On the Charge Corrections of the Semi-empirical Parameters in the Pariser-Parr-Pople Method. II. Molecules Containing Oxygen and Nitrogen

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In an extension of the modified Pariser-Parr-Pople approximation, the numerical values of the parameters W and γ have been varied with charge. Calculations have been made on phenol, furan, benzaldehyde, aniline, pyrrole, pyridine, *sym*-triazine, imidazole, and the pyridinium cation. For comparison CNDO calculations have also been made.

The necessity of varying some parameters with charge in the Pariser-Parr-Pople method (PPP) is discussed in an earlier paper¹ where calculations on formaldehyde, acrolein, formic acid, and formate ion are made with W_μ and $\gamma_{\mu\mu}$ values dependent on the charge on the atom. The present paper is a continuation of this study and includes calculations on oxygen containing molecules, *viz.* phenol, furan, and benzaldehyde, and on nitrogen containing molecules, *viz.* aniline, pyrrole, pyridine, *sym*-triazine, imidazole, and the pyridinium cation.

METHOD

As in the earlier paper,¹ two different alternatives for determining the parameters have been used. In Alt. 1 the parameters determined in Refs. 2–5 are assumed to be valid for formally neutral atoms. In Alt. 2 the uncorrected values in Refs. 2–5 are assumed to be valid for the net atomic charge predicted by their use on the chosen reference molecules. In both alternatives two different functions giving the variation of W with charge are used, *viz.* $F_1(q)$ and $F_2(Z_{\text{eff}})$.

In $F_1(q)$ the difference between the valence

Fig. 1. I: Phenol, II: furan, III: benzaldehyde, IV: pyridine, V: pyrrole, VI: aniline, VII: *sym*-triazine, VIII: imidazole.

state ionization potentials (IP) of the anion, the neutral atom, and the cation have been used to estimate the variation of W with q , the charge on the atom. These ionization potentials are given in Table 1 and Ref. 1.

In $F_2(Z_{\text{eff}})$ the variation of the valence state IP is considered a function of Z_{eff} , calculated according to Slater's rules. The IP's of three isoelectronic atoms have been taken as fixed points. These values are found in Table 2 and Ref. 1.

Table 1. Valence state ionization potentials for atoms and atomic ions, obtained from tables in Refs. 6–8 directly or by combination of values in these tables. All values in eV. It has been possible to get values only for the uncharged atom and for either the negatively or positively charged atom. To get the third value in the series the IP value of an isoelectronic atom with different charge of the core has been transformed according to Brown and Hefferman.⁹ These transformed values are given in parentheses. A corresponding table for carbon and oxygen has been given in Ref. 1.

C ⁻ $t_1t_2t_3z^2 \rightarrow t_1t_2t_3z$ 0.62 ^a (N ⁻ 0.78)	N (pyrrole) $t_1t_2t_3z^2 \rightarrow t_1t_2t_3z$ 12.25 ^a	N ⁺ $t_1t_2t_3z \rightarrow t_1t_2t_3$ 28.72 ^{b,c}
N ⁻ $t_1^2t_2t_3z^2 \rightarrow t_1^2t_2t_3z$ 1.20 ^a	N (pyridine) $t_1^2t_2t_3z \rightarrow t_1^2t_2t_3$ 14.51 ^a	O ⁺ $t_1^2t_2t_3z \rightarrow t_1^2t_2t_3$ 34.50 ^{a,b,c} (N ⁺ 28.75)

^a Ref. 6; ^b Ref. 7; ^c Ref. 8.

Table 2. The left hand side of the table gives valence state ionization potentials for isoelectronic series obtained from tables in Refs. 6–8 directly or by combination of values in these tables. Values are given in eV. The atoms in one series differ both in Z_{eff} and in core charge. Ionization potentials obtained after correcting for the difference in core charge according to Brown and Hefferman⁹ are given in the right hand side of the table. A corresponding table for carbon and oxygen has been given in Ref. 1.

	C ⁻	N	O ⁺		N, core charge 5		
Core charge	4	5	6	Z_{eff}	2.90	3.90	4.90
Pyrrole nitrogen $t_1t_2t_3z^2 \rightarrow t_1t_2t_3z$ IP., eV	0.62 ^a	12.25 ^a	31.1 ^{b,c}		0.78	12.25	25.90
Pyridine nitrogen $t_1^2t_2t_3z \rightarrow t_1^2t_2t_3$ IP, eV	2.14 ^{a,c}	14.51 ^a	34.5 ^{a,b,c}		2.67	14.51	28.75

^a Ref. 6; ^b Ref. 7; ^c Ref. 8.

The numerical values of the one-center two-electron integrals for different charges on the atom have been determined by linear interpolation. The data for the anion, the neutral atom, and the cation used for C and O are given in Ref. 1. The values used for nitrogen in eV are N⁻ 13.58, N 15.44, and N⁺ 17.31.

A more detailed description of Alt. 1 and Alt. 2 and the two F -functions is given in the earlier paper.¹

In determining the parameters for uncharged atoms according to Alt. 2, one or two reference molecules must be chosen for which the parameters are assumed to be valid for the predicted charge.

In the earlier paper¹ formaldehyde was chosen as the reference molecule for determining

the parameters for the keto oxygen. In that paper both carbon and oxygen parameters were corrected according to Alt. 2. In the present paper, for the ether bond in phenol, where oxygen is bound only to one carbon, only Alt. 1 has been used since the charges are small. In the ether bond in furan, where oxygen is bound to two carbon atoms, the charge on the oxygen atom with uncorrected parameters has been calculated to 0.26 and the charge on the neighbour carbon to -0.08. On this molecule both alternatives have been used for oxygen, but only Alt. 1 for the carbon atom.

For pyridine nitrogen, where the charges are small, only Alt. 1 has been used. In pyrrole the charges are large on nitrogen and both alternatives have been used for this atom. Aniline, with

Table 3. The semi-empirical W values used for uncharged atoms and standard distances ($R_{C-O}=1.22$ Å, $R_{C-OH}=1.35$ Å and $R_{CN}=1.338$ Å). The values in Alt. 2 have been calculated as described in text, the other values are taken from Refs. 2–5, where also the dependence on bond length is given. Values given in eV.

W_C°	-9.84						
$\Delta W_{C(N)}$	0.03						
	Ether oxygen			Keto oxygen			
	Alt. 1	Alt. 2		Alt. 1	Alt. 2		
		$F_1(\rho)$	$F_2(Z_{eff})$		$F_1(\rho)$	$F_2(Z_{eff})$	
$\Delta W_C(O)$	-0.09	-0.09	-0.09	$\Delta W_C(O)$	-0.71	4.56	0.90
W_O°	-11.18	-15.74	-12.62	$W_O^\circ + \Delta W_O(C)$	-19.60	-26.17	-21.50
$\Delta W_O(C)$	1.52	6.08	2.96				
	Pyridine nitrogen			Pyrrole nitrogen			
	Alt. 1			Alt. 1	Alt. 2		
					$F_1(\rho)$	$F_2(Z_{eff})$	
W_N°	-12.57			-8.52	-10.22	-9.05	
$\Delta W_N(C)$	0.14			0.14	3.60	1.23	

one carbon bound to nitrogen, and pyrrole, with two carbons bound, have been used as reference molecules. The choice of parameters of the pyridinium cation merits a special description. It has been assumed that the charge contributed to the system by adding H^+ becomes equally distributed on the N and the H atoms. The net charge on the N atom is therefore assumed to be $+0.5 + \pi$ -electron charge, cf. Table 4. This net value has been employed in the determination of W and γ . The possible distribution of charge within this ion and different types of calculations are discussed in great detail by Mataga and Mataga²⁹ and will not be repeated here. For the lowest transitions these authors obtained the values 38.3 and 49.5 kK.

The semi-empirical W_μ values used with zero atomic charges are given in Table 3.

It seems to be valuable to compare the results obtained with the method described above with results obtained with a method that takes σ -electrons in consideration explicitly. Therefore calculations have been made with the CNDO method (complete neglect of differential overlap) with parameters given by Höjer and Meza.¹⁰

The SCF-MO's in the PPP-method have been evaluated using a program written by B. Roos and M. Sundborn. This program also calculates the energy levels of the excited states by mixing all on the configurations obtained from single excitations (max. 140 configurations). Oscillator strengths for the dipole transitions, according to formula by Mulliken and Rieke,¹¹ and eigenvectors for the multi-configurational problem

are also given in computer output. The program used for the CNDO calculations has been written by G. Höjer and S. Meza. The computer IBM 360/75 at Stockholm's data central has been used for the calculations.

For C–C and C–O bonds, bond lengths have been calculated from the bond orders between nearest neighbours using eqns. 6–8 in Ref. 1; and for C–N, the relation

$$R_{\mu\nu}(CN) = 1.458 - 0.18 p_{\mu\nu} \quad (1)$$

has been used according to Ref. 3.

The charges on the atoms, but not the bond lengths, have been varied to self-consistency. The structure of the molecules are taken from experimental data.

RESULTS

The ground state properties, *i.e.* net charges on the atoms, bond orders, bond lengths, and dipole moments, together with ionization potentials calculated with Koopmans' theorem, are given in Table 4. Calculated values of singlet π - π^* transition energies and of oscillator strengths are given in Table 5. In both tables some typical experimental values obtained by different workers are given. Most of the experimental values on IP's are adiabatic. All the experimental values of transition energies are determined in the vapour phase except the values for *sym*-triazine given by Favini *et al.*,²⁵ for imidazole,^{27,28} and for the pyridinium ion.

Comparing the results of calculations made

Table 4. π -Electron net charges, bond orders, bond distances (in Å), dipole moments (in Debye) and ionization potentials (in eV), predicted by use of different sets of charge-corrected parameters for the PPP method. For the CNDO method both π -electron and total net charges and total dipole moments are given. For the description of the methods, see text. IP's calculated according to Koopmans' theorem.

Phenol	PPP-method		Alternative 1		CNDO method		Exp. values
	Uncorr.		$F_1(q)$	$F_2(Z_{\text{eff}})$	π	total	
Net charge							
C ₁	0.01		0.00	0.01	0.08	0.16	
C ₂	-0.03		-0.02	-0.03	-0.09	-0.14	
C ₃	0.00		-0.01	0.00	0.04	-0.03	
C ₄	-0.02		-0.01	-0.01	-0.06	-0.10	
O ₇	0.06		0.05	0.06	0.07	-0.22	
Bond order C ₁ -C ₂	0.645		0.649	0.647			1.395 ^a
Bond dist.	1.401		1.400	1.401			
Bond order C ₂ -C ₃	0.670		0.669	0.669			1.395 ^a
Bond dist.	1.396		1.397	1.397			
Bond order C ₃ -C ₄	0.665		0.665	0.665			1.395 ^a
Bond dist.	1.397		1.397	1.397			
Bond order C ₁ -O ₇	0.251		0.228	0.240			1.379 ^a 1.364-69 ^b
Bond dist.	1.366		1.370	1.368		1.68	1.40 ^c
Dipole moment	0.74		0.65	0.72			8.46 ^d ad. 8.75 ^e vert.
IP	8.45		8.58	8.50	8.29		9.34 ^d ad. 9.45 ^e vert.
	9.14		9.11	9.11	9.64		11.30 ^d ad.
	10.75		11.08	10.89			
	12.55		12.64	12.57	14.19		
Furan	PPP-method		Alternative 1		Alternative 2		Exp. values
	Uncorr.*		$F_1(q)$	$F_2(Z_{\text{eff}})$	$F_1(q)$	$F_2(Z_{\text{eff}})$	
Net charge							
O ₁	0.26		0.15	0.20	0.24	0.25	
C ₂	-0.08		-0.04	-0.06	-0.06	-0.07	
C ₃	-0.05		-0.03	-0.04	-0.06	-0.05	
Bond order O ₁ -C ₂	0.408		0.316	0.367	0.397	0.404	
Bond dist.	1.334		1.353	1.343	1.337	1.335	1.362 ^g
Bond order C ₂ -C ₃	0.831		0.865	0.847	0.837	0.833	
Bond dist.	1.367		1.361	1.365	1.366	1.367	1.361 ^g
Bond order C ₃ -C ₄	0.494		0.460	0.478	0.487	0.492	
Bond dist.	1.428		1.434	1.431	1.429	1.428	1.431 ^g
Dipole moment	1.66		0.95	1.34	1.71	1.66	0.66 ^c 0.72 ^c
IP	8.72		8.50	8.63	8.20	8.58	8.89 ^d ad. 8.94 ^e vert.
	9.33		9.96	9.65	9.00	9.25	10.25 ^d ad. 10.34 ^e vert.
	12.16		12.99	12.41	11.76	12.06	14.44 ^d vert.

* The same values are obtained with Alt. 2 when only O₁ is corrected for the charge

Table 4. Continued.

	PPP-method		Alt. 1 for all atoms		Alt. 2 for C ₇ and O ₈ , Alt. 1 for the other		CNDO-method		Exp. values
	Uncorr.	F ₁ (Q)	F ₂ (Z _{eff})	F ₁ (Q)	F ₂ (Z _{eff})	π	total		
Benzaldehyde									
Net charge									
C ₁	0.08	0.03	0.06	0.04	0.05	-0.01	0.01		
C ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-0.06	
C ₃	0.01	0.00	0.01	0.02	0.01	0.00	0.00	-0.07	
C ₄	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-0.06	
C ₅	0.01	0.00	0.00	0.00	0.00	0.00	0.00	-0.06	
C ₆	-0.05	-0.05	-0.02	-0.02	-0.03	0.01	0.01	-0.07	
C ₇	0.49	0.15	0.31	0.47	0.48	0.11	0.06		
O ₈	-0.56	-0.20	-0.37	-0.53	-0.54	-0.14	-0.14		
Bond order C ₁ -C ₂	0.639	0.639	0.638	0.641	0.639				
Bond dist.	1.402	1.402	1.402	1.402	1.402				
Bond order C ₂ -C ₃	0.669	0.669	0.669	0.669	0.669				
Bond dist.	1.397	1.397	1.397	1.397	1.397				
Bond order C ₃ -C ₄	0.665	0.666	0.666	0.666	0.666				
Bond dist.	1.397	1.397	1.397	1.397	1.397				
Bond order C ₄ -C ₅	0.663	0.661	0.662	0.662	0.662				
Bond dist.	1.398	1.398	1.398	1.398	1.398				
Bond order C ₅ -C ₆	0.672	0.674	0.674	0.673	0.673				
Bond dist.	1.396	1.396	1.396	1.396	1.396				
Bond order C ₆ -C ₁	0.636	0.635	0.635	0.638	0.637				
Bond dist.	1.403	1.403	1.403	1.402	1.402				
Bond order C ₁ -C ₇	0.280	0.286	0.288	0.277	0.281				
Bond dist.	1.467	1.466	1.465	1.467	1.466				
Bond order C ₇ -O ₈	0.800	0.939	0.890	0.817	0.809				
Bond dist.	1.221	1.196	1.205	1.218	1.219				
Dipole moment	3.39	1.45	2.38	3.37	3.36				
IP	9.51	9.26	9.35	9.55	9.53	9.04	2.14	ca. 2.7 ^{liq.} 9.46 ^{ad.} 9.80 ^{vert.} 11.48 ^{ad.}	
	9.78	9.49	9.62	9.74	9.75	9.71			
	12.56	12.21	12.35	12.45	12.52				
	13.66	13.59	13.57	13.45	13.59	13.98			

Table 4. Continued.

	PPP-method Uncorr.	Alternative 1 $F_1(q)$	$F_2(Z_{eff})$	CNDO-method		ab initio ^r	total	Exp. values
				π	π			
Pyridine								
Net charge								
N_1	-0.07	-0.03	-0.05	-0.04	-0.04	-0.11	-0.63	
C_2	0.03	0.00	0.02	0.02	0.02	0.05	0.25	ca. 0.08 ⁱ
C_3	0.00	0.01	0.00	-0.03	-0.03	-0.04	-0.18	" 0.00 ⁱ
C_4	0.01	0.00	0.01	0.04	0.04	0.07	-0.04	" 0.04 ⁱ
Bond order N_1-C_2	0.670	0.671	0.671					1.3394 ^b
Bond dist.	1.337	1.337	1.337					1.3958 ^b
Bond order C_2-C_3	0.657	0.657	0.657					1.3936 ^b
Bond dist.	1.399	1.399	1.399					2.15 ^c 2.25 ^c
Bond order C_3-C_4	0.671	0.671	0.671					9.28 ^d
Bond dist.	1.396	1.396	1.396					10.54 ^{d**}
Dipole moment	0.30	0.22	0.27		2.04		2.49	12.22 ^d
IP	9.33	9.37	9.35	9.43		9.52		
	9.74	9.66	9.70	10.02		10.38		
	12.81	12.78	12.80	17.68		14.74		
Pyridinium ion								
Net charge								
N_1^*		-0.26	-0.15	-0.35	-0.35			
C_2		0.09	0.06	0.10	0.10			
C_3		0.02	0.01	-0.02	-0.02			
C_4		0.03	0.02	0.19	0.19			
Bond order N_1-C_2		0.647	0.663					
Bond dist.		1.342	1.339					
Bond order C_2-C_3		0.661	0.658					
Bond dist.		1.398	1.399					
Bond order C_3-C_4		0.669	0.671					
Bond dist.		1.397	1.396					
IP		9.87	9.42	16.26				
		10.78	10.07	17.78				
		13.88	13.12					

* Assuming half of the charge on the ion to be located on N and half on the H, W and γ are determined for the charge 0.50-0.26=0.24.** Interpreted as σ lone pair.

Table 4. Continued.

PPP-method		Alternative 1		Alternative 2		CNDO-method		Exp. values
Uncorr.*	$F_1(Q)$	$F_2(Z_{\text{eff}})$	$F_1(Q)$	$F_2(Z_{\text{eff}})$	π	total		
Pyrrole								
Net charge								
N ₁	0.34	0.19	0.27	0.32	0.33	0.43	-0.07	
C ₂	-0.07	-0.04	-0.05	-0.08	-0.07	-0.10	-0.06	
C ₃	-0.10	-0.06	-0.08	-0.08	-0.09	-0.11	-0.11	
Bond order N ₁ -C ₂	0.472	0.364	0.427	0.455	0.465			1.374 ^f
Bond dist.	1.373	1.392	1.381	1.376	1.374	0.793		
Bond order C ₂ -C ₃	0.790	0.836	0.811	0.797	0.793			1.381 ^f
Bond dist.	1.375	1.366	1.371	1.374	1.374	0.539		
Bond order C ₃ -C ₄	0.541	0.501	0.523	0.538	0.539			1.417 ^f
Bond dist.	1.420	1.427	1.423	1.420	1.420		2.23	1.55-1.84 ^e
Dipole moment	2.55	1.45	2.08	2.22	2.46			8.22 ^d
IP	8.23	7.92	8.12	7.58	8.03	7.74		9.03 ^d
	9.08	9.48	9.32	8.50	8.94	9.00		12.38 ^d
	12.27	13.32	12.61	11.74	12.13	18.19		
Aniline								
Net charge								
C ₁	0.05	0.01	0.03	0.00	0.03	0.08	0.13	
C ₂	-0.08	-0.03	-0.05	-0.03	-0.05	-0.09	-0.13	
C ₃	0.01	0.00	0.00	-0.02	0.00	0.04	-0.03	
C ₄	-0.03	-0.02	-0.02	-0.02	-0.03	-0.06	-0.10	
N ₁	0.12	0.09	0.11	0.12	0.12	0.31	-0.28	
Bond order C ₁ -C ₂	0.623	0.637	0.630	0.628	0.626			1.392 ^m
Bond dist.	1.405	1.402	1.404	1.404	1.404			
Bond order C ₂ -C ₃	0.673	0.671	0.672	0.673	0.673			1.392 ^m
Bond dist.	1.396	1.396	1.396	1.396	1.396			
Bond order C ₃ -C ₄	0.663	0.664	0.663	0.663	0.663			1.392 ^m
Bond dist.	1.398	1.397	1.398	1.398	1.398			
Bond order C ₁ -N ₁	0.355	0.297	0.329	0.338	0.346			1.431 ^m
Bond dist.	1.394	1.405	1.399	1.397	1.396			1.49 ^e
dipole moment	1.60	1.18	1.44	1.65	1.58		1.68	7.71 ^d ad 8.04 ^e vert.
IP	7.66	8.03	7.82	7.54	7.63	7.83 ^{**}		8.95 ^d ad 9.11 ^e vert.
	9.03	8.91	8.99	8.84	8.95	9.13 ^{**}		10.49 ^d ad 10.70 ^e vert.
	10.17	10.60	10.34	10.12	10.17	9.50		

* The same values are obtained with Alt. 2, when only N is corrected for the charge.

** 7.83 not pure π ; 9.13 σ mixed up with π .

Table 4. Continued.

	PPP-method		Alternative 1		Alternative 2		CNDO-method		ab initio ^a		Exp. values
	Uncorr.*	$F_1(Q)$	$F_2(Z_{eff})$	$F_1(Q)$	$F_2(Z_{eff})$	$F_1(Q)$	π	total	π	total	
<i>sym</i> -Triazine											
Net charge	C	0.07	0.02	0.04							
	N	-0.07	-0.02	-0.04							
Bond order C-N		0.665	0.667	0.666					0.17	0.49	
Bond dist.		1.338	1.338	1.338					-0.17	-0.62	
IP		10.08	10.09	10.09							1.338 ^a
											10.01 ^a ** ad. 10.4 ^c vert.
											11.69 ^d ad. 12.0 ^e vert.
											13.26 ^f ad. 13.3 ^g vert.
Imidazole											
Net charge	C ₁	-0.07	-0.03	-0.05		-0.07	-0.11	-0.08			
	C ₂	-0.09	-0.06	-0.08		-0.08	-0.11	-0.10			
	N ₃	-0.14	-0.07	-0.11		-0.10	-0.19	-0.10			
	C ₄	-0.04	-0.03	-0.03		-0.07	-0.04	-0.01			
	N ₅	0.34	0.20	0.27		0.32	0.45	-0.08			
Bond order C ₁ -C ₂		0.781	0.824	0.802		0.784					
Bond dist.		1.376	1.369	1.373		1.376					1.358 ^p
Bond order C ₃ -N ₃		0.552	0.521	0.538		0.554					
Bond dist.		1.359	1.364	1.361		1.358					1.378 ^p
Bond order N ₃ -C ₄		0.779	0.825	0.802		0.788					
Bond dist.		1.318	1.309	1.314		1.316					1.326 ^p
Bond order C ₄ -N ₅		0.479	0.367	0.428		0.456					
Bond dist.		1.372	1.392	1.381		1.376					1.349 ^p
Bond order N ₅ -C ₁		0.477	0.372	0.430		0.466					
Bond dist.		1.372	1.391	1.381		1.374					1.369 ^p
dipole moment		2.87	1.62	2.27		2.42		4.13			3.9-6.2 ^e benzene 4.0-4.9 ^f dioxane
IP		8.36	8.11	8.29		7.62	8.11				
		9.49	10.00	9.80		8.73	9.33				
		12.57	13.46	12.87		11.86	18.62				

* The same values are obtained for imidazole with Alt. 2 when only N₅ is corrected for the charge.** Interpreted as σ lone pair.^a Ref. 12; ^b Ref. 13; ^c Ref. 14; ^d Ref. 15; ^e Ref. 16; ^f Ref. 17; ^g Ref. 18; ^h Ref. 19; ⁱ Ref. 20; ^j Ref. 21; ^k Ref. 22; ^l Ref. 23; ^m Ref. 24; ⁿ Ref. 25; ^p Ref. 26; ^q Ref. 27; ^r Ref. 28.

with the PPP method with different parameter sets, it is seen that the values of charge densities and the connected dipole moments have the largest percent differences from set to set of the other calculated quantities.

Unfortunately there are no experimental data on the charge densities. Furthermore the values calculated with the PPP method give only π -electron densities, not total densities. Thus the comparison between calculated and experimental values on dipole moments lacks significance.

As mentioned above, calculations with the CNDO method have been made for comparison; cf. Table 4. In this method both σ - and π -densities are calculated and, therefore, comparison between calculated and experimental dipole moments is relevant.

For some of the molecules, *ab initio* calculations have been made by other investigators and their values on electron densities, dipole moments, and ionization potentials are given in Table 4. The values of total ($\sigma + \pi$) densities differ very much from the values obtained by CNDO calculations, while the dipole moments do not differ at all so much. This depends on the definitions of the densities, where the *ab initio* calculations give gross atomic densities. Since the purpose of the study is to determine the dependence on charge of the semi-empirical W values, it seems to be more significant to compare the charges on the atoms obtained with the PPP method with those obtained with CNDO method, and not with the *ab initio* calculations. The reason for this is that both CNDO and PPP are ZDO (zero differential overlap) methods and thus the charge densities obtained with these methods are comparable. In the *ab initio* calculations, on the other hand, a non-orthogonal basis is employed together with Mulliken population analysis.

It seems reasonable, with guidance from Table 4 and 5, to vary W and γ with charge only when the absolute value of the charge on the atom is > 0.2 .

Molecules where no charge is > 0.2 are phenol, aniline, pyridine, and *sym*-triazine. In phenol and aniline the hetero-atom (O resp. N) is not a ring atom and it gives two electrons to the π -system. In pyridine and *sym*-triazine the hetero-atom is a ring nitrogen which gives one electron to the π -system.

Molecules where W and γ ought to be corrected, charges on some atoms being large, are benzaldehyde, furan, pyrrole, and imidazole. In benzaldehyde, oxygen, being outside the ring, gives one electron to the π -system. The parameters for both oxygen and the carbon next to it should be corrected. In furan, pyrrole, and imidazole, the hetero-atom for which the parameters should be corrected is a ring oxygen or a ring nitrogen, giving two electrons to the π -system.

Alt. 2 as opposed to Alt. 1 seems to give the best results for all the molecules except in determining the charge densities for benzaldehyde. This conclusion is drawn from comparing PPP results both with experimental data for bond lengths, ionization potentials, and spectra and with CNDO calculated charge densities as discussed above.

When Alt. 2 is used, in most cases there are no large differences in results between calculations with $F_1(q)$ and $F_2(Z_{\text{eff}})$. $F_2(Z_{\text{eff}})$ seems, however, to give better results, and furthermore it seems theoretically to be correct to use $F_2(Z_{\text{eff}})$ when the electrons contributing to the charge are explicitly taken into consideration in the calculation, i.e. π -electrons.

To get charge densities in benzaldehyde which are in best accordance with the CNDO calculations, in Alt. 1, $F_1(q)$ has to be used.

To complete the investigation we have made CNDO calculations on the molecules treated by Grabe and Skancke.¹ Just as in the case of benzaldehyde, Alt. 1 $F_1(q)$ gives charge densities in best accordance with the CNDO calculations for formaldehyde and acrolein. For the formate ion, Alt. 2 is best, as was also the conclusion in Ref. 1 drawn from calculations of bond lengths.

CONCLUSIONS

In making calculations on other molecules with oxygen and nitrogen the intention is to use the W° and ΔW values for uncharged atoms in Table 3; Alt. 2 $F_2(Z_{\text{eff}})$ for ether oxygen, keto oxygen, and pyrrole nitrogen; and Alt. 1 for pyridine nitrogen. The corrections are to be made according to $F_2(Z_{\text{eff}})$. To get densities for keto bonds, however, the values for uncharged atoms for Alt. 1 are to be used and the corrections are to be made according to $F_1(q)$ for both

Table 5. Transition energies and oscillator strengths predicted by use of different sets of charge-corrected parameters. For description of methods, see text.

Molecule	Alternative 1				Alternative 2				Exp. values	
	Uncorrected	$F_1(q)$	Osc. strength f	Osc. strength f	$F_1(q)$	Osc. strength f	$F_2(Z_{\text{eff}})$	Osc. strength f	(vapour) ν_{max} kK	Osc. strength f
Phenol	37.9	38.2	0.01	0.01	38.0	0.01	37.0 ^a	0.02	37.0 ^a	0.02
	47.1	48.0	0.16	0.11	47.5	0.13	46.9 ^a	0.13	46.9 ^a	0.13
	53.7	54.5	0.83	0.99	54.1	0.91	54.0 ^a	0.64	54.0 ^a	0.64
	54.7	55.0	1.04	1.11	54.8	1.08	55.9 ^a	0.47	55.9 ^a	0.47
	62.5	64.7	0.30	0.14	63.5	0.22				
Furan	63.2	64.8	0.08	0.03	64.0	0.05				
	45.5	44.2	0.29	0.31	44.8	0.30	45.2	0.29	46 ^b	log ϵ
	48.4	49.7	0.12	0.05	49.0	0.08	48.7	0.11	48.9 ^b	2.9 shoulder
	59.5	61.3	0.81	0.93	60.1	0.86	59.4	0.83	52.2 ^b	3.6
	62.0	69.1	0.22	0.13	65.2	0.18	62.3	0.21	59.6 ^b	4.1
Benzaldehyde									62.8 ^b	3.8
	37.4	37.1	0.01	0.01	37.2	0.01	37.5	0.01	38.4 ^c	f
	44.3	43.2	0.39	0.45	43.2	0.44	44.6	0.40	43.1 ^c	0.02
	51.6	50.4	0.56	0.38	50.6	0.44	51.7	0.54	51.3 ^c	0.26
	53.5	52.9	0.90	0.67	53.1	0.75	53.6	0.92	(53.8) ^c	1.7
	60.7	58.9	0.31	0.46	59.5	0.40	60.6	0.32	56.2 ^c	
	62.2	59.6	0.04	0.31	60.5	0.18	62.2	0.08	60.6 ^c	
	63.8	63.3	0.51	0.44	63.1	0.53	63.8	0.45		

Table 5. Continued.

Pyrrole	47.3 49.1	0.32 0.06	45.4 49.4	0.36 0.03	46.3 49.3	0.35 0.04	46.8 49.0	0.33 0.06	46.9 49.2	0.33 0.05	47.4 ^d 54.7 ^d 58.5 ^d	>0.12 >0.08 >0.60
Aniline	36.1 44.1 51.3 54.3 60.0 61.7	0.05 0.29 0.38 0.92 0.69 0.11	37.4 46.1 53.2 54.6 62.9 63.5	0.02 0.21 0.79 1.03 0.31 0.06	36.6 44.9 52.1 54.4 61.0 62.4	0.04 0.26 0.55 0.97 0.54 0.08	36.2 43.8 51.0 54.3 60.5 61.7	0.04 0.29 0.45 0.91 0.64 0.11	36.1 44.0 51.2 54.3 60.2 61.7	0.05 0.28 0.43 0.92 0.66 0.10	<i>f</i> 35.5 ^a 43.5 ^a 51.6 ^a 55.5 ^a (63.5) ^a	0.03 0.14 0.51 0.57 (0.68)
Imidazole	47.6 52.5 61.4 69.7	0.33 0.03 0.83 0.39	45.9 52.4 64.2 78.1	0.37 0.02 0.89 0.26	46.7 52.4 62.6 73.6	0.36 0.03 0.87 0.32	47.2 52.0 61.9 71.0	0.35 0.05 0.82 0.36	47.4 52.3 61.6 70.2	0.34 0.04 0.83 0.38	<i>f</i> (in ethanol) log ϵ (48.2) ⁱ (48.4) ^j	3.70 3.32
<i>sym</i> -Tri- azine	44.0 59.7 62.3	0 0 1.17	43.8 59.6 62.3	0 0 1.18	43.9 59.6 62.3	0 0 1.18	43.9 59.6 62.3	0 0 1.18	43.9 59.6 62.3	0 0 1.18	<i>f</i> kK log ϵ (in hexane) ~46 ^e 55.8/ ^f	45.1 ^g 54.3 ^g 2.23 ^g 4.12 ^g
Pyridine	40.7 52.1 57.5 59.3	0.01 0.15 1.16 1.00	40.7 52.1 57.5 59.3	0.001 0.15 1.17 1.00	40.7 52.1 57.5 59.3	0.003 0.15 1.16 1.00	40.7 52.1 57.5 59.3	0.003 0.15 1.16 1.00	40.1 ^d 51.4 ^d 57.5 ^d	0.04 0.10 1.3	<i>f</i>	0.04 0.10 1.3
Pyridini- um ion			40.0 52.0 58.4 58.5	0.09 0.10 1.01 1.02	40.4 52.2 57.9 59.2	0.03 0.14 1.11 0.99	40.4 52.2 57.9 59.2	0.03 0.14 1.11 0.99	(in ethanol-ether) 38.0 ^h 43.5 ^h			

s = shoulder. ^a Ref. 29; ^b Ref. 30; ^c Ref. 31; ^d Ref. 32; ^e Ref. 33; ^f Ref. 34; ^g Ref. 35; ^h Ref. 36; ⁱ Ref. 37; ^j Ref. 38; Some experimental values are given in eV in the reference papers. The conversion factor 1 eV = 8.06573 kK is used here.

carbon and oxygen. Only charges > 0.2 are to be corrected.

Calculations on lumiflavin after these lines have been completed and the results will be given in a following paper.

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