π-ELECTRON STRUCTURE, REACTIVITY, AND ABSORPTION SPECTRA OF ANTHRAPYRIDONE*

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The π-electronic spectra, heats of atomization, and electronic indexes of the lactam and lactim forms of anthrapyridone were calculated by the Pariser–Parr–Pople method with allowance for 25 one-electron configurations. An examination of the π-bond orders and the charges on the atoms showed that a system with a π-electron distribution close to the distribution in anthraquinone and in α-pyridone for the lactam tautometer and in α-hydroxypyridine and anthraquinone for the lactim form is formed in the lactam and lactim of anthrapyridone. The electronic absorption bands were assigned. An analysis of the calculated values demonstrated that the long-wave band in the spectrum of the anthrapyridone is due to charge transfer from the amide group to the ketone group. The reactivity and localization energy indexes of aromatic substitution reactions calculated by the Hückel MO method are in satisfactory agreement with the experimental data.

It has been shown [1] that, of the two possible forms – lactam and lactim – anthrapyridone exists primarily in the lactam form in solution. The electronic structure and the abosrption spectra of these tautomers have not been studied. Some bands of these forms were presented in [1]. 2-Methoxyanthrapyridine was selected as a model of the lactim form. This was done because the percentage of the lactim form in solution is so low that one cannot record its electronic spectrum. Replacement of the hydroxyl group by a methoxy group does not lead to substantial changes in the electronic spectra. The present paper is devoted to a study of the electronic structures and absorption spectra of the tautomers of the lactam and lactim forms by the Pariser-Parr-Pople (PPP) method. The calculation was made with allowance for the interaction of 25 one-electron configurations by the method in [2]. The reactivity indexes were calculated by the Hückel MO method. The heats of atomization were calculated with a program that we worked out with realization of the Dewar algorithm.

π-Electronic Structures

The relative stabilities of the lactam and lactim forms can be estimated from the heats of atomization (ΔH) and, in special cases, from the $E_{\sigma b}$- and $E_{\pi b}$-bond energies. It is seen from Table 1 that the lactim form is somewhat more favorable than the lactam form with respect to the atomization energies. On the other hand, according to the experimental data, the lactam form is more favorable [1]. The bond energies of the two tautomers are approximately identical. The contradictory conclusions regarding the stabilities of the tautomers with respect to the experimental and calculated values can be explained as follows. The calculations were made for the gas phase without allowance for the intermolecular interactions. The experimental data were obtained from solutions or from crystals, in which hydrogen bonds and the other intermolecular interactions may lead to a shift in the equilibrium [3]. The experimental data on α-pyridone, according to which α-pyridone exists in the lactim form in the gas phase but in the lactam form in the crystalline state and in solution [4], constitute a confirmation of this explanation.

TABLE 1. Energy Characteristics of Anthrapyridone Tautomers

Molecule	$E_{\pi b}$, eV	$E_{\sigma b}$, eV	ΔH, eV
I	28,55	81,25	149,50
II	28,49	81,26	149,68

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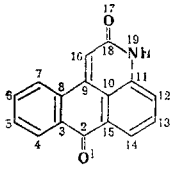
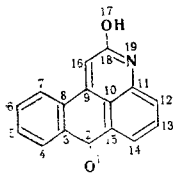
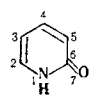
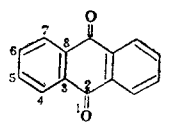
TABLE 2. π-Electron Characteristics and Bond Lengths

Compound	Atom No.	Charge (Q_i) ground state	Charge (Q_i) excited state	Bond	Ground state bond order, P_{rs}	Ground state bond length, Å	Excited state bond order
	1	−0,406	−0,500	1—2	0,834	1,257	0,741
	2	0,284	0,205	2—3	0,303	1,459	0,354
	3	−0,017	−0,041	2—15	0,299	1,460	0,387
	4	0,046	0,040	3—4	0,643	1,400	0,626
	5	0,010	−0,009	3—8	0,599	1,408	0,574
	6	0,022	0,010	4—5	0,664	1,396	0,678
	7	0,010	−0,006	5—6	0,661	1,397	0,645
	8	0,007	−0,024	6—7	0,666	1,396	0,682
	9	0,042	−0,051	7—8	0,638	1,401	0,616
	10	−0,027	0,033	8—9	0,323	1,456	0,371
	11	0,014	0,033	9—10	0,368	1,448	0,495
	12	−0,007	−0,067	9—16	0,823	1,369	0,660
	13	0,018	0,006	10—11	0,615	1,405	0,446
	14	0,040	0,125	10—15	0,578	1,411	0,520
	15	−0,012	−0,075	11—12	0,617	1,405	0,540
	16	0,002	−0,076	11—19	0,303	1,394	0,545
	17	−0,476	−0,340	12—13	0,688	1,392	0,660
	18	0,251	0,152	13—14	0,640	1,401	0,579
	19	0,200	0,590	14—15	0,662	1,397	0,599
				16—18	0,357	1,450	0,418
				17—18	0,789	1,265	0,121
				18—19	0,382	1,380	0,466
	1	−0,413	−0,485	1—2	0,827	1,258	0,745
	2	0,282	0,200	2—3	0,302	1,459	0,356
	3	−0,014	−0,041	2—15	0,312	1,458	0,374
	4	0,044	0,050	3—4	0,639	1,401	0,632
	5	0,005	0,021	3—8	0,602	1,407	0,544
	6	0,017	−0,006	4—5	0,668	1,396	0,657
	7	0,001	0,017	5—6	0,658	1,397	0,625
	8	0,007	−0,002	6—7	0,671	1,395	0,692
	9	0,044	−0,012	7—8	0,635	1,401	0,582
	10	−0,016	0,017	8—9	0,322	1,456	0,412
	11	0,069	0,142	9—10	0,499	1,425	0,451
	12	0,021	−0,034	9—16	0,721	1,386	0,638
	13	0,007	−0,009	10—11	0,569	1,413	0,420
	14	0,052	0,131	10—15	0,515	1,422	0,555
	15	−0,024	−0,054	11—12	0,521	1,421	0,498
	16	−0,028	−0,147	11—19	0,514	1,356	0,574
	17	0,061	0,195	12—13	0,750	1,381	0,701
	18	0,151	0,191	13—14	0,579	1,411	0,564
	19	−0,270	−0,272	14—15	0,707	1,389	0,687
				16—18	0,547	1,417	0,525
				17—18	0,263	1,351	0,452
				18—19	0,708	1,322	0,547
	1	0,387	0,424	1—2	0,476	—	0,427
	2	0,005	−0,148	1—6	0,460	—	0,399
	3	−0,063	0,096	2—3	0,797	—	0,562
	4	0,044	−0,174	3—4	0,499	—	0,632
	5	−0,020	−0,127	4—5	0,817	—	0,496
	6	0,183	0,151	5—6	0,412	—	0,466
	7	−0,535	−0,221	6—7	0,730	—	0,717
	1	−0,408	−0,533	1—2	0,834	—	0,707
	2	0,293	0,165	2—3	0,298	—	0,384
	3	−0,009	0,058				
	4	0,045	0,027				
	5	0,021	0,099				
	6	0,021	0,099				
	7	0,045	0,027				
	8	−0,009	0,058				

It is seen from the P_{rs} and Q_i values that the distribution of the electron density in the ketone and amide groups and in the adjacent C=C bonds in the anthrapyridone molecule is close to the π distribution in the corresponding bonds of anthraquinone and α-pyridone (Table 2). The distribution of the electron density and of the charges in the heteroring of the molecule of the lactim form is close to that in pyridine.

Pronounced redistribution of the electron density occurs in the first excited state. The π-dipole moment of the molecule in the excited state ($\mu = 9.88$) is almost double the dipole moment ($\mu = 5.61$) in the ground state. The bond orders in the rings are equalized to a considerable degree due to a shift in the electron density from the pyridone or pyridol rings towards the ketone group. A large positive charge (+0.125, Table 2) appears on the carbon atom in the 6 position (Table 3). Consequently, this position should undergo nucleophilic attack.

TABLE 3. Reactivity Indexes

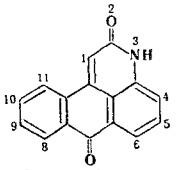
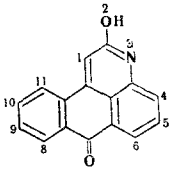
Compound	Position of atom	L_E	L_N	L_R	f_E	f_N	F_r
Anthrapyridone 	1	1,816	1,900	1,858	0,162	0,159	0,543
	4	2,281	2,295	2,288	0,025	0,086	0,449
	5	2,343	2,515	2,464	0,034	0,037	0,401
	6	2,328	2,343	2,335	0,079	0,052	0,436
	8	2,361	2,541	2,451	0,007	0,016	0,226
	9	2,386	2,483	2,435	0,013	0,029	0,205
	10	2,408	2,587	2,497	0,002	0,034	0,404
	11	2,330	2,415	2,370	0,007	0,010	0,425
2-Hydroxyanthrapyridine 	1	1,968	2,137	2,052	0,023	0,109	0,481
	4	2,110	2,355	2,232	0,150	0,102	0,460
	5	2,445	2,543	2,494	0,011	0,027	0,402
	6	2,173	2,483	2,328	0,118	0,082	0,386
	8	2,340	2,550	2,446	0,013	0,011	0,423
	9	2,383	2,467	2,425	0,049	0,037	0,405
	10	2,410	2,587	2,498	0,002	0,035	0,403
	11	2,320	2,405	2,363	0,013	0,013	0,425

TABLE 4. Calculated and Experimental Electronic Spectra of the Lactim Form of Anthrapyridone

Band	Calc. ΔE value, λ_{max}, nm	Exptl. ΔE value, λ_{max}, nm	Calc. oscillator force, f	Exptl. intensity, log ε	Polarization, $\angle y\mu$	Weights of the excited configurations
I	397,3	390	0,211	3,742	134°	81,0 (10—11); 6,2 (9—11)
II	347,1	347	0,341	4,122	4	68,8 (9—11); 10,2 (8—11); 4,8 (10—11)
III	315,4	—	0,100		168	62,4 (8—11); 10,2 (7—11); 8,4 (9—11); 4,8 (9—12)
IV	308,3	308,3	0,553	3,989	224	68,9 (7—11); 10,2 (10—12); 6,8 (9—11); 4,0 (9—12)
V	265,3		0,708		6	32,4 (10—13); 22,9 (10—12); 8,4 (9—13); 7,3 (10—11)
VI	261,0	261,0	0,586	4.062	79	17,7 (10—13); 16,6 (9—12); 16,6 (9—13); 15,0 (8—11); 13,8 (10—14)
VII	252,9	252,9	0,045	4,057	24	33,6 (10—13); 21,2 (9—12); 11,8 (10—12); 6,80 (9—13)
VIII	246,9	246,9	0,145	4,136	352	31,2 (10—14); 22,2 (9—12); 15,2 (9—12); 13,9 (9—14)
IX	239,7		0,104		312	28,1 (9—14); 29,6 (10—14); 6,1 (8—12)
X	230,9		0,642		122	5,8 (7—12); 5,6 (10—14); 4,5 (8—12); 4,5 (8—13); 45,0 (6—11); 8,9 (9—12); 10,5 (9—13)
XI	221,9		0,165		24	25,0 (9—14); 15,3 (7—12); 27,0 (8—12); 10,0 (9—13)
XII	214,8		0,162		56	11,0 (7—12); 5,5 (9—13); 7.4 (7—13); 58,8 (10—15)
XIII	212,0		0,677		115	6,6 (9—14); 5,9 (7—13); 13,6 (7—9); 11,0 (10—15); 11,5 (8—13); 28,8 (8—14)

Aromatic Substitution Reactions

According to the experimental data, anthrapyridone readily undergoes nucleophilic substitution reactions (1 position > 6 position > 4 position) and electrophilic substitutions (1 position > 6 position) [5, 6].

In examining the reactivities by the MO method within the π-electron approximation, one usually proceeds from reactions occurring through the formation of intermediate π and σ complexes. In the first case, it is assumed that electrophilic (f_E) attack is directed to the atom with the maximum π-electron density, while nucleophilic (f_N) attack is directed to the atom with the minimum π-electron density. However a more correct approach is a discussion of the principles of the orientations of aromatic substitution proceeding from the limiting electron densities [7]. It is seen from an examination of the electron densities in the 1, 4, 5, and 6 positions (Table 3) that their values are not in agreement with the experimental order of aromatic substitution. It follows from the calculated values of the limiting densities (f_E and f_N) for the

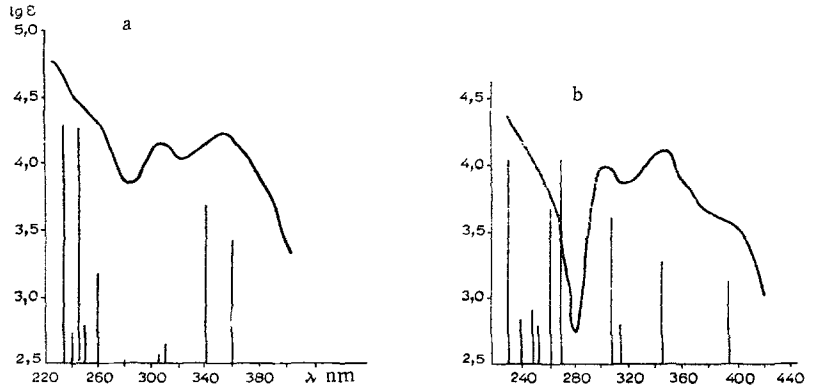


Fig. 1. Experimental and calculated electronic spectra of 50% ethanol solutions: a) lactim form of anthrapyridone (2-methoxyanthrapyridine); b) lactam form of anthrapyridone (anthrapyridone).

TABLE 5. Calculated and Experimental Electronic Spectrum of the Lactim Form of Anthrapyridone

Band	λ_{max}, nm: Calc. ΔE value	λ_{max}, nm: Exptl. ΔE value	Calc. oscillator force, f	Exptl. intensity, log ε	Polarization, ∠yi	Weight of the excited configuration
I	368,6	351	0,290	4,47	268°	68,0 (10—11); 6,0 (8—11); 4 (10—14); 23,0 (9—11)
II	339,2	—	0,399	—	33	30,0 (10—11); 8,1 (10—14); 49,8 (9—11)
III	307,4	311	0,051	4,28	341	7,0 (10—12); 62,2 (8—11); 13,3 (7—11)
IV	305,0	—	0,031	—	49	8,8 (10—12); 23,8 (8—11); 8,0 (8—12); 42,0 (7—11)
V	256,5	—	0,245	—	108	57,1 (10—12); 6,0 (9—12); 10,0 (7—11)
VI	248,4	—	0,080	—	192	13,0 (10—12); 35,0 (10—13); 25,0 (9—12)
VII	246,1	—	0,629	—	325	19,0 (10—13); 31,0 (10—14); 18,0 (9—11); 18,0 (9—12)
VIII	240,8	—	0,095	—	331	6,0 (7—12); 5,0 (9—15); 12,0 (10—13); 9,0 (10—14); 9,0 (8—12); 21,0 (6—11)
IX	233,0	—	0,627	—	229	20,0 (9—14); 8,0 (10—13); 16,0 (10—14); 28,0 (8—12); 9,0 (10—15)

lactam form that the most reactive site for electrophilic and nucleophilic substitution reactions is the 1 position [1], followed by the 6 position for electrophilic substitution and the 4 position for nucleophilic substitution; this is in agreement with the experimental data.

In the case of the σ complex, the reactivity is characterized by the localization energies, which usually give a better description of aromatic substitution than the reactivity indexes of the isolated molecule [8].

It is seen from Table 3 that, according to the magnitudes of the localization energies of electrophilic (L_E) and nucleophilic (L_N) substitution, the most reactive site for both electrophilic and nucleophilic attack of the lactim and lactam forms in neutral media is the carbon atom in the 1 position. This is in good agreement with the experimental data. According to the L_E and L_R values (Table 3), attack then proceeds at the 4 and 6 positions. Inasmuch as the L_E and L_R values are close, one should assume that the reactivities in these positions are approximately identical.

Absorption Spectra of the Lactam and Lactim Forms

It is apparent from the data in Table 4 that the calculated and experimental λ_{max} values are in satisfactory agreement (Fig. 1). This attests to the correct selection of the computational parameters. According to the weights of the excited configurations, 81% of the long-wave I band (Table 4) pertains to transition

from the upper occupied MO (UOMO) or ψ_{10} to the lower vacant MO (LVMO) or ψ_{11}. From an examination of the coefficients of resolution of the UOMO and LVMO with respect to the atomic orbitals, this transition pertains to an $S_{\pi\pi^*}$ transition polarized at 134° relative to the y axis. According to the change in the electron distribution of the charges in the molecular diagrams in the ground and excited states, the transition is realized through charge transfer from the amide group to the keto group. This band can therefore be called an intramolecular charge transfer band. The oscillator force (f) is 0.21. According to CI, 69% of the II band (347 nm) is due to the $\psi_9 \rightarrow \psi_{11}$ transition. The assignment of the other bands is presented in Table 4.

The long-wave band of the lactim form is due primarily (68%) to transition between the $\psi_0 \rightarrow \psi_{11}$ MO and (23%) the $\psi_9 \rightarrow \psi_{11}$ transition and is polarized at 268° relative to the y axis (Table 5). According to the matrix of the coefficients of expansion in the formation of the $\psi_{10} \rightarrow \psi_{11}$ MO, the participation of the MO of the carbon atoms and the MO of the heteroatoms is almost identical. The hydroxyl oxygen atom makes the greatest contribution to the ψ_9 MO. It is apparent from a consideration of the change in the charges in the molecular diagrams on passing from the ground state to the excited state that the electron charges migrate from the lactim ring to the anthraquinone system during the long-wave transition. The second band (339 nm) is polarized at 33° relative to the y axis and is 1.5 times more intense than the long-wave band; this is in good agreement with the experimental results. According to the CI, it is due primarily to transition between ψ_{10} and ψ_{11} (30%) and transition between ψ_8 and ψ_{11} (50%). The rest of the bands are presented in Table 5.

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