MO SELF-CONSISTENT-FIELD CALCULATIONS OF QUINOLINE AND ITS DERIVATIVES

I. CALCULATION OF THE ELECTRONIC SPECTRA OF QUINOLINE AND 8-HYDROXYQUINOLINE BY THE CNDO (COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP) METHOD

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The electronic spectra and electronic structures of quinoline, the hydroxy form of 8-hydroxyquinoline, and the zwitterion form of 8-hydroxyquinoline, and the 8-hydroxy-N-methylquinolinium ion were calculated by the MO self-consistent-field method within the CNDO (complete neglect of differential overlap) approximation.

Molecular orbital self-consistent-field (MO SCF) calculations within the π-electron approximation, which satisfactorily describe the electronic spectra of neutral quinoline and 8-hydroxyquinoline molecules [1-3], poorly convey the electron transitions of the protonated forms [1], particularly the zwitterion form of 8-hydroxyquinoline [2].

In the present paper we present the calculation of quinoline and the hydroxy and zwitterion forms of 8-hydroxyquinoline by the MO SCF method within the CNDO/2 (complete neglect of differential overlap) approximation [4] (with the Del Bene and Jaffe parametrization [5]) with allowance for 40 single excited configurations. The two-center two-electron integrals were calculated within the Mataga–Nishimoto approximation [6]. The geometry of the quinoline molecule was selected in accordance with the data in [7], and the following bond lengths and angle were used: C–O 1.35 Å, O–H 1.04 Å, N–H 1.04 Å, C–N 1.47 Å, angle COH 109°.

The calculation of the hydroxy form of 8-hydroxyquinoline was made for the cis configuration [8].

The observed and calculated (by the Pariser–Parr–Pople (PPP)] method [1, 3] energies and oscillator forces of the singlet–singlet electron transitions of quinoline, 8-hydroxyquinoline, and 8-hydroxy-N-methylquinolinium ion are compared in Table 1. The results of calculation of the $\pi \rightarrow \pi^*$ electron transitions within the CNDO and PPP approximations are in good agreement with the electronic spectra of neutral quinoline and 8-hydroxyquinoline molecules. In addition, the $\sigma - \pi$ interaction in these molecules does not lead to substantial changes in the energies of the $\pi \rightarrow \pi^*$ electron transitions. Allowance for the $\sigma - \pi$ interaction in the case of the neutral quinoline molecules, in contrast to 8-hydroxyquinoline, is also not reflected in the configurational interaction during the formation of lower excited states. The ${}^1L_b$ (α state) excited state in quinoline is formed primarily from the ${}^1\chi_{m,\, m+2}$ and ${}^1\chi_{m-1,\, m+1}$ configurations, whereas the ${}^1L_a$ state (p state) is formed primarily from the ${}^1\chi_{m,\, m+1}$ configuration. The transition with an energy of 4.26 eV in 8-hydroxyquinoline also has pronounced p character. The α state in 8-hydroxyquinoline is expressed less distinctly. The ${}^1\chi_{m,\, m+2}$, ${}^1\chi_{m-1,\, m+1}$ (α state of quinoline) and ${}^1\chi_{m,\, m+1}$ configurations basically form this excited state in 8-hydroxyquinoline.

The $\pi \rightarrow \pi^*$ electron transitions of quinoline manifest different sensitivities to exocyclic substitution. In 8-hydroxyquinoline the energy of the $\pi \rightarrow \pi^*$ electron transitions, to which the p and β bands correspond in quinoline, is considerably reduced. The energy of the $\pi \rightarrow \pi^*$ transition in the lower excited state (α band) decreases to a lesser degree in the substitution of quinoline. As a result, the α and p bands merge in the spectrum of neutral 8-hydroxyquinoline molecules. Asymmetry of the long-wave absorption band is distinctly noticeable in the spectrum of 8-methoxyquinoline (Table 1).

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TABLE 1. Singlet–Singlet Electron Transitions in the Quinoline and 8-Hydroxyquinoline Molecules

CNDO		PPP		Assignment	Experiment	
E, eV	*f*	*E*, eV	*f*		*E*, eV	*f*
			Quinoline			
4,18	0,016			$n\to\pi^*$		
4,20	0,025	$3{,}99^1$	0,052	$\pi\to\pi^*(\alpha)$	$3{,}96^9$	0,04
4,53	0,222	$4{,}48^1$	0,197	$\pi\to\pi^*(p)$	$4{,}59^9$	0,08
5,59	0,002			$\sigma\to\pi$		
5,52	0,746	$5{,}31^1$	0,636	$\pi\to\pi^*$ } (β)	$5{,}51^9$	0,60
5,79	0,219	$5{,}78^1$	1,050	$\pi\to\pi^*$ }		
5,99	0,000			$\sigma\to\pi^*$		
5,99	0,785	$6{,}19^1$	0,843	$\pi\to\pi^*(\beta')$		
			8-Hydroxyquinoline (hydroxy form)			
4,08	0,022	$3{,}92^3$	0,110	$\pi\to\pi^*(\alpha)$ }	$(3{,}90)^a$	
4,20	0,016			$n\to\pi^*$ }	$4{,}06^2$	0,05
4,26	0,178	$4{,}17^3$	0,166	$\pi\to\pi^*(p)$ }	$(4{,}98)^a$	
5,29	0,889	$5{,}21^3$	0,871	$\pi\to\pi^*(\beta)$	$5{,}18^2$	0,64
5,56	0,001			$\sigma\to\pi^*$		
5,58	0,070	$5{,}68^3$	0,087	$\pi\to\pi^*$		
5,98	0,633	$5{,}79^4$	0,602	$\pi\to\pi^*$ } (β′)		
6,18	0,404	$5{,}99^3$	0,278	$\pi\to\pi^*$ }	6,20	0,78
			8-Hydroxyquinoline (zwitterion form)			
1,81	0,038	$1{,}13^3$	0,039	$\pi\to\pi^*(p)$	$2{,}88^b$	
2,86	0,001			$n\to\pi^*$		
3,39	0,106	$3{,}01^3$	0,118	$\pi\to\pi^*$		
4,19	0,004			$n\to\pi^*$		
4,21	0,641	$3{,}86^3$	0,384	$\pi\to\pi^*$		
4,68	0,190	$4{,}32^3$	0,481	$\pi\to\pi^*$		
		$4{,}39^3$	0,144			
4,89	0,009			$\sigma\to\pi^*$		
5,25	0,003			$\sigma\to\pi^*$		
5,03	0,040	$5{,}07^3$	0,106	$\pi\to\pi^*$		
5,28	0,144	$5{,}39^3$	0,091	$\pi\to\pi^*$		
5,49	0,002			$\sigma\to\pi^*$		
5,99	0,532	$6{,}14^3$	0,917	$\pi\to\pi^*$		
			8-Hydroxy-N-methylquinolinium ion (zwitterion form)			
1,94	0,047			$\pi\to\pi^*(p)$	$2{,}28^c$	0,02
					$2{,}80^b$	0,02
2,55	0,002			$n\to\pi^*$		
3,40	0,108			$\pi\to\pi^*$	$3{,}32^c$	0,07
					$3{,}57^b$	0,02
4,02	0,002			$n\to\pi^*$	$3{,}72^b$	0,01
4,28	0,655			$\pi\to\pi^*$ }	$4{,}25^c$	0,62
4,69	0,192			$\pi\to\pi^*$ }	$4{,}54^b$	0,25
4,60	0,003			$\sigma\to\pi^*$		
5,20	0,033			$\pi\to\pi^*$ }	$5{,}00^c$	0,19
5,33	0,113			$\pi\to\pi^*$ }	$4{,}82^b$	0,36
5,29	0,005			$\sigma\to\pi^*$		
5,62	0,001			$\sigma\to\pi^*$		
5,97	0,315			$\pi\to\pi^*$		

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[a] Long-wave absorption of 8-methoxyquinoline.

[b] Spectrum of the zwitterion forms of 8-hydroxyquinoline and the 8-hydroxy-N-methylquinolinium ion in water.

[c] Spectrum of the 8-hydroxy-N-methylquinolinium ion in chloroform.

The lowest-energy transition (4.18 eV) in quinoline has $n\to\pi^*$ character. In 8-hydroxyquinoline the sequence of the transitions changes – the first transition (4.08 eV) has $\pi\to\pi^*$ character, and the energy of the $n\to\pi^*$ transition is 4.20 eV. However, the $n\to\pi^*$ band is not observed in the spectrum of either quinoline or 8-hydroxyquinoline because of overlapping with the intense $\pi\to\pi^*$ absorption.

The zwitterion form of 8-hydroxyquinoline [10-12], which is formed only in aqueous solution [13], is of greatest interest from the point of view of elucidation of the nature of the electron transitions and the structure in this series of compounds. The electronic spectrum of the zwitterion form of 8-hydroxyquinoline was calculated by the PPP method and compared with the spectrum of the zwitterion form in water [2]. However, the available experimental results for the zwitterion form of 8-hydroxyquinoline in water) are not at all suitable for this sort of comparison. It is known that the electronic spectra of similar systems are extremely sensitive to the properties of the solvent. Thus, for example, in the case of the zwitterion form of 8-mercaptoquinoline the shift in the long-wave absorption band for the water–acetone solvent pair is 0.60 eV [13]. The low concentration of the zwitterion form of 8-hydroxyquinoline in water (2% [13]) also does not give a complete representation of its electronic spectrum.

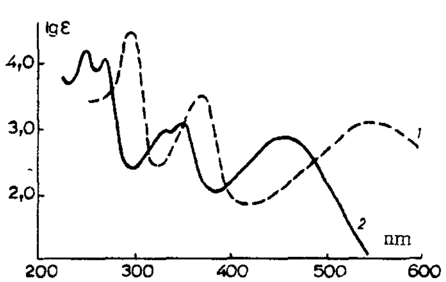

Fig. 1. Electronic absorption spectrum of the 8-hydroxy-N-methylquinolinium ion in chloroform (1) and in water (2).

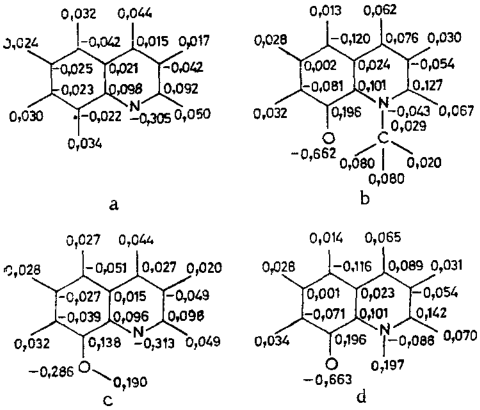

Fig. 2

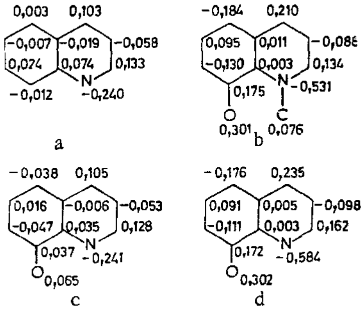

Fig. 3

Fig. 2. Distribution of the total electron density (Q) in molecules of quinoline (a), the 8-hydroxy-N-methylquinolinium ion (b), and the hydroxy (c) and zwitterion (d) forms of 8-hydroxyquinoline.

Fig. 3. Distribution of the π-electron density (Q_π) in molecules of quinoline (a), the 8-hydroxy-N-methylquinolinium ion (b), and the hydroxy (c) and zwitterion (d) forms of 8-hydroxyquinoline.

The spectrum of the 8-hydroxy-N-methylquinolinium ion [11] in chloroform (Table 1) was used as the standard for the electronic spectrum of the zwitterion form in the present research. This compound exists in the zwitterion form both in the crystalline state (red substance) and in solution. However, in this case it is also necessary to take into account the effect of the solvent (Fig. 1).

The results of the present research show that the electronic spectrum of the zwitterion form of the 8-hydroxy-N-methylquinolinium ion in chloroform is modeled satisfactorily within the framework of the CNDO approximation (Table 1). In the zwitterion form the low-energy $\pi \rightarrow \pi^*$ transitions are due primarily to single-configuration transitions. The analogous (to the neutral form of 8-hydroxyquinoline) excited states responsible for bands of the α and β type are absent. The long-wave absorption of the 8-hydroxy-N-methylquinolinium ion (2.28 eV) is due to a $\pi \rightarrow \pi^*$ transition of the p type. This transition is accompanied by charge transfer basically from the 2p AO of oxygen to the quinoline ring. This absorption is shifted to the shortwave region (2.80 eV) in the spectrum of a solution of the 8-hydroxy-N-methylquinolinium ion in water (Fig. 1). The corresponding $\pi \rightarrow \pi^*$ band in the spectrum of the zwitterion form of 8-hydroxyquinoline in water is found at 2.88 eV (1.81 eV, according to the calculation). The extremely substantial difference from the calculated value of the energy of the long-wave transition in alcohol of the zwitterion form of 8-hydroxyquinoline ($\Delta E = 1.07$ eV) and the 8-hydroxy-N-methylquinolinium ion ($\Delta E = 0.86$ eV) in water (Table 1) is due to solvation of the polar molecule of the zwitterion form by molecules of the polar solvent (water). In conformity with the concept of the interaction of the solvent and the dissolved substance (dipole–dipole interaction, formation of hydrogen bonds), water molecules stabilize the ground state of the zwitterion form (8-hydroxyquinoline and the 8-hydroxy-N-methylquinolinium ion), the calculated dipole moment (μ_c) of which is 10.4 D, to a greater extent as compared with the stabilization of the lower excited state ($\mu_c = 4.1$ D). The calculation, in which the effect of the medium was disregarded, satisfactorily models the electron transitions of the zwitterion form of the 8-hydroxy-N-methylquinolinium ion in a less polar medium (chloroform), i.e., in the case where the perturbation of the medium on the energy levels of the molecule reduces to a minimum. This explains the considerably greater deviation of the energy of the long-wave $\pi \rightarrow \pi^*$ transition of the zwitterion form of 8-hydroxyquinoline and the 8-hydroxy-N-methylquinolinium ion in water as compared with chloroform (for the 8-hydroxy-N-methylquinolinium ion) and the calculated energy of the corresponding $\pi \rightarrow \pi^*$ transition.

As noted above, in the case of 8-hydroxyquinoline, the zwitterion form is not generated in weakly polar solvents. However, considering the analogy in the electronic structures and the nature of the electron transitions of the zwitterion form of the 8-hydroxy-N-methylquinolinium ion and 8-hydroxyquinoline, it can be asserted a priori that the calculated electronic spectrum of the zwitterion form of 8-hydroxyquinoline can be adopted as the model spectrum of this form in weakly polar solvents.

The $n \rightarrow \pi^*$ transitions in the spectra of the zwitterion form of 8-hydroxyquinoline in water and of the 8-hydroxy-N-methylquinolinium ion in chloroform are masked by intense $\pi \rightarrow \pi^*$ absorption. In a solution of the zwitterion form of the 8-hydroxy-N-methylquinolinium ion in water the absorption band found at 3.32 eV in the spectrum of a solution in chloroform is split into two bands at 3.57 eV (348 nm) and 3.72 eV (333 nm) (Table 1 and Fig. 1). According to the calculation, this region contains an $n \rightarrow \pi^*$ transition, to which, considering the lower intensity and higher hypsochromic shift (formation of a hydrogen bond), one can assign the band at 3.72 eV.

Molecular Diagrams

The molecular diagrams of the distribution of the total (Q) and π-electron (Q_π) densities in the molecules of quinoline, the 8-hydroxy-N-methylquinolinium ion, and the hydroxy and zwitterion forms of 8-hydroxyquinoline are presented in Figs. 2 and 3.

According to the results of the calculation in the present research, the unshared pair of electrons in quinoline and 8-hydroxyquinoline is delocalized to a considerable degree over the σ system of the molecules. One may note the extremely distinct correlation between the electron densities on the AO of the unshared pair (q_n) entering into the composition of the upper filled σ-MO and the basic pK_{NH^+} properties of quinoline ($pK_{NH^+} = 4.94$ [9], $q_n = 0.883$) and 8-hydroxyquinoline ($pK_{NH^+} = 5.13$ [9], $q_n = 0.945$).

The positive charge of the σ framework in the zwitterion form of 8-hydroxyquinoline and the 8-hydroxy-N-methylquinolinium ion is localized primarily on the nitrogen atom (+0.5). This charge is compensated by a shift in the electron density along the π MO. As a result of this, protonation of the nitrogen atom caused by polarization of the σ and π electrons leads to a slight decrease in Q on the nitrogen atom as compared with the hydroxy form of 8-hydroxyquinoline (Fig. 2).

The greatest deficit in the π- and total electron densities in the molecules of the zwitterion form of 8-hydroxyquinoline and the 8-hydroxy-N-methylquinolinium ion exists on the 2 and 4 carbon atoms of the quinoline ring. The negative charge in the zwitterion form is localized primarily on the AO of the oxygen atom (Fig. 2).

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