Calculated: C 88.0; H 4.7; N 7.3%; M 382. The next substance isolated was 0.05 g of adduct VIa (for an overall yield of 58%).

B) A total of 0.53 g (42%) of adduct VIa and 0.39 g (33%) of adduct VIb were obtained from 1 g (3 mmole) of IV and 2.12 g (40 mmole) acrylonitrile after heating in a sealed ampul at 185-195°C for 1 h.

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ELECTRONIC ABSORPTION SPECTRA AND STRUCTURES OF THE CONJUGATE ACIDS OF 5-HYDROXY- AND 5-AMINOANTHRAQUINONEPYRIDINES

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UDC 541.651:543.422.6:547.837

The structures of 5-hydroxy and 5-amino derivatives of naphtho[2,3-h]quinoline-7,12-dione (anthraquinonepyridine) and their conjugate acids were investigated by experimental and computational [Pariser–Parr–Pople (PPP)] methods. The hydroxy derivative exists in the keto form, while the cation of the hydroxy form is formed during protonation; the amino derivative exists in the amino form but is converted to a cation with an imino structure upon protonation. In both cases the addition of a proton is accompanied by rearrangement of the π-electon structure of the molecules. The assignment of the S_{π,π^*} transitions in the electronic spectra of the bases and their conjugate acids is given on the basis of a quantum-chemical calculation.

Anthraquinonepyridine (naphtho[2,3-h]quinoline-7,12-dione) compounds that contain a substituent in the 5 position with a hydrogen atom that has proton lability are capable of tautomerism due to transfer of the proton to the heteroring nitrogen atom. This sort of tautomerism has been demonstrated for 5-hydroxy-substituted compounds (I) [1] and has been proposed for 5-amino-substituted compounds (II) [2]. In the present research we made an attempt to estimate the relative stabilities of the possible tautomers and their conjugate acids on the basis of quantum-chemical calculations and compared the calculated electronic spectra with the experimental spectra.

Stabilities of the Tautomers

It is apparent from Table 1 that of the three tautomeric forms of I and II, according to the heats of atomization ΔH, the most stable form for I is Ib, while structure IIa is the most stable form for II. It follows from an analysis of the energies of the σ and π bonds that the π-bond energy is responsible for the greatest stability of one of the three forms. In fact, the σ-bond energy for all forms of I and II remains virtually unchanged, while the π-bond energy undergoes considerable changes; E_π has the greatest value for form Ib in the case of the 5-hydroxy derivative, while E_π has the greatest value for form IIa in the case of the 5-amino derivative. A second stabilizing factor of the corresponding tautomer in solutions and in the condensed state is the solvation energy. It follows from the calculation that the coefficient of solvation (M_{solv}) of form Ib in the case of the hydroxy derivative is greater by a factor of approximately two than in the case of the remaining forms. For the stable tautomer of the 5-amino derivative, on the other hand, the coefficient of solvation is smaller by a factor of approximately two than for the next energically advantageous tautomer.

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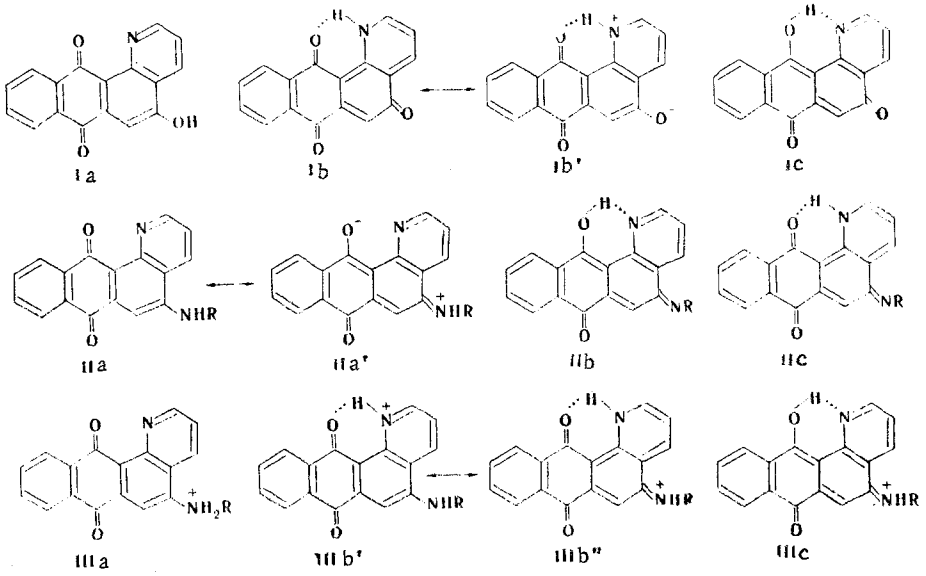
TABLE 1. Energy Characteristics of Compounds

Structure	Heat of atomization, ΔH, eV	π-Bond energy, E_π, eV	σ-Bond energy, E_σ, eV	Total energy, $E_{\sigma\pi}$, eV	Coeff. of solvation, M_{solv}
Anthraquinonepyridine	156,824	32,096	84,790	116,886	1,946
Ia	162,256	33,555	88,825	122,381	2,527
Ib	162,588	34,038	88,848	122,886	5,562
Ic	162,009	33,253	88,817	122,070	2,881
IIa	165,943	33,884	88,155	122,040	2,905
IIb	165,194	32,803	88,074	120,877	2,175
IIc	165,736	33,551	88,108	121,659	4,803
IIIa	168,542	32,591	88,154	121,045	2,088
IIIb'	170,574	34,356	88,215	122,571	3,687
IIIb"	170,388	34,287	88,200	122,487	6,067
IIIc	169,648	33,441	88,168	121,609	3,363
IV	161,455	32,566	84,852	117,418	2,698
V	173,176	33,360	88,216	121,576	2,849
VI	166,948	34,023	88,886	122,909	3,296

This indicates the necessity for allowance for the effect of the solvent on the ratio of the tautomers.



The monoprotonated conjugate acids of the 5-amino derivatives can exist in the IIIa-c forms. According to the greatest ΔH value, structure IIIb' is the most stable structure, and resonance structure IIIb" is quite close to it. Considering the fact that the coefficient of solvation for structure IIIb" is greater by a factor of approximately two, one should expect that its contribution is significant in solutions and in the condensed state. The existence of protonated forms in the form of the IIIb'↔IIIb" tautomer was confirmed experimentally by means of the IR spectra. A band of stretching vibrations of an NH bond at 3452 cm^{-1} and one band of stretching vibrations of a C=O bond at 1672 cm^{-1} are observed in the IR spectrum of the 5-cyclohexylamino-substituted compound (II, R = C_6H_{11}) in $CHCl_3$. In the IR spectrum of the hydrohalide salt of the same compound in solution in $CHCl_3$ and in the crystalline state the band at 3452 cm^{-1} vanishes, the band of C=O groups is split into two components ($\nu C{=}O_{free}$ 1678 cm^{-1} and $\nu C{=}O_{assoc}$ 1633 cm^{-1}), and two absorption bands appear at 3206 and 3000-3100 cm^{-1}. In analogy with the band in the spectra of 1-alkylaminoanthraquinones, the band at 3206 cm^{-1} was assigned to the stretching vibration of an NH bond tied up in an intramolecular hydrogen bond. In fact, the position of the band at 3206 cm^{-1} and the magnitude of the $\Delta\nu C{=}O$ splitting in the spectrum of protonated II (R = C_6H_{11}) are close to the position of νNH and the splitting in the IR spectra of 1-alkylaminoanthraquinones [3]. The broad band at 3000-3100 cm^{-1} is due to vibrations of the $\overset{+}{N}H$ bond.

Electronic Spectra

Anthraquinonepyridine. The calculated electronic spectra of this compound coincides satisfactorily with the experimental spectrum (Fig. 1 and Table 2). The low-intensity shoul-

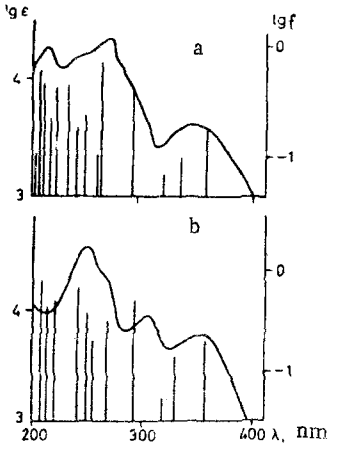


Fig. 1

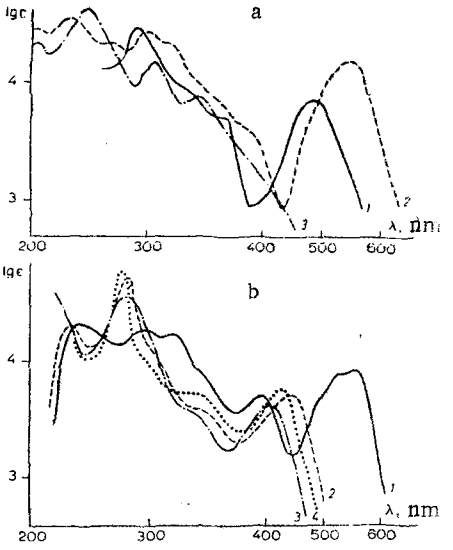


Fig. 2

Fig. 1. Experimental and calculated (vertical lines) electronic spectra of anthraquinonepyridine in 50% alcohol (a) and in 0.01 N HCl in alcohol (b).

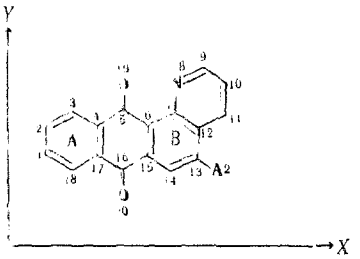
Fig. 2. Electronic spectra: a) 5-cyclohexylaminoanthraquinonepyridine (II) in $CHCl_3$ (1), in 3 N H_2SO_4 in alcohol (2), and in 50% H_2SO_4 in alcohol (3); b) 5-hydroxyanthraquinonepyridine (I) in 50% alcohol (1), in 0.5 N HCl in 50% alcohol (2), 5-methoxyanthraquinonepyridine in 50% alcohol (3), and in 0.5 N HCl in 50% alcohol (4).

der at ∿440 nm undergoes a decrease in intensity upon protonation, and this proves that this band belongs to an S_{n,π^*} transition [4]. According to the calculation, 66% of the intense band at 350 nm pertains to a transition from an upper occupied molecular orbital (UOMO) (Ψ_m) to a lower vacant molecular orbital (LVMO) (Ψ_{m+1}), while 18% pertains to a transition from Ψ_{m-1} to Ψ_{m+1}; the polarization of the transition is −8° relative to the X axis. It follows from an analysis of the atomic coefficients of the MO that participate in the transition and the charge distribution in the ground and first excited states that the carbonyl groups (ΔQ = −0.35) act as electron-acceptor fragments in this transition, while the quinoline fragment (ΔQ = 0.39) is an electron donor. The second S_{π,π^*} transition differs from the first with respect to the direction of polarization (by 74°); it is made up of 53% $S_{\Psi_{m-1},\Psi_{m+1}}$, and 16% $S_{\Psi_m,\Psi_{m+1}}$, and 14% $S_{\Psi_{m-2},\Psi_{m+1}}$. As in the case of the first S_{π,π^*} transition, the carbonyl groups (ΔQ = −0.34) are electron acceptors, while the quinoline fragment (ΔQ = 0.27) is an electron donor. The third and fourth S_{π,π^*} transitions are transitions involving charge transfer from the benzene ring that is not condensed with the pyridine ring to the carbonyl groups (the third S_{π,π^*} transition) and the quinoid system of bonds (the fourth S_{π,π^*} transition).

The electron transitions in the absorption spectrum of anthraquinonepyridine cation IV are approximately the same as in the spectrum of the neutral molecule. The polarization of the first S_{π,π^*} transition in the spectrum of cation IV undergoes a change of 18°, and the electron donor fragment is primarily the benzene ring condensed with the heteroring, i.e., the protonated nitrogen atom is no longer the electron donor (Table 2).

5-Aminoanthraquinonepyridine (II). A long-wave band at 465 nm (in CCl_4) is observed in the spectrum of II (R = C_6H_{11}) as compared with the spectrum of unsubstituted anthraquinonepyridine. This band vanishes in the spectra obtained in strongly acidic media; this constitutes evidence in favor of its assignment to an S_{n,π^*} transition. According to the calculation, the degree of participation of the nitrogen atom of the amino group in the formation of an UOMO is 26%, while the orbitals of the carbon atoms of the benzene and pyridine rings make the remaining contribution. A total of 92% of the transition is realized between the UOMO and LVMO. The band is polarized in a direction from the amino group to the quinoid system. It follows from an analysis of the coefficients of expansion of the MO with respect

TABLE 2. Electronic Spectra of Anthraquinonepyridine Derivative:



Structure	Absorption maximum, λ_{max}, nm		Oscillator force, f	Angle (in degrees) between direc. of polariza. and the X axis	Localization of the transition			
	calc.	exptl.			acceptor	$-\Delta Q$	donor	ΔQ
1	2	3	4	5	6	7	8	9
Anthraquinonepyridine	359	350[a]	0,172	−8	C = O group	0,35	Quinoline fragment	0,39
	335		0,102	66	C = O group	0,34	Quinoline fragment	0,27
	319		0,066	4	C = O group	0,34	Benzene ring (A)	0,45
	291	295	0,373	−72	Quinoid system		Benzene ring (A)	0,45
	262	267	0,645	32				
	259	256	0,104	13				
	248	240	0,240	7				
IV	359	347[a]	0,242	10	C = O group	0,27	Benzene ring (B)	0,34
	332		0,120	78	C = O group	0,33	Benzene ring (B)	0,20
	320	305	0,056	10	C = O group	0,34	Benzene ring (A)	0,47
	293	295	0,400	−73	Quinoid system		Benzene ring (A)	0,43
	269	265	0,272	58				
	255		0,165	−14				
	249	248	0,386	17				
IIa	446	465[b]	0,226	−35	C = O group	0,40	Amino group and adjacent benzene ring	0,50
	350	362	0,072	−15	Pyridine ring	0,24	Amino group and adjacent benzene ring	0,29
	327	330 sh	0,010	−54	Pyridine ring	0,40	Amino group and adjacent benzene ring	0,63
	314		0,128	18	C = O group	0,31	Benzene ring (A)	0,38
	293	304	0,363	0				
	282		0,671	53				
	265		0,220	82				
IIIb″	494	555[c]	0,185	−38	Pyridine ring	0,45	N_{21} and benzene ring (B)	0,43
	415	380 sh	0,339	1	C = O group	0,36	N_{21} and benzene ring (B)	0,55
					Benzene ring (A)	0,20		
	373		0,191	38	Pyridine ring	0,42	O_{19}—C_5—C_6—C_{15}—C_{14}—C_{13}—N_{21}	0,49
	311	316	0,050	0	Oxygen atoms	0,96	Benzene ring (A)	0,45
					N_{21} atoms	0,57	N_8 atom	0,60
	291	298	0,084	−25				
	274		0,359	34				
	265	271	0,532	81				

to the AO and an analysis of the π charges and bond orders in the molecular diagrams in the ground and first excited states that the carbonyl groups ($\Delta Q = -0.40$) are electron acceptors, while the amino group and the adjacent benzene ring ($\Delta Q = 0.50$), where the nitrogen atom of the amino group ($\Delta Q = 0.20$) constitute an electron donor.

The second S_{π,π^*} transition is polarized at an angle of −15° relative to the X axis. The pyridine ring ($\Delta Q = -0.24$) is an electron acceptor, while the benzene ring condensed with it and the amino group constitute a donor, i.e., this transition is localized primarily in the aminoquinoline fragment of the molecule. The third S_{π,π^*} transition has the same

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9
V	383	345[d]	0,209	−24	C = O group	0,32	N_{21} and adjacent benzene ring	0,45
	336		0,160	63	C = O group	0,21	Benzene group (B)	0,20
	317		0,059	13	C = O group	0,33	Benzene group (A)	0,44
	304	309	0,101	−25	Pyridine ring	0,38	Benzene ring (B)	0,38
	285	298	0,369	−86				
	260	250	0,977	32				
Ib	490	553[e] 525	0,150	−44	Pyridine ring	0,45	Benzene ring (B) and C = O group	0,52
	425	415	0,381	0	Benzene ring (A) and quinone C = O group	0,22 0,36	O_{21} atom and adjacent benzene ring	0,53
	383	364 sh	0,218	37	Pyridine ring	0,39	O_{19}—C_5—C_6—C_{15}—C_{14}—C_{13}—O_{21}	0,47
	309	323	0,034	3	Carbonyl groups	0,26	Benzene ring (A)	0,30
	288	298	0,044	−40				
	275		0,173	−11				
	263	260 sh	0,659	69				
	255	245	0,167	11				
VI	411	440[f]	0,223	−35	Carbonyl groups	0,32	OH and adjacent benzene ring	0,46
	342	351 sh	0,058	81	Pyridine ring	0,31	OH and adjacent benzene ring	0,32
	323	324 sh	0,058	33	Carbonyl groups	0,23	OH and adjacent benzene ring	0,41
					Pyridine ring	0,20		
	315	304 sh	0,089	18	Carbonyl groups	0,32	Bentene ring (A)	0,42
	288		0,278	−52				
	273	278	1,168	43				
	246		0,270	−33				
Ia	413	410[g]	0,210	−34	C = O group	0,40	OH and adjacent benzene ring	0,47
	338	345 sh	0,022	−58	C = O group	0,14	OH and adjacent benzene ring	0,20
					Pyridine ring	0,06		
	315	333 sh	0,114	15	C = O group	0,31	Benzene ring (A)	0,41
	306		0,077	−13	Pyridine ring	0,41	OH and adjacent benzene ring	0,58
	289		0,208	−36				
	273	282	1,102	46				

[a]In 20% alcohol [8].
[b]Spectrum of 5-cyclohexylaminoanthraquinonepyridine in CCl_4.
[c]Spectrum of 5-cyclohexylaminoanthraquinonepyridine in 3 N H_2SO_4 in 50% alcohol.
[d]Spectrum of 5-cyclohexylaminoanthraquinonepyridine in 50% H_2SO_4 in 50% alcohol.
[e]Spectrum of 5-hydroxyanthraquinonepyridine in 50% alcohol.
[f]Spectrum of 5-hydroxyanthraquinonepyridine in 0.5 N HCl in 50% alcohol.
[g]Spectrum of 5-methoxyanthraquinonepyridine in 50% alcohol.

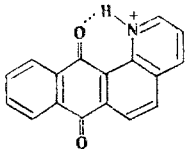
character. In the fourth S_{π,π^*} transition the carbonyl groups are acceptors, and the benzene ring is a donor.

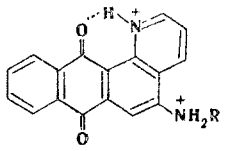
Protonation of II gives rise to a bathochromic shift in the electron absorption spectrum [2]. To explain the observed red shift let us examine the expected character of the electronic spectra of structures III. Protonation of the amino nitrogen atom with the formation of structure IIIa (of the ammonium type) should lead to the disappearance of the $S_{\pi l,\pi^*}$ band in the spectrum of II as a consequence of blocking of the unshared pair of electrons of the nitrogen atom and its exclusion from conjugation. The result of this should be a blue shift, which contradicts the experimental observation. The calculated electronic spectrum of IIIa is in agreement with this: a long-wave band is found at 386 nm. Consequently, structure IIIa does not explain monoprotonation. The spectrum of protonated form IIIb should not differ markedly from the spectrum of the unprotonated molecule. In fact, numerous data show

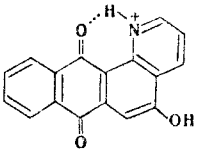
that protonation of the nitrogen atom in the aromatic ring of the amino derivative (for example, in 6-aminoquinoline, which is not capable of tautomeric conversion) gives rise to a small red shift of the long-wave band [5]. The calculation is in agreement with these data: the long-wave band of cation IIIb' is shifted 5 nm to the red region. Consequently, structure IIIb' does not reflect the result of monoprotonation of II. Finally, monoprotonation may be accompanied by rearrangement of the π-electron structure (forms IIIb" and IIIc). The spectra should be characterized by a red shift of the long-wave band as compared with the spectrum of II. The indicated shift is experimentally observed [for II, $\Delta\lambda = \lambda_{max}(CCl_4)-\lambda_{max}$ (3 N H_2SO_4 in 50% alcohol) = 90 nm]. The calculation of structures IIIb" and IIIc with the use of the same parameters as in the calculation of structures I, II, IIIa, and IIIb also gives a red shift of the indicated band ($\Delta\lambda$ = 57 and 30 nm), and this confirms the correctness of the assumption presented above.

Consequently, according to an analysis of the absorption spectra, II exists in the IIIb" or IIIc form in an acidic medium. As we demonstrated above, the data on the heats of atomization and from the IR spectra provide evidence in favor of the IIIb" structure.

The long-wave band in the spectrum of resonance structure IIIb" is related to the $S_{\psi_m,\psi_{m+1}}$ (77%) and $S_{\psi_m,\psi_{m+2}}$ (19%) transitions; the polarization is −38°. The pyridine ring (ΔQ = −0.45) acts as an electron acceptor in IIIb", while the benzene ring condensed with it and the exocyclic nitrogen atom (ΔQ = 0.43) act as an electron donor, i.e., charge transfer takes place within the quinoline fragment. Consequently, the long-wave transition in the spectrum of IIIb" is due to the participation of other fragments than those in the IIa structure. The second S_{π,π^*} band is a band of charge transfer from the exocyclic nitrogen atom and the associated (with it) benzene ring to the carbonyl groups and the other benzene ring. The characteristics of the remaining transitions are presented in Table 2.


IV


V


VI

As the acidity of the medium is increased further, the intensity of the long-wave band decreases, and this band vanishes in 50% H_2SO_4. The spectrum becomes similar to the spectrum of anthraquinonepyridine cation IV, i.e., a dication with the V structure is formed (Fig. 2). The calculated spectrum of the dication coincides satisfactorily with the experimentally observed spectrum (Table 2).

5-Hydroxyanthraquinonepyridine (I). The structure of 5-hydroxyanthraquinonepyridine can be represented by structures Ia-c. According to the calculation, the spectrum of form Ia is characterized by a long-wave band at 412 nm; this is in agreement with the observed spectrum of fixed form Ia, viz., 5-methoxyanthraquinone pyridine (λ_{max} 410 nm in 50% alcohol). The long-wave band in the spectrum of I lies at 525-553 nm (in 50% alcohol). Consequently, structure Ia does not reflect the structure of I, and it may be represented as resonance between quinoline (Ib) and dipolar (Ib') structures [1].

The spectrum calculated for the Ib form is in qualitative agreement with the spectrum obtained experimentally (Table 2). The first long-wave transition is localized primarily in the quinoline fragment and is accompanied by charge transfer to the pyridine ring, i.e., it is similar to the transition in the IIIb" structure. The second S_{π,π^*} transition is accompanied by charge transfer from the exocyclic oxygen atom and the benzene ring linked to it to the anthraquinone system and to the carbonyl groups, i.e., it is also similar to the second transition in the spectrum of the cation of the 5-amino derivative (IIIb") (Table 2). However, the calculation of the spectrum of the Ib' form is not in agreement with the experimental spectrum: one band at 432 nm was found by calculation above 400 nm, while two bands were found in this region in the experimental spectrum.

Compound I exists in cationic form VI in an acidic medium [1]. The calculated electronic spectrum is in satisfactory agreement with the experimental spectrum (Table 2). One band, which is shifted hypsochromically relative to the long-wave band of the neutral form, is found in the long-wave region. This transition is primarily (90%) due to a transition from an UOMO to an LVMO and is accompanied by charge transfer from the hydroxy group and the benzene ring linked with it (ΔQ = 0.46) to the pyridine ring (ΔQ = −0.09) and to the carbonyl groups (ΔQ =

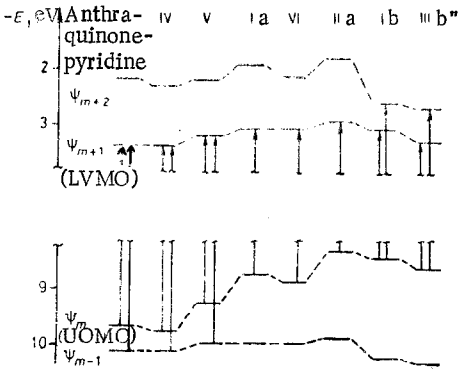


Fig. 3. Energy levels of the MO and long-wave transitions in anthraquinonepyridine derivatives.

—0.32). The second band is a band of charge transfer from the hydroxy group and the adjacent benzene ring (ΔQ = 0.32) to the pyridine ring (ΔQ = —0.31).

Effect of Substituents and Protonation on the MO. It is apparent from Fig. 3 that the introduction of an electron-donor substituent (NH, OH) in the 5 position of anthraquinonepyridine leads to a simultaneous increase in the energies of the UOMO (Ψ_m) and LVMO (Ψ_{m+1}). However, the increase in the energy of the UOMO is two to three times greater than that of the LVMO, and this explains the red shift of the long-wave band in the spectra of I and II relative to the analogous band in the spectrum of anthraquinonepyridine.

The levels of diprotonated form V are somewhat increased relative to the MO of anthraquinonepyridine. A peculiarity of the levels of the MO of the monoprotonated molecules is the pronounced increase in the UOMO relative to the levels of the MO of anthraquinonepyridine, similar to introduction of a strong electron donor.

EXPERIMENTAL

The synthesis and purification of the investigated compounds were accomplished by the methods in [1, 2]. The electronic absorption spectra were recorded with a Specord UV-vis spectrometer. The IR spectra of KBr pellets and solutions in $CHCl_3$ were recorded with a UR-20 spectrometer. The calculation was carried out by the Pariser—Parr—Pople (PPP) method in the Dewar variation with the use of 25 singly excited configurations [6, 7]. The energies of the intramolecular hydrogen bonds were not taken into account in the calculation.

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