QUANTUM-CHEMICAL INVESTIGATION OF THE π-ELECTRONIC STRUCTURE OF 3-HYDROXY-4-PHENYLAZOQUINOLINE AND 4-HYDROXY-3-PHENYLAZOISOQUINOLINE*

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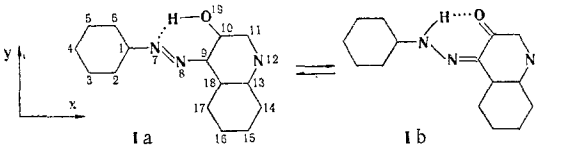
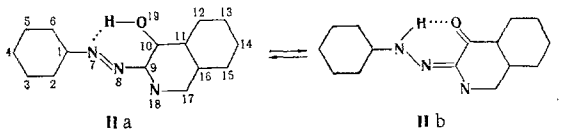
The total bond energies, the atomization energies, the molecular diagrams in the ground and first excited states, the interatomic distances in the ground state, and the electronic spectra of the azo and quinonehydrazone forms of 3-hydroxy-4-phenylazoquinoline and 4-hydroxy-3-phenylazoisoquinoline were calculated by the MO LCAO method within the Pariser–Parr–Pople approximation with the utilization of optimization of the internuclear distances with respect to the minimum of the atomization energy. It follows from an analysis of the ΔH values that the azo form in the first case is energetically more advantageous than the quinonehydrazone form, while the opposite is true in the second case. The calculated interatomic distances and bond orders of the tautomers correspond to those in the azo and quinonehydrazone structures. The absorption bands in the electronic spectra were assigned. The long-wave band in the absorption spectra of the quinonehydrazone tautomers is due primarily to charge transfer from the bridge-amino-nitrogen atom to the quinoid system.

3-Hydroxy-4-phenylazoquinoline (I) exists primarily in the azo form (Ia), while 4-hydroxy-3-phenylazoisoquinoline (II) exists primarily in the quinonehydrazone form (IIb).



Ia Ib



IIa IIb

An evaluation of the stabilities of the tautomers of I and II, obtaining of data on the electronic structures and the structures of the tautomers, and assignment of the absorption bands in the electronic spectra seem of interest. In order to achieve this, we performed a quantum-chemical calculation of the ground and excited states of the tautomers by the Pariser–Parr–Pople (PPP) method with introduction of the "approximation of the variable β" [2]. The interaction of 25 singly excited configurations was taken into account in the calculation of the spectra. The values of the orbital-ionization potentials (I), the one-center interelectronic repulsion integrals (γ) (for the calculation of the excited states), and the β-variation parameters

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TABLE 1. Energy Indexes of the Tautomeric Forms of I and II

Form	$E_{\pi b}$, eV	$E_{\sigma b}$, eV	E_b, eV	ΔH, eV	$\Delta H_{azo} - \Delta H_{qh}$, eV
Ia	32,571	74,241	106,812	155,626	0,468
Ib	32,214	74,367	106,581	155,158	
IIa	32,510	74,236	106,745	155,559	−0,191
IIb	32,785	74,389	107,174	155,750	

TABLE 2. Charges on the Atoms (q_r) of the Tautomeric Forms of I and II in the Ground (Ia, Ib, IIa, and IIb) and First Excited (Ia*, Ib*, IIa*, and IIb*) States

Atom	q_r							
	Ia	Ia*	Ib	Ib*	IIa	IIa*	IIb	IIb*
1	0,019	0,048	0,028	0,056	0,021	0,040	0,011	0,043
2	0,022	0,009	−0,046	0,040	0,021	0,005	−0,032	0,033
3	−0,001	0	0,002	0,010	−0,001	−0,002	0,003	0,010
4	0,013	0,008	−0,028	0,064	0,009	−0,004	−0,018	0,062
5	−0,002	0,002	0,003	0,014	−0,003	0	0,004	0,014
6	0,015	−0,009	−0,044	0,033	0,012	−0,018	−0,033	0,020
7	−0,083	−0,240	0,146	0,601	−0,092	−0,241	0,238	0,587
8	−0,070	−0,262	−0,165	−0,396	−0,063	−0,278	−0,149	−0,393
9	0,020	0,132	0,127	0,103	0,038	0,162	0,081	0,134
10	0,053	0,121	0,265	0,118	0,065	0,147	0,255	0,155
11	0,091	0,029	0,158	0,078	−0,002	−0,043	0,001	−0,044
12	−0,207	−0,221	−0,167	−0,249	0	0,032	0,045	0,034
13	0,050	0,056	0,034	0,025	0,008	0,006	0,018	0,002
14	0,002	0,037	0,014	0,006	0,004	−0,003	0,019	−0,005
15	0,003	0,044	0,017	0,019	0,011	0,046	0,016	0,022
16	0,001	−0,016	0,009	−0,011	−0,002	−0,047	−0,003	−0,041
17	0,002	0,066	0,025	0,035	0,109	0,209	0,166	0,114
18	0,002	−0,041	−0,025	−0,039	−0,206	−0,252	−0,218	−0,255
19	0,068	0,236	−0,349	−0,508	0,071	0,242	−0,403	−0,492

were taken from [3]. The I and γ values (for the calculation of the ground state) and the parameters for the determination of the σ-bond energies were taken from [4]. Optimization of the internuclear distances with respect to the minimum of the atomization energy (ΔH) was used in the calculations. The optimization was carried out with respect to a program that we composed that realizes the Dewar algorithm [4]. In the calculations it was assumed that all of the molecules are planar systems with angles between the bonds of close to 120°. The positive direction of the angle of rotation of the vector of the moment of the transition was selected as being clockwise from the x axis.

π-Electronic Structures

The position of the tautomeric equilibrium between forms Ia⇌Ib and IIa⇌IIb is determined by the energetic advantageousness of the corresponding forms. The bond energies of all forms should be compared in order to evaluate it [5]. Within the approximation of independence of the σ and π electrons, the bond energy (E_b) is represented in the form of the sum of the π-bond ($E_{\pi b}$) and σ-bond ($E_{\sigma b}$) energies, i.e., $E_b = E_{\pi b} + E_{\sigma b}$. A more correct value for evaluation of the energetic stability of the tautomers is the atomization energy ΔH [4]. The absolute values of all of the calculated energy values are presented in Table 1.

It follows from Table 1 that the E_b and ΔH values for the azo tautomer of I are larger than for the quinonehydrazone tautomer, while the relationship between E_b and ΔH is just the opposite of this for II. Consequently, the azo form of I is more favorable than the quinonehydrazone form, while the quinonehydrazone tautomer is more favorable for II. These conclusions are confirmed by the experimental data [1]. It should be noted that one cannot draw conclusions regarding the stability of the tautomers only from the π-bond or only from the σ-bond energies, inasmuch as the bond lengths of the tautomers differ markedly from one another, and an analysis only of these energies leads to conclusions that contradict the experimental results and the relationship between the E_b and ΔH values. The energetic advantageousness of form IIb as compared with IIa is probably due to the special position of the nitrogen atom in the ring.

Molecular Diagrams

It is apparent from the data on the bond lengths (R_{rs}) and orders (P_{rs}) and also from the charges on the atoms (q_{rs}) of the molecules (Tables 2-4) that a unified π-electron system of bonds is formed in the azo

TABLE 3. Bond Orders and Lengths (P_{rs} and R_{rs}) of the Tautomeric Forms of I in the Ground (Ia, Ib) and First Excited (Ia*, Ib*) States

Bond	P_{rs} (R_{rs})			
	Ia	Ia*	Ib	Ib*
1—2	0,612 (1,406)	0,546	0,631 (1,402)	0,513
1—6	0,609 (1,406)	0,546	0,631 (1,402)	0,515
1—7	0,386 (1,379)	0,496	0,316 (1,392)	0,563
2—3	0,677 (1,394)	0,699	0,674 (1,395)	0,710
3—4	0,661 (1,397)	0,637	0,662 (1,397)	0,626
4—5	0,656 (1,398)	0,633	0,662 (1,397)	0,624
5—6	0,683 (1,393)	0,703	0,674 (1,395)	0,711
7—8	0,834 (1,269)	0,562	0,207 (1,380)	0,336
8—9	0,409 (1,375)	0,559	0,850 (1,295)	0,638
9—10	0,663 (1,397)	0,430	0,282 (1,463)	0,396
9—18	0,489 (1,427)	0,460	0,340 (1,453)	0,434
10—11	0,549 (1,416)	0,540	0,299 (1,460)	0,412
10—19	0,264 (1,351)	0,476	0,847 (1,255)	0,683
11—12	0,740 (1,316)	0,707	0,871 (1,293)	0,786
12—13	0,520 (1,355)	0,480	0,378 (1,381)	0,423
13—14	0,523 (1,421)	0,554	0,613 (1,405)	0,601
13—18	0,561 (1,414)	0,555	0,591 (1,409)	0,551
14—15	0,757 (1,380)	0,707	0,684 (1,393)	0,690
15—16	0,569 (1,413)	0,595	0,645 (1,400)	0,625
16—17	0,751 (1,381)	0,706	0,679 (1,394)	0,697
17—18	0,539 (1,418)	0,549	0,625 (1,403)	0,580

TABLE 4. Bond Orders and Lengths (P_{rs} and R_{rs}) of the Tautomeric Forms of II in the Ground (IIa, IIb) and First Excited (IIa*, IIb*) States

Bond	P_{rs} (R_{rs})			
	IIa	IIa*	IIb	IIb*
1—2	0,613 (1,405)	0,542	0,631 (1,402)	0,517
1—6	0,610 (1,406)	0,541	0,631 (1,402)	0,518
1—7	0,389 (1,380)	0,503	0,308 (1,393)	0,551
2—3	0,677 (1,394)	0,702	0,675 (1,395)	0,713
3—4	0,661 (1,397)	0,624	0,662 (1,397)	0,620
4—5	0,656 (1,398)	0,630	0,662 (1,397)	0,629
5—6	0,682 (1,393)	0,705	0,674 (1,395)	0,714
7—8	0,835 (1,269)	0,563	0,365 (1,352)	0,373
8—9	0,405 (1,376)	0,541	0,797 (1,306)	0,614
9—10	0,667 (1,396)	0,428	0,321 (1,456)	0,377
9—18	0,503 (1,358)	0,493	0,385 (1,379)	0,476
10—11	0,506 (1,424)	0,498	0,330 (1,455)	0,392
10—19	0,271 (1,350)	0,493	0,815 (1,261)	0,713
11—12	0,535 (1,419)	0,542	0,624 (1,403)	0,604
11—16	0,567 (1,413)	0,533	0,508 (1,408)	0,552
12—13	0,750 (1,381)	0,728	0,680 (1,394)	0,690
13—14	0,575 (1,412)	0,575	0,644 (1,400)	0,623
14—15	0,748 (1,382)	0,716	0,687 (1,392)	0,698
15—16	0,542 (1,418)	0,562	0,612 (1,406)	0,588
16—17	0,495 (1,426)	0,462	0,376 (1,447)	0,442
17—18	0,768 (1,311)	0,731	0,842 (1,298)	0,741

forms of I and II due to conjugation of the azo group with the aromatic rings. It follows from a comparison of the P_{rs} values that the conjugation of the quinoline ring with the azo group is greater by a factor of 1.5 than the conjugation with the hydroxyl group. It should be noted that the P_{rs} and R_{rs} values in the rings are different. Thus, while all of the P_{rs} and R_{rs} values in the phenyl rings are approximately equal, the P_{rs} and R_{rs} values in the quinoline ring take on a slight quinoid character. In the first excited state ('B), the P_{C-N} and $P_{N=N}$ values are equalized, the negative charges on the nitrogen atoms of the azo group increase markedly, and the oxygen atoms acquire an additional positive charge. This attests to the participation in the $^1A \rightarrow {}^1B$ transition of charge transfer from the oxygen atom in the π-conjugated system primarily to the azo group, during which the quinoid character of the phenyl rings also increases, while the π bonds in the quinoline ring become more delocalized. Because of redistribution of the charges on the atoms during the $^1A \rightarrow {}^1B$ transition, the π dipole moments (μ_π) increase markedly, and their direction changes.

The $P_{C=N}$ and $P_{C=O}$ values in the ground state of the quinonehydrazone form of Ib and IIb, like the $R_{C=N}$ and $R_{C=O}$ values, attest to considerable multiplicity of these bonds. The orders of the C—C and C—N bonds adjacent to C=O and C=N have depressed values (0.282-0.385). The P_{rs} and R_{rs} values of all of the bonds in the benzene rings of Ib and IIb are approximately equal, and this attests to a considerable degree of delocalization of the π bonds. The charges on the atoms of the bridge-amine-nitrogen atom are

TABLE 5. π Dipole Moments (μ_π) and Their Directions ($\varphi°$) for the Tautomeric Forms of I and II in the Ground (Ia, Ib, IIa, and IIb) and First Excited (Ia*, Ib*, IIa*, and IIb*) States

Form	Ia	Ia*	Ib	Ib*	IIa	IIa*	IIb	IIb*
μ_π	1,570	2,189	3,187	10,196	1,986	6,568	3,568	7,071
$\varphi°$	41	161	219	177	125	185	196	5

TABLE 6. Calculated Characteristics of the Electron Transitions of the Tautomeric Forms of I and II: Wavelengths (λ), Oscillator Forces (f), Polarizations ($\varphi°$), and Eigenvector of the Configurational Interaction Matrix (CIM)

Compound	State	λ, Å	f	$\varphi°$	CIM eigenvector		
Ia	$'B$	4156	0,85	185	0,98(10—11)		
	$'G+$	3288	0,33	55	0,91 (9—11)	+0,29(10—13)	+0,19(9—12)
	$'C-$	2924	0,11	11	0,91 (8—11)	−0,21 (9—11)	−0,14(7—11)
		2533	0,23	260	0,53(10—13)	−0,50(10—12)	+0,46(9—12)
	$'G-$	2298	0,17	269	0,69(10—14)	−0,51 (7—11)	−0,35(8—14)
	$'G-$	2188	1,10	75	0,69(10—13)	−0,64 ((9—12)	−0,17(6—13)
Ib	$'B$	4988	0,52	6	0,98(10—11)	−0,12(10—12)	
	$'C$	3560	0,22	277	0,98 (9—11)		
	$'C+$	2812	0,43	234	0,85(10—12)	+0,36 (7—11)	+0,18(9—12)
	$'G+$	2605	0,13	267	0,75(10—14)	+0,52 (8—11)	+0,33(8—15)
		2243	0,37	241	0,77(10—13)	−0,35 (7—12)	+0,33(9—12)
	$'(CH)-$	2190	0,20	208	0,78(10—15)	−0,44 (6—11)	−0,30(8—14)
IIa	$'B$	4147	1,05	177	0,98(10—11)	−0,11(10—12)	
	$'(CG)-$	2796	0,61	212	0,74 (9—11)	−0,41(10—12)	−0,31(7—12)
	$'G+$	2206	0,28	270	0,80(10—14)	+0,48 (8—11)	+0,28(9—14)
	$'(GC)$	2161	0,10	150	0,56 (9—12)	−0,49 (7—12)	+0,42(6—11)
IIb	$'B$	4623	0,89	180	0,98(10—11)	+0,12(10—13)	
	$'(GC)$	2711	0,15	219	0,82(10—12)	−0,42 (7—11)	+0,20 (8—11)
	$'G-$	2579	0,11	265	0,70 (9—11)	−0,62(10—14)	−0,30 (9—15)
	$'(CG)$	2494	0,61	193	0,77(10—13)	+0,31(10—15)	−0,30 (7—11)
	$'(GH)$	2244	0,37	155	0,52 (8—12)	−0,44 (7—12)	+0,36(10—13)
		2107	0,16	73	0,75 (7—12)	+0,34 (8—12)	+0,32(10—15)

0.146 and 0.238, respectively, for forms Ib and IIb. The positive charge on this nitrogen atom in the first excited state ('B) increases by a factor of 2.5 for Ib and by a factor of 1.6 for IIb. This leads to an increase in μ_π from 3.187 to 10.196 D for Ib and from 3.568 to 7.071 D for IIb (Table 5). Moreover, the μ_π directions change by almost 180°. Consequently, during the $'A \rightarrow {}'B$ transition there is pronounced charge transfer from the bride-amine-nitrogen atom to the π-conjugated system of the molecule. The quinoid character of the phenyl rings increases, while the quinoid character of the quinoline rings decreases. The decrease in $P_{C=O}$ and the increase in P_{C-N} in the first excited state attests to an increase in the conjugation of the bridge amine nitrogen atom with the benzene ring.

Assignment of the $\pi \rightarrow \pi^*$ Absorption Bands

The absorption bands in the electronic spectra of the investigated compounds were assigned with allowance for the following data: the agreement between the calculated characteristics and the experimental values, the type of orbitals between which the electron transition, determined from the coefficients of expansion of the MO with respect to the AO, is realized, allowance for the configurational interaction, the magnitude and the direction of the shift of the π-electron density during transition of the molecule to the excited state, localization of the electron transition within the limit of certain fragments of the molecule, and the direction (polarization) and intensity (oscillator force) of the transition.

According to the literature data [6], the long-wave absorption bands in the electronic spectra of azo compounds can be classified as $S_{n\pi}$ and $S_{\pi\pi^*}$ transitions. The $S_{n\pi^*}$ bands are of low intensity and are frequently overlapped by the more intense bands of the $S_{\pi\pi^*}$ transitions. Considering the structural peculiarities of the molecule, the $S_{\pi\pi^*}$ transitions can be divided into several series according to the classification in [7, 8]: a band associated with the long-wave transitions over the entire π-conjugated system – $'A \rightarrow {}'B$ ($S_{\bar{\pi}\text{-}\pi^*}$ or $S_{2p_z\pi^*}$), bands associated with the remaining transitions over the entire π system – $'A \rightarrow {}'C$ ($S_{\pi\pi^*}$), bands associated with transitions localized in the aromatic rings – $'A' \rightarrow H$ ($S_{\Phi\Phi^*}$), and bands associated with transi-

tions between the MO of the entire π-conjugated system of the molecule and the MO of the aromatic rings – $^1A \rightarrow {}^1G$ ($S_{\pi\Phi^*}$ and $S_{\Phi\pi^*}$).

The calculated λ_{max} values of the intensities and polarizations of the absorption bands are in satisfactory agreement with the experimental values [1]. This attests to a reliable selection of the computational parameters. The characteristics of the most intense absorption bands related to the transitions with an oscillator force of no less than 0.10 are presented in Table 6.

The long-wave band in the spectrum of the azo form of I at 432 nm is related to the $^1A \rightarrow {}^1B$ transition with a small amount of participation of charge transfer (~9%) of the unshared pair of electrons of the oxygen atom to the π system. According to the calculations, this band is due (96%) to transition from the upper occupied π MO (π_{UOMO}) to the lower vacant π^* MO (π^*_{LVMO}), and the transition is polarized along the x axis. The calculated wavelength of this band (λ_{max} 416 nm) is somewhat lower than the experimental value (432 nm). This can be explained by the effect of the intramolecular hydrogen bond (IHB), which was not taken into account in the calculations. The band at 326 nm is related to the $^1A \rightarrow {}^1G$ transition consisting (to the extent of 83%) of transition between the π MO of the quinoline system and the π MO of the entire system of the molecule. The oscillator forces of both transitions are in satisfactory agreement with the experimental values ($f_{theor}/f_{exp} = 3.7\text{-}3.9$).

According to the calculations, the quinonehydrazone form of I is characterized by a long-wave band at 499 nm, which is related to the $^1A \rightarrow {}^1B$ transition polarized along the x axis. It follows from an analysis of the coefficients of expansion of the MO with respect to the AO that this band is due to an $S_{2p_z\pi^*}$ transition from π_{UOMO} to π^*_{LVMO}. The $2p_z$-AO of the bridge-amine-nitrogen atom makes the greatest contribution (29%) to π_{UOMO}. The second intense band at 356 nm is related to the $^1A \rightarrow {}^1C$ transition. The remaining bands that characterize both tautomers of I are presented in Table 6.

It is known [1] that II exists primarily in the form of the quinonehydrazone tautomer. Correlation of the calculated and experimental spectra of the azo form of II is therefore difficult. According to the calculations, the long-wave band that characterizes the azo form of II should appear at 415 nm. It is related to the $^1A \rightarrow {}^1B$ transition from π_{UOMO} to π^*_{LVMO} ($S_{\pi\pi^*}$) polarized along the x axis. Taking the IHB into account, it can be assumed that this band should undergo a bathochromic shift of 15-20 nm; this is confirmed by expansion of the electronic absorption spectra of II into Gaussian components [1].

The spectrum of the quinonehydrazone form of II is of greatest interest. The calculated spectrum of this form is characterized by the long-wave band of the $^1A \rightarrow {}^1B$ transition polarized along the x axis. The band at 462 nm is due primarily to transition from π_{UOMO} to π^*_{LVMO}. Inasmuch as 29% of π_{UOMO} consists of the $2p_z$ AO of the bridge-amine-nitrogen atom and a pronounced shift of the electron density from this nitrogen atom to the quinoline ring occurs during this transition, it can be classified as an $S_{2p_z\pi^*}$ transition with charge transfer from the bridge-amine-nitrogen atom primarily to the π system of the quinoline ring. The remaining intense bands are caused by a shift of the $^1A \rightarrow {}^1G$ and $^1A \rightarrow {}^1C$ transitions with alternating predominance of one or another excited state (Table 6).

LITERATURE CITED

1. B. E. Zaitsev and T. A. Mikhailova, Khim. Geterotsikl. Soedin., 812 (1974).
2. V. P. Zvolinskii (Zvolinsky), G. I. Kagan, G. M. Kagan, M. E. Perel'son (Perelson), and Ju. N. Sheinker, Summaries of the Theory of Electronic Shells of Atoms and Molecules, Vilnius (1969), p. 44.
3. K. Nishimoto and L. S. Forster, Theor. Chim. Acta, 4, 155 (1966).
4. M. Dewar, Molecular Orbital Theory of Organic Chemistry, McGraw-Hill (1969).
5. V. A. Kosobutskii, G. I. Kagan, V. K. Belyakov, and O. G. Tarakanov, Zh. Strukt. Khim., 12, 822 (1971).
6. R. N. Nurmukhametov, Absorption and Luminescence of Aromatic Compounds [in Russian], Khimiya, Moscow (1971).
7. J. R. Platte, J. Chem. Phys., 18, 1168 (1950).
8. J. R. Platte, J. Opt. Soc., Amer., 43, 252 (1953).