nitrogen containing molecules,[3] and chlorine derivatives.[4]

The purpose of the present study is to extend the method further to include the carbonyl group and to demonstrate its application to some carbonyl compounds.

The essential new features introduced in I are the following. Firstly the atomic parameter W_C was made dependent on the surroundings. This makes the method consistent, *i.e.* all parameters may be regarded as approximated to the second order in the overlap integral between neighbouring atoms in a formal OAO basis.[5] Secondly all the parameters were chosen empirically from experimental information on a set of molecules.

DETERMINATION OF SEMI-EMPIRICAL PARAMETERS

The general scheme applied in the evaluation of the parameter values is the one developed in paper I. Here the additional parameters needed for the carbonyl group are introduced and determined.

The formalism used is identical with that described previously. Consequently only a few expressions necessary for the definition of the new parameters will be presented.

In paper I the one-electron parameter W_μ was made dependent on the surroundings of the carbon atom μ. This dependence was introduced by the expression

$$W_\mu = W^0 + \sum_{\nu=1}^{3} \Delta W_\mu (\nu) \tag{1}$$

where W^0 is the ionization potential (IP) of the methyl radical, and where $\Delta W_\mu (\nu)$ represents a change in W^0 due to the presence of neighbouring atoms ν different from hydrogen. This change is made dependent on the nature of the atom ν and also on the interatomic distance $R_{\mu\nu}$:

$$\Delta W_\mu(\nu) = \Delta W_\mu{}^0(\nu) + \delta(R_{\mu\nu} - R_0) \tag{2}$$

In eqn. (2) R_0 is a chosen reference distance, and δ is a coefficient to be determined empirically.

The parameter W_μ for the carbonyl carbon was fitted to the general scheme by assuming that the change due to the neighbouring oxygen atom, $\Delta W_C(O)$, could also be expressed by a linear relation of type (2). According to this assumption the bond distance of the carbonyl group enters as a variable. However, the measured carbonyl bond distances, where available, are close to 1.22 Å in all the molecules studied in the present work. Accordingly this value was assumed for all the molecules, and no distance dependence was introduced. As far as the correction $\Delta W_C(O)$ is concerned eqn. (2) thus reduces to the constant term

$$\Delta W_C(O) = \Delta W_C{}^0(O) \tag{3}$$

The additional terms given by eqn. (1) were evaluated according to the rules suggested in paper I.

As a consequence of the assumption of a fixed carbonyl bond distance, the corresponding oxygen parameter W_O was given the same value in all the molecules studied. The same restriction was put on the remaining two parameters determined empirically, namely the two-electron Coulomb repulsion integral γ_{CO} and the core resonance integral β_{CO}.

The one-center two-electron Coulomb repulsion integral for oxygen, γ_{OO}, was assumed to be 18.89 eV, a value derived from atomic spectral data in a manner leading to the value used for the corresponding integral γ_{CC} in paper I.[6,7]

The remaining parameters needed for the calculations presented here were taken from paper I and from the more recent study of methyl substituted hydrocarbons.[2]

The two-electron two-center Coulomb integrals for non-neighbours were calculated by the uniformly charged sphere approximation.[8] The diameter of the tangent spheres constituting an oxygen π orbital was assumed to be 1.04 Å, a value corresponding to the diameters of 1.47 Å and 1.76 Å introduced previously for the carbon atom and methyl group orbitals, respectively.[2] This method leads to some minor corrections of the carbon atom parameters given in paper I. The adjusted values have been presented elsewhere.[2,3,9]

Table 1. Semi-empirical parameters for the carbonyl group. All values in eV. For notation see text.

$\gamma_{OO} = 18.89$	$W_O = -19.60$
$\gamma_{CO} = 9.33$	$\Delta W_C(O) = -0.71$
$\beta_{CO} = -2.46$	

Five new parameters thus have to be determined from experiments, of these γ_{OO} has been evaluated as mentioned above. The remaining parameters γ_{CO}, β_{CO}, W_O, and $\Delta W_C(O)$ were determined through a simultaneous least squares fit to the ionization potential (IP) and lowest singlet-singlet transitions of formaldehyde(I), acrolein(II), and benzaldehyde(III). Two transitions were used for benzaldehyde, one for each of the other molecules. The parameter set obtained is presented in Table 1.

The IP's and transition energies calculated from these parameter values are given in Table 2 together with the experimental data used in the fitting. Seven experimental values are satisfactorily reproduced by variation of four parameters. Thus the consistency of the computational scheme seems quite good from this point of view.

The experimental IP's quoted in Table 2 are adiabatic values obtained by Watanabe [10] (benzaldehyde) and by Turner,[11] whereas the transition energies, all of which are vacuum UV-values, have been measured by Kimura and Nagakura [12] (benzaldehyde) and by Walsh.[13,14]

The numerical solutions of the SCF-equations were evaluated on a CDC 3300 computer by means of a programme written by Drs. B. Roos and T. Alm, and kindly put at our disposal.

Table 2. Comparison between calculated and experimental data applied in the evaluation of the semi-empirical parameters. All values in eV.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$	$\Delta E_{calc.}$	$\Delta E_{obs.}$
I	14.00	13.99 [a]	7.95	7.95 [c]
II	10.80	10.82 [a]	6.26	6.41 [c,d]
III	9.52	9.51 [b]	4.64	4.52 [e]
			5.49	5.35 [e]

[a] Ref. 11. [b] Ref. 10. [c] Ref. 14. [d] Ref. 13. [e] Ref. 12.

RESULTS AND DISCUSSION

The parameter scheme obtained above was applied in a study of the elec-tronic structure and electronic spectra of some carbonyl compounds. Glyoxal (IV), acetaldehyde (V), acetone (VI), p-benzoquinone (VII), 2,5-dimethyl-p-benzoquinone (VIII), and o-benzoquinone (IX) were chosen for this purpose, in addition to the three reference molecules.

The molecular ground states were described by a single determinant wave function, whereas configurational mixing including all singly excited configurations, was invoked in the description of the excited states.

The carbon-oxygen skeleton of the molecules was assumed to be planar with all angles equal to 120°, except for (IX) where some minor adjustments of the angles were introduced in order to obtain a molecular geometry consis-tent with the chosen bond distances. Fig. 1 gives labelling of molecules and notation of atoms.

In a separate calculation the angle 3—2—7 in (VII) was changed from 120° to the experimental value [15] 117.8°. This gave only negligible changes in the results.

The bond distances used for deriving the values of the distance-dependent parameters are given in the third column of Table 3. Two different calcula-tions were performed in the case of (VIII). Firstly the geometry of molecule (VII) was retained. Secondly four of the ring distances were changed to the values indicated in parentheses in the third column of Table 3. The semi-empirical parameters varying with bond distances were based on these new values, whereas repulsion integrals between non-bonded atoms were kept unchanged. Results from this second calculation on (VIII) are given in paren-theses in Tables 3, 4, 5, and 7.

1. Ground state properties. Theoretical estimates of C—C bond lengths were obtained from the relation [16]

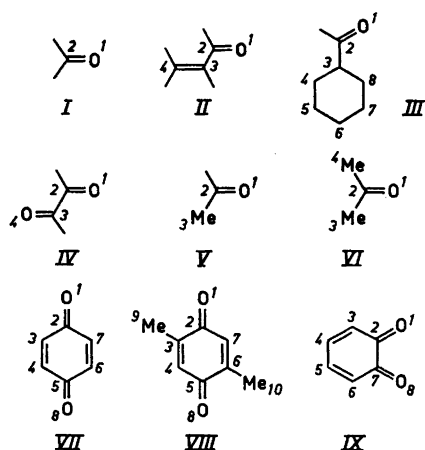$$R_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu} \tag{4}$$

Fig. 1. Labelling of molecules and notation of atoms.

Table 3. Assumed, calculated, and observed bond distances. All values in Å.

Molecule	Bond	$R_{\text{ass.}}$	$R_{\text{calc.}}$	$R_{\text{obs.}}$
I	1—2	1.22	1.207	1.208(0.003); [a] 1.212(0.005) [b]
II [c]	1—2	1.22	1.219	1.219(0.005)
	2—3	1.47	1.468	1.470(0.003)
	3—4	1.345	1.345	1.345(0.003)
III	1—2	1.22	1.221	
	2—3	1.48	1.466	
	3—4	1.40	1.403	
	4—5	1.40	1.396	
	5—6	1.40	1.398	
	6—7	1.40	1.397	
	7—8	1.40	1.397	
	3—8	1.40	1.402	
IV [d]	1—2	1.22	1.219	$R_{12}+R_{23}=2.73(0.01)$
	2—3	1.50	1.491	
V [e]	1—2	1.22	1.215	1.216(0.002)
	2—3	1.52	$p_{23}=0.25$	1.501(0.005)
VI [f]	1—2	1.22	1.223	1.222(0.003)
	2—3	1.52	$p_{23}=0.23$	1.507(0.003)
VII [g]	1—2	1.22	1.228	1.222(0.008)
	2—3	1.48	1.472	1.477(0.006)
	3—4	1.33	1.349	1.322(0.008)
VIII [h]	1—2	1.22	1.229(1.231)	1.223(0.002)
	2—3	1.48(1.50)	1.475(1.477)	1.502(0.002)
	3—4	1.33(1.35)	1.352(1.353)	1.347(0.003)
	4—5	1.48	1.467(1.464)	1.482(0.002)
	3—9	1.52	$p_{39}=0.18$	1.503(0.002)
IX	1—2	1.22	1.225	
	2—3	1.48	1.469	
	3—4	1.34	1.353	
	4—5	1.48	1.458	
	2—7	1.48	1.491	

Observed R-values: [a] Ref. 18. [b] Ref. 19. [c] Ref. 17. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 15. [h] Ref. 23.

where $p_{\mu\nu}$ is the mobile bond order for the bond between carbon atoms μ and ν. For C—O bond lengths a similar relation

will be used here.

$$R_{\text{CO}} = 1.365 - 0.18 p_{\text{CO}} \qquad (5)$$

The coefficient 0.18 in (5) is assumed to be equal to the corresponding value in formula (4). The constant 1.365 is obtained by fitting the formula to

Table 4. Calculated and observed ionization potentials. All values in eV.

Molecule	(IP)$_{calc.}$	(IP)$_{obs.}$[a]
I		10.87
	14.00	13.99
		15.86
II		9.99
	10.80	10.82
	13.77	13.19
		14.56
III	9.52	9.46(9.51[b])
	9.78	
	12.57	11.48
	13.67	
IV	13.79	
	14.90	
V		10.23
	12.14	12.75
	13.86	13.90
		15.09
VI		9.67
	11.89	12.16
	12.28	
	13.82	14.15
		15.55
VII	11.07	
	11.19	
	13.75	
	14.59	
VIII	10.41(10.12)	
	10.52(10.31)	
	12.88(12.88)	
	13.12(13.08)	
	13.66(13.54)	
	14.54(14.34)	
IX	10.16	
	12.40	
	13.22	
	14.52	

For III, the bracket after the (IP)$_{obs.}$ values reads: }(see text)

[a] Ref. 11. [b] Ref. 10.

the calculated mobile bond order and the measured C—O bond distance in (II), for which very accurate experimental results are available.[17]

The calculated bond distances for all the molecules are presented in Table 3 together with experimental values for comparison. The calculated C—O

Table 5. Calculated atomic π-electron charges.

Mole-cule	1	2	3	4	Atom 5	6	7	8	9
I	1.48	0.52							
II	1.55	0.51	0.90	1.04					
III	1.56	0.51	0.93	1.05	0.99	0.99	0.98	0.99	
IV	1.56	0.44							
V	1.54	0.50	1.96						
VI	1.59	0.48	1.96						
VII	1.57	0.51	0.96						
VIII	1.58	0.51	0.89	1.05					1.97
	(1.60)	(0.50)	(0.85)	(1.08)					(1.97)
IX	1.56	0.49	0.97	0.98					

distances are situated in the interval 1.215 Å—1.225 Å except for formaldehyde and the *p*-quinones. Where experimental values exist, the discrepancies are within 0.006 Å.

The experimental C—C bond distances of acrolein [17] are reproduced very nicely. In the case of benzaldehyde and *o*-benzoquinone there does not seem to exist any experimental structure determination.

From a study of the rotational fine structure of the electronic spectrum [20] of glyoxal the sum of the C—O and C—C bond distances in this molecule was determined to be 2.73 ± 0.01 Å. It was found reasonable to assume the value 1.22 ± 0.01 Å for the C—O bond length, which gives 1.51 ± 0.01 Å as an estimate for the C—C distance. Our calculated value is 1.491 Å. Thus the observed difference in C—C bond length between acrolein and glyoxal is satisfactorily reproduced by the present calculation.

Trotter's X-ray data for *p*-benzoquinone [15] show a $C_3—C_4$ distance which is significantly shorter than the C—C distance in ethylene, a result which is impossible to account for in a calculation treating the π-electrons only. Comparison of Trotter's data with those of Hirshfeld and Rabinovich [23] for 2,5-dimethyl-*p*-benzoquinone shows that methylation to the dimethyl compound adds about 0.025 Å to each of the adjacent bond distances in the ring. Our results indicate this elongation on methylation to be only 0.003—0.005 Å. In this way, however, we obtain a good agreement between theory and experiment for the $C_3—C_4$ distance in dimethyl-*p*-benzoquinone.

The C—C bond distances to methyl carbons have not been calculated, but the bond orders obtained (Table 3) indicate that this distance should be a little longer in dimethyl-*p*-benzoquinone than in acetaldehyde and acetone. This conclusion is not supported by available experimental information. However, in view of the approximations introduced in the formal treatment of the methyl group, too much stress should not be put on this disagreement.

Predicted molecular ionization potentials as approximated by Koopmans' theorem are presented in Table 4. The experimental results quoted for the purpose of comparison are adiabatic values given by Turner [11] and by Watanabe [10] (benzaldehyde). The IP data of Table 2 are also included here for the sake of completeness.

Turner concluded that the lowest IP for formaldehyde and acrolein do correspond to the loss of a lone pair electron on the oxygen atom. If this is assumed to be the case also for acetaldehyde and acetone, we obtain a good agreement between theory and experiment for ionization from the highest π level in acetone, and also an acceptable agreement for acetaldehyde. The second calculated IP of acetaldehyde reproduces the observed value very nicely. If we tentatively assume that the second experimental value for acetone (12.16 eV) is composed of two unresolved components, the two remaining calculated values for this molecule are also in good agreement with experiment. The second calculated IP of acrolein is acceptable.

For benzaldehyde Turner [11] obtained the adiabatic IP values 9.46 eV and 11.48 eV. However, in a very recent paper on vertical IP's by Baker, May and Turner,[24] the value 9.80 eV is reported, and from the photoelectron spectrum presented, one or more vertical IP values are found somewhere between 12 and 13 eV. Clearly our calculated values 9.52 eV and 9.78 eV both correspond to the unresolved experimental peak at 9.80 eV, whereas our value 12.57 eV is in much better agreement with these recent data than with the previous experimental value 11.48 eV.

Unfortunately experimental information providing the basis for a similar discussion of the IP's of glyoxal and the quinones is lacking.

Pi-electronic charge distributions are given in Table 5. The atomic charge on oxygen is seen to be as high as 1.5—1.6 electron units in all the molecules. This is a consequence of our method for determining semi-empirical parameters, which resulted in a higher value for W_O than commonly proposed.

Table 6 gives calculated π-electronic dipole moments. Experimental dipole moments are also quoted although they are not directly comparable to the calculated ones which consider π electrons only. It is noted that the difference between calculated and experimental value is in the range 0.03—1.2 D, the calculated value always being the highest.

Unfortunately there is no possibility for testing the goodness of the calculated atomic charges and dipole moments directly by experiment, because we know very little about the magnitude and direction of contributions other than π-electronic to the total dipole moment of a molecule.

Table 6. Calculated and observed dipole moments. In Debye units.

Molecule	calc.	obs.
I	2.78	2.34 [a]
II	3.14	3.11 [b]
III	3.40	2.7 —3.0 [c]
V	3.32	2.69 [d]
VI	3.74	2.90 [e]
IX	6.30	5.1 [f]

[a] Ref. 25. [b] Ref. 26. [c] Ref. 27. [d] Ref. 21. [e] Ref. 37. [f] Ref. 28.

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

Molecule	$\Delta E_{calc.}$	$\Delta E_{obs.}$	$f_{calc.}$	$f_{obs.}$
I [a]	7.95	7.95	0.40	
II [a,b]	6.26	6.41	0.70	
	7.61		0.09	
III [c]	4.64	4.52	0.007	0.02
	5.49	5.35	0.38	0.26
	6.40	6.35	0.56	
	6.64	6.68	0.91	
	7.53	6.97	0.32	} 1.7
	7.71	7.50	0.04	
	7.91		0.52	
IV [a]	7.47	7.44	0.70	
	7.60		forb.	
	10.32		forb.	
V [a,d,e]	7.63	7.52	0.38	0.13
	9.09		0.07	
VI [a]	7.66	8.05	0.38	
	9.05		0.12	
VII [f,g,h]	4.23	4.28(4.49)	forb.	0.008
	5.38	5.17(5.17)	0.72	0.15
	7.14		forb.	
	7.16		forb.	
	7.26		0.001	
	7.94		1.34	
VIII [g]	3.85(3.74)	4.07	forb.	
	5.16(5.09)	4.98	0.72(0.67)	
	6.73(6.79)		0.04(0.06)	
	7.03(7.03)		forb.	
	7.15(7.19)		forb.	
	7.60(7.71)		forb.	
	7.67(7.64)		0.81(1.05)	
IX [i,j]	3.94	3.3—3.4	0.18	0.66
	6.07	4.9	0.12	0.26
	6.44		0.04	
	7.17	6.2	1.27	strong
	7.19		0.33	

Observed values: [a] Ref. 14. [b] Ref. 13. [c] Ref. 12. [d] Ref. 29. [e] Ref. 30. [f] Ref. 34. [g] Ref. 35. [h] Ref. 36. [i] Ref. 31. [j] Ref. 32.

2. Electronic spectra. Table 7 presents predicted electronic transitions, compared with available experimental information. The calculated values given are the lowest singlet-singlet transitions in each molecule.

The over all agreement between calculated and available experimental transition energies is very satisfactory, except for acetone and o-benzoquinone.

The experimental value quoted [14] for acetone represents a rather broad maximum of an absorption peak starting at around 7.5 eV. A closer analysis of this particular band is missing due to heavy overlapping [30] in the observed spectrum.

The most detailed experimental information on the electronic transitions in o-benzoquinone seems to be available in a work by Goldschmidt and Graef.[31] They measured the spectrum in different solvents, but not in the vapour phase. The value 4.9 eV quoted in the table indicates the position of a shoulder observed using ether or chloroform as a solvent. This shoulder is not observed in hexane solution. The experimental value of 6.2 eV is rather uncertain as the corresponding absorption peak has never been observed.[32] The value given is assigned to a strong transition in the neighbourhood of 200 mμ. Our calculated oscillator strength for the predicted transition at 7.17 eV does indicate a strong absorption in this region.

Kimura and Nagakura obtained a series of experimental transition energies for benzaldehyde,[12] the two lowest of which we also quoted in Table 2. They obtained a good agreement between experiment and calculation, except for the two lowest values. Our two lowest values reproduce the experimental data better, because they were used in the parameter determination as discussed above. The remaining experimental transitions are also rather well reproduced by our calculation.

Numerous investigators have measured the electronic absorption spectrum of p-benzoquinone under various experimental conditions. Some of the results obtained are summarized in Ref. 33. The absorption maxima of the two lowest $\pi \rightarrow \pi^*$ transitions are usually found in the intervals 4.1—4.5 eV and 5.0—5.3 eV, respectively. The values given in the table refer to a vapour phase investigation.[34]

The observed values for (VIII) given in the table refer to a spectrum measured in hexane solution.[35] Experimental values for (VII) obtained under the same conditions are indicated in parentheses in the table. The predicted shifts in transition energies due to methylation are 0.38 (0.49) and 0.22 (0.29) eV, respectively. These values should be compared with the observed differences of 0.42 and 0.19 eV.

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