SPECTRAL CHARACTERISTICS AND ACID–BASE EQUILIBRIA OF 4,9-DIHYDROXY-5,10-DIOXO-4,5,9,10-TETRAHYDRO-4,9-DIAZAPYRENE AND ITS 2,7-DERIVATIVES

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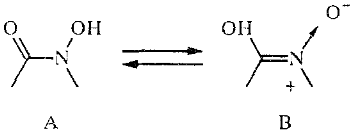
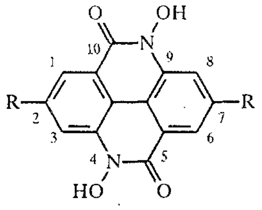
The IR and electronic spectra of 2,7-disubstituted 4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (R = H, I, NH_2, NO_2, OH) are studied. Analysis of the IR bands shows that, in crystalline form and in neutral and basic solutions, the compounds exist predominantly in the hydroxamic form. It is established that in sulfuric acid solutions the oxygen atoms of the C=O groups are protonated. The spectral characteristics of the neutral and ionized forms of the compounds are determined. The acid ionization constants are measured by potentiometric titration.

Derivatives of 4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene find use as intermediates in the manufacture of dyes, polymers, and plastics [1]. The O═CR–NR–OH group can be a specific reagent for metal ions [2]. The structure of this fragment allows for the existence of tautomers:



It is to be expected that the realization of tautomers A and B, as well as of their protonated and deprotonated forms, will depend on the kind of solvent and the pH of the medium. However, this question has not been considered in the literature.

In the present work, we have studied the spectral properties and acid–base equilibria of 2,7-disubstituted 4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene:



I - V

I R=H, II R=I, III R=NH_2, IV R=NO_2, V R=OH

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TABLE 1. Wave Numbers (cm^{-1}) of Some Absorption Bands in the IR Spectra of Compounds I-V and Their Cationic and Anionic Forms

Compound	R	ν_{OH+NH_2}	$\nu_{NC=O}$	$\nu_{C\cdots C}$	ν_{N-OH}	ν_{C-N}	δ_{CH}	pK_{a1}, pK_{a2}
N, N(CH$_3$)$_2$—I	H	—	1645	1590	—	1335	730, 800	
I	H	2860...3390	1645	1585	1420	1345	735, 805	
II	J	2860...3415	1660	1600, 1555	1400	1335	605, 695, 865	4,12; 8,73
III	NH$_2$	2830...3420	1660	1605, 1560 1520*	1380	1310	600, 710, 840	4,25; 6,96
IV	NO$_2$	2850...3450	1675	1600	1410	1325	600, 710, 895	
V	OH	2840...3440	1680	1590	1380	1335	585, 760, 845	
II—Na		2800...3600	1670	1610	1450**	1340	600, 870	
III—Na		2800...3600	1665	1610	1420**	1360 пл	590, 820	
V—Na		2800...3600	1690	1620	1420**	1360 пл	710, 840	
I—cation			—	1610	1430	1360		
III—cation			1670	1615, 1580	1450, 1420	1330		
IV—cation			1675, 1645	1600	1420	1340		

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*Overlapped by ν_{NO_2}.

**ν_{N-O}.

TABLE 2. Maxima of the Long-wavelength Absorption Bands in the Electronic Spectra of Compounds I-V

Compound	Form	λ_1, nm	lgε_1	λ_2, nm	lgε_2	λ_3, nm	lgε_3	λ_4, nm	lgε_4
I	Neutral	366	3,43	349	3,23	333	3,07	312	3,13
	Monoanion	397	3,33	381	3,44	364	3,41	345	3,37
	Protonated	377	4,26	360	4,01	377	4,00	345	3,43
II	Neutral	387	4,13	380	4,19	373	4,15	364	4,08
	Monoanion	397	3,98	380	4,00	373	3,78	356	3,78
	Protonated	417	4,06	397	3,81	336	3,57		
III	Neutral	415	3,99	252	4,02				
	Monoanion	421	4,00	279	3,87				
	Dianion	425	3,98	392	3,86	338	3,68	285	4,37
	Monoprotonated	400	3,78	262	4,11				
	Diprotonated	371	4,27	354	4,07	339	3,78		
IV	Neutral	412	4,29	331	4,25	285	4,67		
	Monoanion	450	4,11	394	3,83	306	4,82		
	Dianion	474	3,64	362	4,41	311	4,82	280	4,69
	Protonated	390		369		350		373	
V	Neutral	392	4,08	375	3,96	295	3,88	270	4,30
	Monoanion	410	3,95	385	3,82	299	3,94		
	Dianion	427	3,88	277	4,48				
	Protonated	520		415		333		319	

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*λ_5 = 302 nm; lgε5 = 3.16; λ_6 = 280 nm, lgε6 = 3.44.

**λ5 = 333 nm; lgε5 = 3.37; λ6 = 299 nm; lgε6 = 3.34.

***λ5 = 320 nm; lgε5 = 3.75; λ6 = 307 nm; lgε6 = 3.75.λ_7 = 294 nm, lgε7 = 3.56.

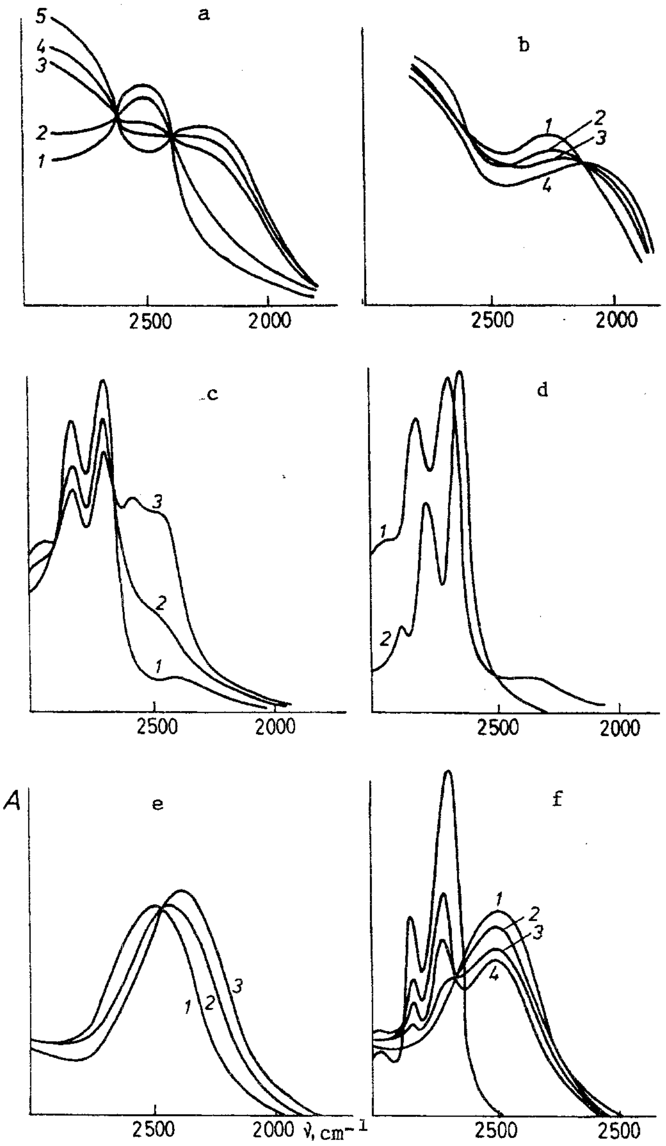


Fig. 1. Electronic absorption spectra of ethanol solutions at various pH values: a) compound IV, $C = 8 \cdot 10^{-5}$ M: 1) pH 7.98; 2) pH 9.23; 3) pH 11.18; 4) pH 11.30; 5) pH 12.33; b) compound IV, $C = 8 \cdot 10^{-5}$ M: 1) pH 12.33; 2) pH 12.70; 3) pH 13.20; 4) pH 13.53; c) compound 1, $C = 3.4 \cdot 10^{-4}$ M: 1) pH 1.48; 2) pH 8.96; 3) pH 12.54; d) compound 1, $C = 3.4 \cdot 10^{-4}$ M: 1) ethanol solution; 2) solution in concd. H_2SO_4; e) compound III, $C = 5 \cdot 10^{-5}$ M: 1) pH 1.10; 2) pH 1.80; 3) pH 2.80; f) compound III, $C = 5 \cdot 10^{-5}$ M: 1) pH 1.10; 2) pH 0.90; 3) pH 0.55; 4) pH 0.20; 5) solution in concd. H_2SO_4.

IR Absorption Spectra. The IR spectra show a very strong absorption band in the region of the carbonyl group stretch (1645-1680 cm^{-1}) for compounds I-V (Table 1). The shift of $\nu_{\mathrm{NC=O}}$ to higher frequencies in the case of the 2,7-disubstituted derivatives of the compounds is probably determined primarily by intermolecular factors. This follows from the similarity of the $\nu_{\mathrm{NC=O}}$ frequencies for compounds IV and V (1675 and 1680 cm^{-1} respectively). The presence of the $\nu_{\mathrm{NC=O}}$ band in the spectra is evidence that these compounds exist in form A.

The $\nu_{\mathrm{N-OH}}$ band is assumed to lie in the 1380-1420-cm^{-1} region. This is confirmed by the shift of the band to higher frequencies in the IR spectra of the sodium salts of the compounds. In the region of hydroxyl and amide group stretches, a broad absorption region is found, 2830-3415 cm^{-1}, with numerous maxima. The strong shift of ν_{OH} to lower frequencies is evidence that the OH groups are involved in hydrogen bond formation. The insolubility of compounds I-V in

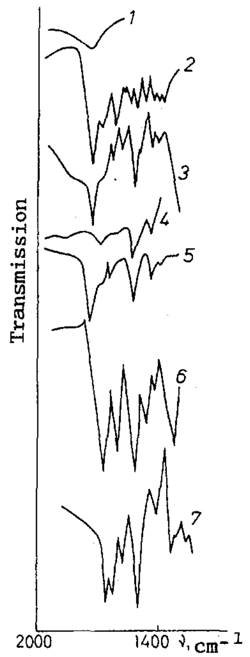


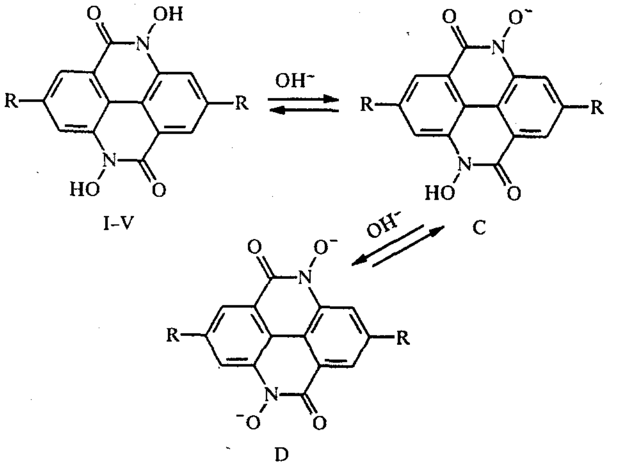
Fig. 2. IR spectra in paraffin oil and in concd. H_2SO_4: 1) background (concd. H_2SO_4); 2) compound III, paraffin oil; 3) compound III, concd. H_2SO_4: 4) compound I, concd. H_2SO_4: 5) compound I, paraffin oil; 6) compound IV, paraffin oil; 7) compound IV, concd. H_2SO_4.

nonpolar solvents prevents more detailed information from being obtained. The assignment of the remaining IR absorption bands is shown in Table 1.

Electronic Absorption Spectra. In the electronic absorption spectra (NaOH, ethanol), a sequence of isosbestic points appears, characterizing the equilibria: neutral form $\rightleftarrows$ monoanion $\rightleftarrows$ dianion (Fig. 1a, b; Table 2). It should be noted that for compounds I and II only one deprotonated form is found in the 7-14 pH range. The size of the shift of the long-wavelength absorption band ($\Delta\lambda_{max}$) on going from the neutral to the monoanionic form (6-38 nm) depends on the kind of substituent in the 2,7 positions and increases in the order: $NH_2 > I > OH > H > NO_2$.

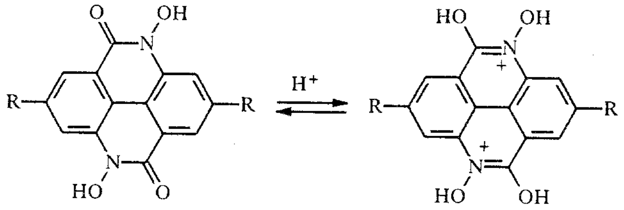
It should be noted that the long-wavelength bands of the neutral and monoanionic forms of compounds I, II, and V are characterized by vibrational fine structure (see Fig. 1c) with differences between the vibrational levels of 1350, 480, and 1120 cm^{-1}, respectively.

The preservation of the $\nu_{NC=O}$ band location and of the shift in the ν_{N-OH} band in the IR spectra of the sodium salts of compounds I-V is evidence that the anions of these molecules exist in the C or D form:



In concentrated sulfuric acid, the long-wavelength band of compounds I, II, IV, and V is characterized by vibrational fine structure. In the case of compounds I, II, and V, the band undergoes a bathochromic shift (see Fig. 1d). In the case of nitro derivative IV, there is a hypsochromic shift of the long-wavelength band. Protonation of amino derivative III occurs even in dilute mineral acids in two steps, as shown by the hypsochromic shift of the long-wavelength band and subsequent appearance of isosbestic points (Fig. 1e, f). Monoprotonation is explained by the addition of a proton to one of the amine groups. In this case, the long-wavelength bands of the neutral and monoprotonated forms do not have fine structure. On further decrease in pH, fine structure appears in the band and it is shifted further to shorter wavelengths (diprotonated from). In concentrated sulfuric acid, the "featureless band" disappears completely, and a long-wavelength band with vibrational structure remains ($\Delta\nu$ = 1320 cm^{-1}), which does not change with a further increase in acid concentration. Consequently, the strong inductive effect of the two $NH_3{}^+$ groups hinders protonation at the oxygen atom of compound III in the A form.

To establish the site of protonation, the IR spectra of the compounds in concentrated sulfuric acid were considered. It can be seen from Table 1 and Fig. 2 that the carbonyl stretching bands in compounds I, II, and V disappear on protonation. This can be explained by the protonation of the oxygen atoms of the C=O groups. The resulting cation apparently contains a C=N double bond with the positive charge on the nitrogen atom.



The IR spectrum of compound IV in sulfuric acid preserves the $\nu_{NC=O}$ band (see Fig. 2). At the same time, as stated above, the long-wavelength band in the electronic spectrum is found to undergo a hypsochromic shift, indicating protonation of the molecule. In view of these data, it can be proposed that the NC=O group is preserved when compound IV is protonated.

On protonation of compound III, the $\nu_{NC=O}$ band is shifted to higher frequencies by 10 cm^{-1}. The preservation and increase in the frequency of $\nu_{NC=O}$ is explained by the existence of compound III in sulfuric acid as the diammonium salt of the hydroxamate form, in full accord with the EAS [electronic absorption spectroscopy] data.

EXPERIMENTAL

The 4,9-dihydroxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (1) and its derivatives (II-V) were prepared by the procedures described in [4]. The compounds were purified by distillation; their purity and identity were monitored by thin-layer chromatography. The IR spectra of the compounds and their sodium salts were taken in KBr pellets, paraffin oil mulls on NaCl plates, and as suspensions in paraffin oil with added sulfuric acid on CaF_2 plates in the 4000-400-cm^{-1} region on a-Specord 75-IR spectrophotometer. The electronic spectra were obtained in ethanol solutions and solutions in concentrated sulfuric acid on a Specord UV-vis instrument in the 200-700-nm region. Acid–base equilibria were studied by the saturation method. The acid ionization constants of the compounds in ethanol solutions were determined potentiometrically at 20°C by the method of Albert and Sargent [5].

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