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Electronic Structure and Spectra of Organic Molecules

Part X*. SCF MO CI Calculations for the Hydroxy Derivative Anions of Some Aromatic Molecules

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The Pariser-Parr-Pople method is used to predict the singlet-singlet ($\pi \rightarrow \pi^*$ type). Electronic transition energies for the anions of hydroxy derivatives of benzene, pyridine and pyrimidine. The core integral for the $-O^-$ substituent was treated as an empirical parameter and its value was chosen to fit results for the phenoxide ion and then applied for the compounds with the $-O^-$ substituents. The results of the calculations for molecules with the $-O^-$ groups are compared with those of the corresponding molecules containing the $-OH$ and $-NH_2$ substituents as well as with the experimental data. No serious deviations between theoretical and experimental data other than those which could be ascribed to steric hindrances occuring in the molecules were found.

Die Pariser-Parr-Pople-Methode wird benutzt, um die Singlett-Singlett-Übergangsenergien ($\pi - \pi^*$-Typ) von Benzol-, Pyridin- und Pyrimidinderivaten zu berechnen, die OH-Gruppen enthalten. Das Rumpfintegral des $-O^-$-Substituenten wurde wie ein empirischer Parameter behandelt. Sein Wert wurde so gewählt, daß er die Meßergebnisse für das Phenolat-Anion richtig wiedergibt. Die Resultate der Berechnungen für Moleküle mit der $-O^-$-Gruppe werden mit denjenigen für die entsprechenden Moleküle mit OH- und NH_2-Substituenten als auch mit den experimentellen Daten verglichen. Es werden keine ernsten Abweichungen zwischen theoretischen und experimentellen Daten gefunden, außer solchen, die einer sterischen Hinderung zugeschrieben werden können.

La méthode de Pariser, Parr et Pople est utilisée pour prédire les transitions électroniques ($\pi \rightarrow \pi^*$) pour les formes anioniques des derivés hydroxy du benzène, pyridine et pyrimidine. La valeur d'integrale de coeur associée du substituant $-O^-$ a été choisie de façon à reproduire les positions des bandes d'absorption de forme anionique du phenol et après elle a été appliquée pour les composés envisagés. Les resultats des calculs pour l'anions sont mis en comparaison avec les resultats obtenus pour les correspondantes derivés aminés et hydroxy et avec les donnés experimentales. Peu de déviations ont été obtenus, en dehors de ceux que l'on peut attribuer à des encombres steriques.

Introduction

An examination of the electronic absorption spectra of organic molecules shows that there are no great differences between the spectra of amino substituted compounds and the corresponding anions of molecules in which an amino group is replaced by a hydroxy one. The absorption bands of the anions mentioned above are slightly shifted towards longer wavelengths and their intensity is somewhat stronger compared to those of amino substituted molecules. According to Ref. [1], for instance, the two near ultraviolet absorption bands of aniline have been recorded at 281 and 230 nm, while the bands of the phenoxide ion have been found at 287 and 235 nm, respectively. The measured values of the molar

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[*] Based in part on a M. Sci. thesis by M. Berndt, N. Copernikus University, Toruń, 1969 (unpublished, in Polish).

extinction coefficients are 1400, 8200 and 2600, 9900 for the corresponding bands of aniline and the phenoxide ion, respectively. This type of analogy between the spectra of molecules containing the $-O^-$ group and the corresponding amino derivatives has been observed in many cases. A particularly good illustration, concerning these experimental facts can be found in Ref. [1].

It is purpose of the present paper to apply the Pariser-Parr-Pople method to discuss the electronic absorption spectra of anionic species of some hydroxyaromatics (substituted benzenes) and hydroxyheterocyclic compounds (substituted pyridines and pyrimidines). We shall also compare the spectra of anions with those of neutral molecules and amionosubstituted ones.

Calculations

In a series of previous papers [2, 3] we showed, when using the Pariser-Parr-Pople method in the SCF MO-LCAO CI form with the zero differential overlap approximation, it was possible to obtain a good agreement between experimental data and theoretical values for the singlet-singlet ($\pi \rightarrow \pi^*$ type) transition energies for a series of molecules (benzenes, pyridines, pyrimidines, purines) containing simple donor groups as OR or NR_1R_2 (here the R's indicate hydrogen atoms or alkyl groups). The substituents mentioned above contain one central atom (oxygen or nitrogen) contributing two π-electrons to the conjugated system. In order to estimate the value of the core integral for the substituent X of this sort we used the following approximation

$$W_X = \langle \phi_X | T(i) + U_X^{++}(i) | \phi_X \rangle = -I(\text{X–H}) - \gamma_{XX},$$

where $I(\text{X–H})$ is the experimental value of the ionization potential of the X–H molecules and γ_{XX} is the one-center two-electron Coulomb repulsion integral for the substituent's central atom.

In the present communication we attempt to apply the described approximation to interpret the π-electronic structure of molecules containing $-O^-$ substituents, i.e. anions of hydroxy derivatives. In the first approximation it can be assumed that the removal of the proton of the $-OH$ group leaves the hybridization undisturbed and that there are two π-electrons of $-O^-$ conjugated with those of the ring. Thus, according to the model mentioned above, it seems that the value of the ionization potential of HO^- (i.e. of the H_2O molecule anion) is needed for the evaluation of the integral W_{O^-}. As far as we are aware, there are no experimental data of $I(HO^-)$ obtainable in the literature. It could, however, be possible to approximate the value of the ionization potential of HO^- using the value of the electron affinity of the hydroxyl radical. The experimental value of the latter has been found in the range of 2.1–2.7 eV[1] [21]. However, we cannot use this value in our calculations as it would give quite unrealistic results for the transition energies of the phenoxide anion. This is connected with the fact that the distribution of the valence electrons of the oxygen atom in the HO^- anion is different from the electron distribution of the oxygen atom of the $-O^-$ substituent in aromatic molecules. In the former case there are two equivalent

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[1] The *ab initio* SCF calculations in a Gaussian basis [4] give quite unrealistic values for the ionization potential of HO^- when using Koopman's theorem.

lone pair electrons in the oxygen atom, while in the case of an aromatic molecule with an $-O^-$ substituent one of the pairs of the oxygen is conjugated with the π-electronic system of the parent molecule. In consequence, the ionization potential of the two lone pair electrons of the oxygen atom in the $-O^-$ substituent are different. Therefore, in the calculations presented here the integral W_{O^-} has been treated as an empirical parameter. If we use the value of 18.0 eV for the γ_{OO} integral, similarly as it has been done in the calculations for the $-OH$ substituent, the quantity $W_{O^-}+\gamma_{OO}=-J(-O^-)$ becomes in fact the necessary empirical parameter. The value of $I(-O^-)$ can be interpreted as the ionization potential of this electron pair of the $-O^-$ substituent which is conjugated with the π-electronic system of the ring. The value of $I(-O^-)$ has been estimated as being equal to 9.6 eV by comparison of the experimental and theoretical transition energies for the phenoxide ion.

As to other semiempirical parameters in our calculations, we adopted the $I-A$ approximation for the one center integrals for both carbon and pyridinic nitrogen atoms. In the evaluation of these integrals for nitrogen in an amino group and oxygen the values of 14.5 and 18.0 eV were used respectively. The two-center Coulomb repulsion integrals were calculated by means of the Nishimoto and Mataga formula. The same values of the resonance integrals as in our previous paper [2] were used expect that for the carbon-substituent bond. In the present calculations the value of -2.20 eV was used for all C–X bonds ($r_{CX}=1.36$ Å).

As to the excited states, all singly excited configurations were allowed to interact.

In all calculations it is assumed that the anionic forms are represented by structures in which the negative charge is concentrated on the oxygen atom. It seems to be evident in the case of the hydroxy derivatives of the benzenes. For the case of hydroxy N-heterocycles, however, which can exist in various tautomeric structures, it can be expected that the corresponding anions have either the so called lactam form in which the negative charge is concentrated on the nitrogen atom or the lactim form with the negative charge on the oxygen atom. Unfortunately, experiments (ultraviolet, infrared and Raman spectroscopical studies) do not give a decisive answer concerning the structures of the anionic species of hydroxy substituted pyridines and pyrimidines, the conclusions being dependent on the criteria used for structure diagnosis.

The study of Raman spectra [5] seems to confirm the predominance of the lactam forms for the anions of 2-hydroxy and 2-, and 4-hydroxypyrimidine as well as the lactim ones for the anions of 3- and 4-hydroxypyridine. According to the ultraviolet spectra [6] the lactam form predominates for the anion of 2-hydroxypyridine and the lactim one for the anion of 4-hydroxypyridine. On the other hand, it has been deduced from infrared spectroscopical studies [7] that the anions of 2- and 4-hydroxypyridine and 2- and 4-hydroxypyrimidine have structures of the corresponding lactim type[2].

It is noteworthy that the predominance of the lactim type structures for all anions mentioned above is confirmed by electron-affinity considerations (the electron-affinity of oxygen is higher than that of nitrogen).

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[2] The only possible lactim form in the case of the anion of 5-hydroxypyrimidine is connected with the rule of valence.

In the case of the anionic forms of cytosine and isocytosine no experimental data concerning their structures seem to be available[3]. By analogy to the considered anions of hydroxypyridines and pyrimidines, however, it has been assumed that the anions of cytosine and isocytosine have structures in which the negative charge is concentrated on the oxygen.

Results and Discussion

The results of the calculations for the singlet excited states of the anionic species of the molecules in question together with the experimental data are given in Tables 1 to 5. For comparison we give the same theoretical quantities calculated for both neutral species of the hydroxy and the corresponding aminosubstituted compounds. Since the ultraviolet spectra of hydroxy and aminosubstituted molecules have been discussed theoretically by a number of investigators, the spectra of molecules under study will be discussed here with regard to the effects of substituents on the parent molecule spectrum.

Substituted Benzenes

As can be seen from Table 1, containing the calculated and experimental transition energies for mono- and disubstituted benzenes, there is a quite satisfactory agreement between the theoretical and experimental data. In all cases the differences between the experimental and calculated transition energies are not higher than 0.15 eV. The comparison between observed and calculated spectral transition energies is better illustrated in Fig. 1. It can be seen that the bands of the neutral forms are shifted towards shorter wavelengths with respect to those of the anionic ones. The calculations also confirm the observed analogy between the spectra of anionic forms of hydroxy compounds and the corresponding amino derivatives.

A comparison of the present results with previous ones[4] (within the SCF MO CI framework) obtained by other people may be made for the phenoxide ion only. Namely, Nishimoto and Forster [9] have recently calculated by means of the β-variable SCF MO CI method the transition energies for the anions of phenol, hydroxynaphthalenes and hydroxyquinolines. The best model they had used for the anion parametrization yielded the values of 4.48 and 5.55 eV for the first two transition energies of the phenoxide ion compared to the experimental values of 4.3 and 5.30 eV, respectively. It should be noted that the comparison does not give a proper idea of the differences in the results of both methods, since in the

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[3] It is noteworthy that the infrared and ultraviolet studies on the anions of 2,4-diketopyrimidines [8] confirm their structures with the negative charge concentrated on the oxygen atom.

[4] Compare the improved LCAO study on the phenoxide ion by Julg and Bonnet [11] and the CNDO calculation for this molecule by Del Bene and Jaffé [12]. After compilation of the present paper we have read the paper by Tyutyulkov *et al.* [22] concerning the SCF MO CI study of phenol and the phenoxide ion. In the paper, the core integral for the oxygen of the $-O^-$ substituent was treated as an empirical parameter. The difference between the value of this parameter and the value of the corresponding integral for oxygen in the $-OH$ group is 3.0 eV. The same difference has been used in the calculations presented here. This result does not appear unexpected because the empirical parameters, used in Ref. [22] are very similar to ours.

Table 1. *Mono and disubstituted benzenes – the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, molar extinction coefficients, ε, transition polarizations, Θ (in degrees)*

Theoretical			Experimental[a]		
ΔE	f	Θ[b]	ΔE	ε	Solvent
(1) 1-OH-benzene					
4.58	0.016	0	4.59	2200	Water
5.75	0.108	90	5.88	6000	
6.64	1.136	90			
6.66	1.011	0			
(2) 1-O^--benzene					
4.34	0.044	0	4.31	2600	Aqueous NaOH, pH = 12.3
5.32	0.332	90	5.28	9900	
6.27	0.523	0			
6.49	0.862	90			
(3) 1-NH_2-benzene					
4.40	0.037	0	4.40	1400	Phosphate buffer, pH = 8.0
5.34	0.316	90	5.39	8200	
6.35	0.614	0	6.31	34500	
6.48	0.847	90			
(4) 1,3-diOH-benzene					
4.49	0.014	60	4.53[c]	1900	KCl/HCl aqueous buffer solution, pH = 1.4
5.62	0.052	−30	5.65	6200	
6.38	1.231	60			
6.46	0.962	−30			
(5) 1-OH-3-O^--benzene					
4.31	0.030	89	4.35	2700	H_3BO_3/NaOH aqueous buffer solution, pH = 10.25
5.30	0.228	20	5.27	7200	
6.10	0.664	−58			
6.15	0.954	42			
(6) 1-OH-3-NH_2-benzene					
4.36	0.025	84	4.37[d]	2300	Cyclohexane + 2% ether
5.33	0.211	19	5.30	8600	
6.14	1.002	65			
6.18	0.664	−24			
(7) 1,3-diO^--benzene					
4.20	0.032	60	4.24	3400	KCl/NaOH aqueous buffer solution, pH = 13,7
5.18	0.113	−30	sh 5.2	8000	
5.73	1.104	60	5.85	32000	
5.76	0.474	−30			
(8) 1,3-diNH_2-benzene					
4.27	0.029	60	4.29	2100	Aqueous Stenhagen and Theorell buffer, pH = 11.75
5.22	0.113	−30	5.21	7800	
5.75	1.069	60	5.89	32000	
5.92	0.540	−30			

[a] Experimental data taken from Ref. [1] unless otherwise indicated. sh indicates a shoulder.

[b] The polarization direction (angle Θ) is measured positive towards C_4 with respect to an axis from C_2–C_6.

[c] Musgrave [14] gives the values of 4.48 and 5.63 eV for the first two transition energies in water.

[d] From Ref. [15]; the first two transition energies (in eV) in water are 4.46 ($\varepsilon = 1900$) and 5.41 ($\varepsilon = 6400$).

Table 2. *Trisubstituted benzenes – the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, molar extinction coefficients, ε, transition polarizations, Θ (in degrees)*

Theoretical			Experimental[a]		
ΔE	f	Θ[b]	ΔE	ε	Solvent
(9) 1-NH_2-2,4-diOH-benzene					
4.19	0.068	−28	4.22	2700	KH_2PO_4/Na_2HPO_4, pH = 7.5
5.13	0.281	72	5.36	5500	
6.17	0.921	−45	6.27	25000	
6.27	0.749	55			
(10) 1-NH_2-2-OH-4-O^--benzene					
4.01	0.088	−21	4.10 5.17 6.03	3700 5500 27000	KH_2PO_4/Na_2CO_3, pH = 10.02
4.96	0.407	79			
6.09	0.749	−76			
6.12	0.574	1			
(11) 1-NH_2-2-O^--4-OH-benzene					
4.07	0.081	−48			
4.91	0.214	37			
5.85	0.963	−78			
5.96	0.601	−6			
(12) 1-NH_2-2,4-diO^--benzene					
3.93	0.093	−37	3.99	4000	Aqueous 10% NaOH
4.83	0.272	56	5.10	5500	
5.67	0.797	−83	5.90	27000	
5.76	0.603	−22			
(13) 1,3-diOH-2-NH_2-benzene					
4.26	0.015	60	4.57	1150	KH_2PO_4/Na_2HPO_4, pH = 7.5
5.07	0.139	−30	sh 5.29	6300	
5.93	0.863	60	6.05	38000	
6.08	0.962	−30			
(14) 1-OH-2-NH_2-3-O^--benzene					
4.13	0.021	−68	4.38	2000	$H_3BO_3/KCl/Na_2CO_3$, pH = 10.85
4.86	0.124	20	sh 5.03	6300	
5.70	0.986	−85	5.81	34000	
5.82	0.718	1			
(15) 1,3-diO^--2-NH_2-benzene					
4.04	0.006	60	4.43	1750	M NaOH
4.74	0.042	−30	sh 5.00	6500	
5.43	0.977	60	5.63	38000	
5.55	0.784	−30			

[a] All data taken from Ref. [1]. sh indicates a shoulder.

[b] The polarization direction (angle Θ) is measured positive towards C_4 with respect to an axis from C_2–C_6.

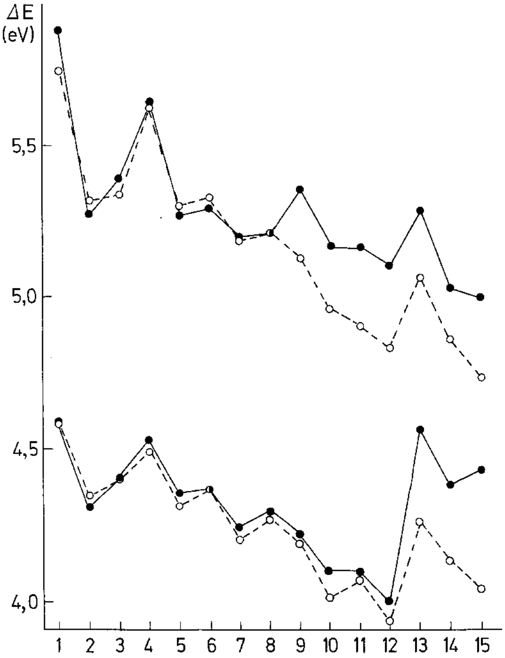

Fig. 1. Comparison between observed and calculated singlet-singlet transition energies for substituted benzenes. Actual data and numbering of molecules in Tables 1 and 2. —●—●— observed values, —○—○— calculated values

calculations reported here the phenoxide ion has been treated as a reference molecule.

In the case of 1,2,4-trisubstituted benzenes we obtain a slightly poorer agreement between theoretical and experimental *ΔE* values than in the case of m-substituted benzenes. There are much more discrepancies between theory and experiment for 1,2,3-trisubstituted benzenes. We ascribe them to steric hindrances occuring in polysubstituted molecules and we do not consider the obtained results to be unexpected.

Substituted Pyridines and Pyrimidines

The results of the calculations for the anionic species of the hydroxy derivatives of pyridine and pyrimidine and the corresponding amino derivatives are given in Tables 3 and 4. The transition energies are in satisfactory agreement with experimental data (see also Fig. 2); the differences between the theoretical and experimental values do not exceed 0.15 eV, except the case of the anion of 4-hydroxypyridine for which the observed value seems to be uncertain (the observed intensity of the first absorption band is very low, this fact being confirmed by the small value of the calculated oscillator strength). From Tables 3 and 4 and Fig. 2 it can be seen that the calculations predict correctly the dependence of the transition energy value on the position of the substituent. The experimental analogy between the spectra of the anionic forms and the corresponding amino derivatives is also confirmed by the present calculations.

Table 3. *Monosubstituted pyridines – the singlet-singlet transition energies, ΔE (in eV),* oscillator *strengths, f, molar extinction coefficients, ε, transition polarizations, Θ (in degrees)*

Theoretical			Experimental[a]		
ΔE	f	Θ[b]	ΔE, (ε, f)		
(16) 2-OH-pyridine[c]			[18]	[17]	[1]
4.60	0.096	13	(Me) 4.57 (f = 0.11)	(Et) 4.59	(He) 4.54 (ε = 3650)
5.86	0.137	−58	5.72 (f = 0.14)	5.79	5.77 (ε = 7300)
6.81	1.023	−40			} 6.77 (ε = 26000)
6.92	0.927	52			
(17) 2-O⁻-pyridine			[16]		
4.35	0.126	19	(W, pH = 13) 4.26 (ε = 5070)		
5.47	0.338	−48	5.39 (ε = 9000)		
6.52	0.315	32			
6.66	0.744	−47			
(18) 2-NH_2-pyridine[d]					
4.40	0.126	16	(Et) 4.2	(Cy) 4.3 (ε = 3800)[e]	
5.48	0.322	−48	5.3–5.4	5.4 (ε = 9400)	
6.57	0.445	13			
6.67	0.672	−63			
(19) 3-OH-pyridine[c]			[18, 20]	[19]	
4.58	0.086	−22	(W, Me) 4.49 (f = 0.08)	(Me) 4.44	
5.76	0.129	38	5.74 (f = 0.28)	5.64	
6.74	0.988	66			
6.84	0.914	−21			
(20) 3-O⁻-pyridine			[16]		
4.25	0.112	−31	(W, pH = 13) 4.16 (ε = 4960)		
5.29	0.312	33	5.25 (ε = 11000)		
6.27	0.433	77			
6.67	0.713	5			
(21) 3-NH_2-pyridine[d]					
4.33	0.109	−29	(Et) 4.1–4.2	(Cy) 4.25 (ε = 3000)[e]	
5.33	0.296	33	5.2–5.3	5.34 (ε = 8200)	
6.36	0.514	78			
6.67	0.696	2			
(22) 4-OH-pyridine[c]			[19]	[20]	
4.73	0.010	0	(Me) 5.17 sh	(W) 5.27 sh	
5.78	0.087	90	5.58	5.58 (f = 0.15)	
6.62	0.890	0			
6.69	1.135	90			

[a] Solvent: Me = methanol, W = water, Cy = cyclohexane, Et = ethanol, He = heptane. sh indicates a shoulder.

[b] The polarization direction (angle Θ) is measured positive towards C_4 with respect to an axis from C_2–C_6 (in pyridines) or N_1–N_3 (in pyrimidines).

[c] Experimental data for methoxy derivative of pyridine.

[d] For complication of the experimental data see Ref. [2].

[e] The values of molar extinction coefficients were taken from the measurements made in water.

Table 3 (continued)

Theoretical			Experimental[a]	
ΔE	f	Θ[b]	ΔE, (ε, f)	
(23) 4-O$^-$-pyridine			[16]	
4.57	5.10^{-4}	0	(W, pH = 13) 4.77 sh (ε = 2200)	
5.30	0.322	90	5.19 (ε = 14150)	
6.14	0.589	0		
6.52	0.865	90		
(24) 4-NH$_2$-pyridine[d]				
4.61	$2\cdot10^{-5}$	0	(Et) 4.5–4.6 sh	(Cy) 4.77 sh (ε = 2400)[e]
5.32	0.312	90	5.1–5.3	5.32 (ε = 14000)
6.22	0.636	0		
6.51	0.835	90		

Table 4. *Monosubstituted pyrimidines – the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, molar extinction coefficients, ε, transition polarizations, Θ (in degrees)*

Theoretical			Experimental[a]	
ΔE	f	Θ[b]	ΔE, (ε, f)	
(25) 2-OH-pyrimidine[c]			[16]	
4.69	0.107	0	(W, pH = 7) 4.69 (ε = 4660, f = 0.072)	
5.99	0.229	90	5.9 (ε = 6000)	
6.94	0.894	0		
7.20	0.872	90		
(26) 2-O$^-$-pyrimidine			[16]	
4.39	0.124	0	(W, pH = 13) 4.24 (ε = 4600)	
5.61	0.433	90	5.63 (ε = 11700)	
6.61	0.051	0		
6.83	0.656	90		
(27) 2-NH$_2$-pyrimidine[d]				
4.45	0.122	0	(Et) 4.2–4.3	(Cy) 4.38 (ε = 3200)[e]
5.59	0.425	90	5.5	5.56 (ε = 13000)
6.70	0.083	0		
6.81	0.615	90		
(28) 4-OH-pyrimidine[c]			[16]	
4.79	0.066	30	(W, pH = 7) 5.0 (ε = 3370, f = 0.066)	
5.92	0.109	−15	5.8 (ε = 6500)	
6.77	0.929	73		
6.92	0.923	−11		
(29) 4-O$^-$-pyrimidine			[16]	
4.60	0.089	49	(W, pH = 13) 4.69 (ε = 3280)	
5.49	0.282	7	5.46 (ε = 11100)	
6.36	0.499	−87		
6.70	0.711	16		
(30) 4-NH$_2$-pyrimidine[d]				
4.63	0.096	44	(Et) 4.5–4.6	(Cy) 4.71 (ε = 5200)[e]
5.49	0.282	8	5.3	5.44 (ε = 18200)
6.40	0.558	88		
6.70	0.664	9		

Footnotes the same as in Table 3.

Table 4 (continued)

Theoretical			Experimental[a]	
ΔE	f	Θ[b]	ΔE, (ε, f)	
(31) 5-OH-pyrimidine			[16]	[16]
4.59	0.115	0	(W, pH = 4.32) 4.58 (ε = 4750)	(Et) 4.49 (ε = 5330)
5.75	0.229	90	5.79 (ε = 9720)	5.68 (ε = 9970)
6.96	0.902	90		
7.05	0.754	0		
(32) 5-O$^-$-pyrimidine			[16]	
4.17	0.133	0	(W, pH = 9.35) 4.07 (ε = 4450)	
5.23	0.382	90	5.20 (ε = 11240)	
6.47	0.118	0		
6.85	0.719	90		
(33) 5-NH$_2$-pyrimidine[d]				
4.27	0.132	0	(Et) 3.94	(W, pH = 7) 4.16 (ε = 3100)[e]
5.27	0.368	90	5.05	5.25 (ε = 11000)
6.57	0.175	0		
6.85	0.712	90		

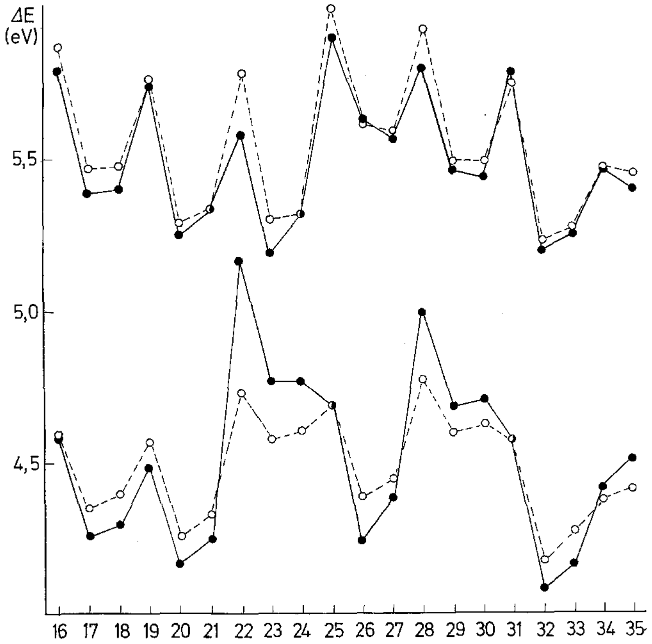

Fig. 2. Comparison between observed and calculated singlet-singlet transition energies for substituted pyridines and pyrimidines. Actual data and numbering of molecules in Tables 3, 4 and 5. —●—●— observed values, —○—○— calculated values

Anions of Cytosine and Isocytosine

Morita and Nagakura [10] have recently measured the electronic absorption spectra of cytosine, isocytosine and their anions and cations in order to compare these observations with the results obtained within the Pariser-Parr-Pople framework. In their calculations some of the integrals were determined in such a way that the calculated transition energies agreed well to the observed ones. For the anions of cytosine and isocytosine, for instance, they considered the two nitrogens in the ring (see Fig. 3) to be equivalent and the valence state ionization potentials of the nitrogen atoms were treated as empirical parameters. Moreover, the values of the ionization potentials of the amino-type nitrogen and of the oxygen were also altered.

The results calculated by Morita and Nagakura [10] and those by the present authors as well as the experimental results are listed in Table 5. As can be seen

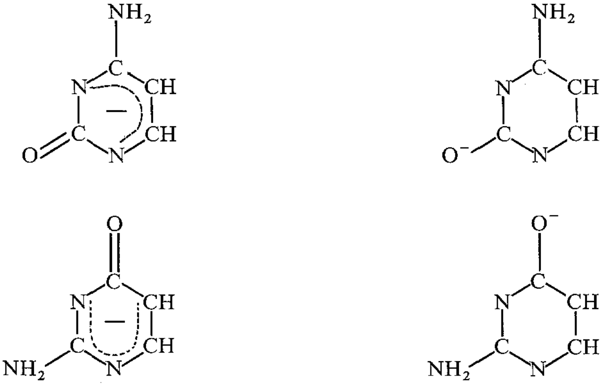

Fig. 3. Structures of anions of cytosine (top) and isocytosine (bottom) assumed in the calculations by Morita and Nagakura [10] (on the left) and in the present calculations (on the right)

Table 5. *Cytosine and isocytosine anions – the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, and transition polarizations, Θ (in degrees)*

Theoretical					Experimental	
Morita and Nagakura results		Present work				
ΔE	f	ΔE	f	Θ[a]	ΔE	f
(34) Cytosine anion						
4.42	0.128	4.38	0.147	26	4.42	0.128
5.55	0.294	5.47	0.192	−40	5.46	0.124
6.41	0.787	5.90	0.778	74		
6.69	0.315	6.22	0.356	18		
(35) Isocytosine anion						
4.39	0.103	4.41	0.141	30	4.52	0.117
5.59	0.312	5.45	0.216	−40	5.40	0.141
6.58	1.135	5.91	0.766	73		
6.63	0.106	6.18	0.362	15		

[a] Measured counterclockwise from the line N_1–N_3.

from these figures the maximal deviation between the theoretical and experimental ΔE values in the case of the present calculation is 0.12 eV compared to 0.19 eV in Ref. [10]. So the agreement between theory and experiment seems to be slightly improved compared to the results of Morita and Nagakura. We do not, however, consider the good agreement between the last calculation and the experiment to be unexpected since the anions of both cytosine and isocytosine were, in fact, treated as the reference compounds in the paper by Morita and Nagakura [10]. Contrary to this, all parameters used in our calculations for the cytosine and isocytosine anions had been determined on other reference molecules.

It may be interesting to compare the relationship between the values of the transition energies for the cytosine and isocytosine anions predicted by the two calculations mentioned above. Namely, for the first transition the observed ΔE value for the isocytosine anion is higher than that for the cytosine anion and the same fact is found in the calculations reported here[5], while this is not in the case of Morita and Nagakura results. For the second transition the experimental energy for the cytosine anion is slightly increased compared to that of the isocytosine anion and this fact seems to be predicted in the present calculations, while the results obtained by Morita and Nagakura suggest an opposite sequence rather.

The Effect of the $-O^-$ *Group on the Spectrum of Molecules*

A few words on the effect of the $-O^-$ group on the spectrum of molecules should be said. As we know [2, 3, 13] the conjugation between the π-electrons of the substituents (here: benzene, pyridine, pyrimidine) is sensitive in the first place to the value of the sum of $W_X + \gamma_{XX}$ for the substituent atom, i.e. to the value of the ionization potential of the lone pair of the substituent. The spectroscopic evidence shows that the $-OH$ group has weaker electron donor properties than both the $-NH_2$ and $-O^-$ groups. In the present study, the comparison of the calculated singlet-singlet transition energies of molecules considered gives the same results for the relative strengths of these substituents. It is also interesting to compare the experimental shifts (δE) of the first absorption band of the parent molecule caused by the substituents with the calculated charge (ΔQ) transferred from the substituents to the ring of the molecules. As we see from the Fig. 4 these shifts are accompanied by the transfer of the π-electronic charge from the central atom of substituents to the ring. It is also evident that the change in the π-electron density at the oxygen atom of the $-O^-$ group and at the nitrogen atom of the corresponding amino group has a similar effect on δE. We note that the relationship between the values of δE and the corresponding ΔQ values is almost linear; serious deviations are observed only for 4-substituted pyridines (uncertain positions of the first absorption bands) and for trisubstituted benzenes and the later are probably due to steric effects.

As we see from the results described in this paper, the semiempirical Pariser-Parr-Pople type calculations can be succesfully used to interpret the electronic absorption spectra of anions of molecules containing hydroxy groups. We have obtained, in general, a very good agreement between the calculated and experi-

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[5] This fact is only indicated as a trend by the computed transition energies.

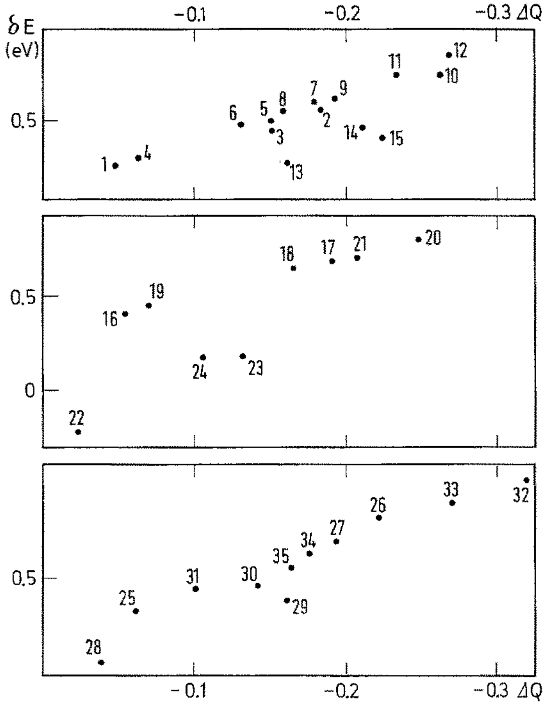

Fig. 4. Observed shifts δE of the first absorption band of benzene, pyridine and pyrimidine caused by the substitutions versus the calculated charge transfered from substitutions to the ring (top-benzenes, middle-pyridines, bottom-pyrimidines)

mental singlet-singlet transition energies for the anions under study. In spite of the satisfactory results obtained, it should be remembered that the calculations presented here cannot be treated as an evidence indicating that the anions of hydroxy *N*-heterocycles exist in lactim forms.

Acknowledgement. The authors would like to thank a referee for drawing their attention to the paper by Page and Sugden (see Ref. [21]).

Note Added in Proof: After the manuscript of this paper had been sent to the Editor of the Theoretica Chimica Acta, we read the paper by M. Tichý and R. Zahradník [J. physik. Chem. **73**, 534 (1969)] concerning the theoretical study of the electronic absorption spectra of amino and hydroxy derivatives of benzenoid hydrocarbons and corresponding anionic forms of phenols. Their results agree well with the experimental data.

Quite recently the Pariser-Parr-Pople type calculations (similar to those presented in this paper) have been performed for the anions of some aromatic and heterocyclic compounds with substituents containing sulfur (J. S. Kwiatkowski, M. Berndt and J. Fabian: Acta physica polon., to be published). Theoretical results are in a good agreement with experiment.

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