π-ELECTRON STRUCTURES AND REACTIVITIES OF 2,3- AND 2,5-DIHYDROXYPYRIDINES

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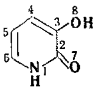
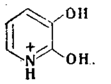
The π-electron structures and reactivities of 2,3- and 2,5-dihydroxypyridines in neutral, acidic, and alkaline media were investigated by the Hückel MO method. Satisfactory correlations of the indexes of the π-electron structures with the reactivities and other properties of these molecules were obtained.

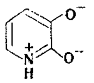
It has been shown [1] by UV and IR spectroscopic methods that 2,3- and 2,5-dihydroxypyridines exist in forms Ia, IIa, Ib, IIb, Ic, and IIc, respectively, in neutral, acidic, and alkaline media:



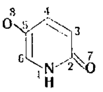
Ia



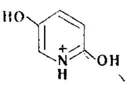
Ib



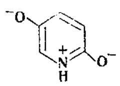
Ic



IIa



IIb



IIc

The electronic structures and reactivities of I and II have not been studied by quantum-chemical methods. The aim of the present study was to obtain indexes of the π-electron structures and to correlate them with the reactivities and other properties of I and II.

The calculations were performed by the Hückel MO LCAO method [2] with the parameters presented in Table 1.

It follows from the total π-electron energies (E_π), delocalization energies (ED_π), and delocalization energies per π electron (ED_π/n) presented in Table 2 that forms Ia and IIa are the most stable.

It is usually assumed [2, 3] that the long-wave $\pi \rightarrow \pi^*$ band in the electronic spectra of molecules is associated with the transition (ΔE) of a π electron from an upper occupied molecular orbital (E_{UOMO}) to a lower vacant MO (E_{LVMO}). The λ_{max} values calculated from the ΔE values for the long-wave $\pi \rightarrow \pi^*$ band from the formula [3]

TABLE 1. Parameters for the Calculation of 2,3- and 2,5-Dihydroxypyridines by the Hückel MO Method

Compound and its form	Coulombic			Resonance			
	h_1	h_7	h_8	k_{C-C}	k_{C-N}	$k_{3,8}$	$k_{2,7}$
Ia	0,27	1,6	2,0	1	1	0,64	2,50
Ib	0,34	2,0	2,0	1	1	0,60	0,60
Ic	0,34	1,2	1,2	1	1	0,50	0,50
IIa	0,27	1,6	2,0	1	1	0,64	2,50
IIb	0,34	2,0	2,0	1	1	0,80	0,80
IIc	0,34	1,2	1,2	1	1	0,72	0,72

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TABLE 2. Energy Characteristics of 2,3- and 2,5-Dihydroxypyridines

Compound and its form	E_{UOMO}, β_0	E_{LVMO}, β_0	$-\Delta E\times\beta_0$	Calc. λ_{max}, nm	Exptl. λ_{max}, nm	Calc. J, eV	$E_\pi\times\beta_0$	$ED_\pi\times\beta_0$	$\frac{ED_\pi}{n}\times\beta_0$
Ia	0,265	−0,973	1,238	308	300	−8,75[1]	17,730	3,950	0,395
Ib	0,836	−0,913	1,749	290	290	−8,84	16,588	2,188	0,219
Ic	0,719	−0,912	1,631	310	310	−8,56	13,370	2,170	0,217
IIa	0,265	−0,937	1,202	320	330	−8,800[1]	17,726	3,946	0,395
IIb	0,715	−0,909	1,624	313	313	−8,55	16,762	2,362	0,236
IIc	0,552	−0,912	1,462	347	347	−8,15	13,188	1,988	0,199

TABLE 3. Electronic Characteristics and Bond Lengths for Three Forms of 2,3- and 2,5-Dihydroxypyridines

Compound and its form	Atom No.	q_r	Bond r−s	p_{rs}	Calculated r_{rs}, Å	Compound and its form	Atom No.	q_r	Bond r−s	p_{rs}	Calculated r_{rs}, Å
Ia	1	1,372	1—2	0,430	1,372	IIa	1	1,363	1—2	0,427	1,372
	2	0,821	1—6	0,663	1,330		2	0,821	1—6	0,667	1,329
	3	1,167	2—3	0,404	1,442		3	1,218	2—3	0,417	1,440
	4	1,014	3—4	0,743	1,382		4	0,993	3—4	0,731	1,385
	5	1,192	4—5	0,594	1,408		5	1,155	4—5	0,608	1,402
	6	0,964	5—6	0,672	1,395		6	0,971	5—6	0,659	1,397
	7	1,501	2—7	0,760	1,270		7	1,505	2—7	0,759	1,270
	8	1,969	3—8	0,158	1,369		8	1,973	3—8	0,150	1,370
Ib	1	1,157	1—2	0,651	1,332	IIb	1	1,173	1—2	0,639	1,334
	2	0,943	1—6	0,657	1,331		2	0,932	1—6	0,658	1,331
	3	0,998	2—3	0,641	1,400		3	1,039	2—3	0,641	1,400
	4	0,989	3—4	0,661	1,397		4	1,004	3—4	0,676	1,393
	5	1,018	4—5	0,663	1,396		5	0,985	4—5	0,641	1,400
	6	0,963	5—6	0,669	1,395		6	0,985	5—6	0,651	1,398
	7	1,967	2—7	0,180	1,366		7	1,938	2—7	0,256	1,353
	8	1,964	3—8	0,194	1,363		8	1,943	3—8	0,238	1,356
Ic	1	1,158	1—2	0,649	1,333	IIc	1	1,180	1—2	0,630	1,336
	2	0,950	1—6	0,657	1,331		2	0,945	1—6	0,659	1,331
	3	1,004	2—3	0,637	1,400		3	1,044	2—3	0,632	1,402
	4	0,990	3—4	0,660	1,397		4	1,009	3—4	0,679	1,394
	5	1,020	4—5	0,663	1,396		5	0,996	4—5	0,633	1,402
	6	0,964	5—6	0,668	1,395		6	0,990	5—6	0,644	1,400
	7	1,955	2—7	0,214	1,360		7	1,914	2—7	0,299	1,345
	8	1,960	3—8	0,198	1,362		8	1,922	3—8	0,277	1,349

$$\Delta E = E_{LVMO} - E_{UOMO} = \frac{28.635\cdot10^3}{\lambda\ (\mathrm{nm})}\left(\frac{\mathrm{kcal}}{\mathrm{mole}}\right) = \frac{1241}{\lambda\ (\mathrm{nm})}\left(\frac{\mathrm{eV}}{\mathrm{mole}}\right)$$

for $\beta_0 = -2.445$ eV for forms Ib, Ic, IIb, and IIc and for an average $\beta_0 = -3.240$ eV for forms Ia and IIa lead to the experimental λ_{max} values [1] for this band.

The calculated ionization potentials (Table 2) from the E_{UOMO} values for forms Ib, Ic, and IIc are close to the ionization potential of phenol (I=−8.50 eV) [4]. However, it is assumed that identification of −I with the UOMO energy is valid only for MO in the SCF method. In [1], we calculated the E_{UOMO} values for forms Ia and IIa by the MO method within the Pariser−Parr−Pople (PPP) approximation. The I values obtained from these values for Ia and IIa (Table 2) are also close to I for phenol.

It is seen from Table 3 that the values of the effective π-electron charges ($Q_N^{\cdot} \approx +0.632$ and $Q_O^{\cdot} \approx -0.503$) in forms Ia and IIa are in good agreement with the experimental data: the high value of the intensity of the absorption band of the C=O group in α-pyridones [1, 5] and the dipole moment of α-pyridone, which is equal to 1.73 D [6]. The high value of the positive charge on the cyclic nitrogen atom of the pyrrole type attests to the participation of the unshared pair of electrons in the overall π-electron system. Moreover, the π-electron density is markedly shifted to the pyridone C=O group. The positive charge on the oxygen atom in the 3 and 5 positions attests to the conjugation of these atoms with the ring. The uneven distribution of the π-electron density (q_r) in the heterorings is due to the effect of the nitrogen and oxygen atoms (Table 2).

The bond lengths (r_{rs}) calculated from the bond orders (p_{rs}) from the formulas in [7] are in agreement with the known experimental data for 2-pyridone, pyridine, and phenol [8]. It follows from a compari-

TABLE 4. Reactivity Indexes for Three Forms of 2,3- and 2,5-Dihydroxypyridines

Compound and its form	Atom No., r	Q_r	f_r^+	f_r^-	f_r^0	F_r	L_r^+	L_r^-	L_r^0
Ia	4	−0,014	0,004	0,225	0,114	0,398	2,594	2,502	2,548
	5	−0,192	0,260	0,003	0,131	0,469	3,087	1,858	2,472
	6	+0,036	0,040	0,280	0,160	0,400	2,488	2,426	2,457
Ib	4	+0,011	0,010	0,313	0,161	0,411	2,556	2,462	2,509
	5	−0,018	0,174	0,052	0,113	0,403	2,586	2,470	2,528
	6	+0,037	0,206	0,124	0,165	0,409	2,546	2,454	2,500
Ic	4	+0,010	0,108	0,315	0,166	0,412	2,530	2,468	2,504
	5	−0,020	0,114	0,052	0,083	0,404	2,584	2,454	2,519
	6	+0,036	0,142	0,124	0,133	0,410	2,520	2,450	2,485
IIa	3	−0,218	0,255	0,255	0,255	0,587	2,520	1,652	2,086
	4	+0,007	0,038	0,250	0,144	0,396	1,574	1,534	1,554
	6	+0,029	0,040	0,280	0,160	0,409	1,454	1,394	1,424
IIb	3	−0,039	0,114	0,164	0,139	0,418	2,576	2,384	2,480
	4	−0,004	0,049	0,290	0,170	0,418	2,500	2,488	2,494
	6	+0,015	0,142	0,230	0,186	0,426	2,446	2,438	2,442
IIc	3	−0,044	0,084	0,167	0,125	0,424	2,246	2,166	2,206
	4	−0,009	0,049	0,290	0,169	0,423	2,076	2,024	2,050
	6	+0,010	0,112	0,235	0,173	0,432	1,974	1,930	1,952

son of the calculated r_{rs} values for the forms of I and II that hydroxyl groups have a slight effect on the change in the bond length in the heterocycle, while the carbonyl group markedly alters them.

According to the experimental data, aromatic substitution in alkaline media in I is directed initially to the 6 position and then to the 4 position [9], while the 6 position is the most reactive one in II [10]. The electrophilic reactions of I and II, which proceed in acidic media, are directed to the 6 position [11].

It is apparent from Table 4 that the calculated π-electron charges (Q_r) for the reactive centers of forms Ib, Ic, IIb, and IIc prove to be unsuitable to explain the electrophilic substitution in acid and alkaline media. However, the calculated localization energies (L_r^+) for forms Ib, Ic, IIb, and IIc are in agreement with the experimentally observed sequence of electrophilic substitution in I and II in acid and alkaline media. The values that we obtained for the boundary electron densities (f_r^+) are also in agreement with the experimental data on electrophilic substitution. The L_r^+ values for forms Ia and IIa indicate the same sequence of electrophilic substitution as for forms Ib and Ic and IIb and IIc, respectively.

It is known [2] that when one examines the reactivity in the MO method, the q_r or Q_r values characterize the occurrence of substitution reactions through the intermediate π complex, in which the π-electron density does not undergo significant changes; however, the localization energies (L_r^+) characterize the occurrence of substitution reactions through an intermediate σ complex, in which the change in the π-electron density is considerable. Since the L_r^+ values are in complete agreement with experiment while the Q_r values are not in agreement in I and II, there is some basis to assume that substitution in acid and alkaline media proceeds through the formation of an intermediate σ complex.

There is no information in the literature regarding the nucleophilic and radical substitution reactions in I and II. The reactivity indexes for nucleophilic substitution (Q_r, f_r^-, and L_r^-) and radical substitution (f_r^0, the free valence index F_r [2, 3], and L_r^0) were calculated for the reaction centers of the heterorings of all forms of I and II and are presented in Table 4.

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