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Phototransformations of 6-X-5-Nitroquinoxalines

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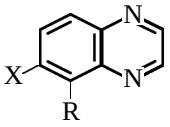
Abstract — Photophysical properties and photochemical activity of 6-X-5-nitroquinoxalines with electron-donor substituents (X = H, CH_3, Cl, OC_2H_5, NH_2) *ortho* to the nitro group were studied. The quantum yield of the formation of 5-hydroxyquinoxaline from the corresponding nitro derivative depends on the nature of the substituent and irradiation conditions. Phototransformations can go through nitro-nitrite rearrangement with the participation of two alternative $T(n\pi^*)$ levels, depending on the size and electronic effects of the substituent. The latter factor is largely determined by the population on excitation of different charge-transfer states involving the nitro group.

We earlier showed [1, 2] that photolysis of 5-nitroquinoxalines and its methyl derivatives in organic and aqueous media provides hydroxy derivatives. Two mechanisms of phototransformations were proposed, depending on the energy of the absorbed quantum: homolytic Ar–NO_2 bond rupture and nitro–nitrite rearrangement. The available published data [3] suggest that the rate of the latter process depends on the size of the substituent *ortho* to the nitro group. Taking into account that this substituent also affects electronic properties of the molecule, thus forming a state diagram, we undertook photophysical and photochemical research on 6-X-5-nitroquinoxalines with substituents X differing from each other both in size and in electronic properties (compounds **I**–**V**). As models we used 6-X-quinoxalines **VI**–**VIII**.



I–**VIII**

R = NO_2, X = H (**I**); R = NO_2, X = CH_3 (**II**); R = NO_2, X = Cl (**III**); R = NO_2, X = OC_2H_5 (**IV**); R = NO_2, X = NH_2 (**V**); R = H, X = Cl (**VI**); R = H, X = OC_2H_5 (**VII**); R = H, X = NH_2 (**VIII**).

Photophysical properties. The electronic absorption spectra of compounds **I**–**V** (Table 1) are rather difficult to interpret because of the admixture to local excited electronic states of these molecules of additional charge-transfer configurations and new $n\rightarrow\pi^*$ transitions compared with unsubstituted quinoxaline [4–6].

Compounds **I**–**III** are close in their optical properties to 2,3,6-trimethyl-5-nitroquinoxaline we studied previously [2]. The spectra characteristically contain strong absorption bands at 220–230 nm, less structured compared with those in the spectrum of 2,3,6-trimethyl-5-nitroquinoxaline, as well as medium-intensity bands at 300–320 nm. Both strong and medium bands undergo a bathochromic shift in the series X = H–CH_3–C (0–1300–700 and 0–200–300 cm^{-1}) and a hypsochromic shift compared with models ([7], Table 1): quinoxaline **I** (2000, 200 cm^{-1}) and quinoxalines **VI**, **III** (400, 1000 cm^{-1}). With account for published data [2, 7, 8], they can be assigned to transformed π–π^* bands of quinoxaline, formed by the $S_0\rightarrow S_4$ and ($S_0\rightarrow S_3$ + $S_0\rightarrow S_2$) transitions with a certain contribution of the X$\rightarrow$nucleus (CT-1) and $NO_2\rightarrow$nucleus (CT-2) charge transfers. The long-wave $n\rightarrow\pi^*$ band formed by the $S_0\rightarrow S_1$ transition appears as a shoulder at 330–340 nm on the neighboring $\pi\pi^*$ band. In ethanol, the spectra of the three compounds all preserve their patterns, except that in the spectra of methyl and chloro derivatives **II** and **III** in which the CT-1 process is realized we observe enhanced intensity of $\pi\rightarrow\pi^*$ transitions and no $n\pi^*$ band in the latter case. In aqueous solutions, all $\pi\pi^*$ bands are diffuse, and the shoulder at 340 nm is preserved only for the simplest nitro derivative **I**.

Compounds **I**–**III** do not fluoresce at room temperature both in hexane and in ethanol. The model compounds, quinoxaline and compound **VI**, very weakly fluoresce under these conditions (quantum yield φ_f ~10^{-4}, fluorescence maximum λ_f ~400 nm). At 77 K in ethanol glasses of compounds **I**–**III** no more than phosphorescence is observed, whose band parameters (maxima, principal vibration frequency) and lifetime τ_{ph} are close to those of quinoxaline (see [2] and

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Table 1. Spectral properties and basicity of 6-X-5-nitroquinoxalines **I**–**V** and 6-X-quinoxalines **VI**–**VIII**[a]

Comp. no	Absorption, λ_a ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}), 295 K				pK_a	Phosphorescence (fluorescence), 95% ethanol, 77 K	
	heptane	95% ethanol	water, pH 7	H_2SO_4[b]		λ_{ph} (λ_f)	τ_{ph}
I	222 (26.3), 230 sh, 304 (5.96), 317 (6.36), 335 sh	222 (25.4), 307 (5.75), 317 (6.19), 340 sh	220 (26.0), 315 (6.38), 340 sh	222 (19.2), 328 (7.8)	–1.1	470 sh, 485 sh, 509, 530 sh	–
II	229 (25.1), 311 (5.39), 319 (6.30), 333 sh	230 (24.8), 308 (6.46), 318 (7.63), 340 sh	230 (24.8), 317 (7.63)	233 (17.2), 333 (8.76)	–1.0	474, 508, 547	0.22
III	233 (28.1), 311 (6.02), 322 (6.42), 340 sh	232 (28.0), 311 sh, 322 (7.00)	232 (26.8), 321 (7.19)	232 (23.4), 325 (8.46)	–1.9	480, 516, 547	0.21
IV	238 (28.4), 336 (6.30), 350 sh	237 (26.5), 337 (6.68)	237 (23.9), 340 (6.89)	255 (19.2), 340 (6.83), 375 (6.67)	–0.88	487, 523, 563	0.24
V	245, 285, 340 sh, 372	250 (31.3), 295 sh, 351 sh, 392 (8.82)	247 (25.5), 300 (4.24), 345 (7.60), 397 (8.09)	245 (15.7), 272 (14.1), 350 (10.2), 465 (10.3)		525, 560 (492)	0.19
VI	235, 238 sh, 322, 333 sh	236 (25.7), 322 (5.76)	237 (24.4), 322 (5.66)	245 (26.1), 337 (8.27)	0.32	487, 520, 555 sh	–
VII	240 (26.3), 333 (7.08), 347 sh	246 (24.1), 342 (6.70)	246 (23.5), 345 (6.55)	255 (25.2), 330 (4.85), 382 (7.06)	1.24	476, 488, 510 (395)	0.42
VIII	247 (27.0), 253 sh, 280 sh, 363 (5.85)	257 (31.4), 290 sh, 394 (6.31)	255 (24.5), 290 sh, 375 (5.17)	272 (21.0), 320, 460 (6.51)	2.75	540 sh, 580 (484)	0.26

[a] (λ_a, λ_f, λ_{ph}) Absorption, fluorescence, and phosphorescence maxima, respectively, nm; (τ_{ph}) phosphorescence lifetime, s. [b] Conjugate acid; concentration, N: 10 (**I**–**IV**), 36 (**V**), 5 (**VI**), and 1 (**VII, VIII**).

Table 1). As the electron-donor power of substituent X increases (compounds **IV** and **V**, X = EtO, NH_2), the $\pi\pi^*$ bands shift bathochromically by 1800–4600 cm^{-1} because of increased contribution of CT-1. As a result, inversion of the $S(\pi\pi^*)$ and $S(n\pi^*)$ levels may occur, favored by highly polar solvents [7]. Thus, models **VII** and **VIII** fluoresce at room temperature with the following parameters, λ_f (nm) (φ_f): 396 (0.001) and 405 (0.02) in heptane and 418 (0.03) and 524 (0.53) in ethanol, respectively. Nitro derivative **V** fluoresces, too, but only when frozen (77 K) (Table 1, Figs. 1a and 2). On the other hand, as judged from data for naphthalenes [9, 10], one more, additional charged-transfer configuration $X \rightarrow NO_2$ (CT-3) is possible in molecules **IV** and **V**. Evidence for this suggestion comes from the observation in the absorption spectra of compound **V** of a band at 340–350 nm, which is lacking in the spectra of amine **VIII** (Table 1, Figs. 1a and 1b, curve *1*).

Low-temperature measurements show that the $S_1 \rightarrow S_0$ and $T \rightarrow S_0$ bands of model **VIII** and nitro derivative **V** are close to each other (Figs. 1a and 1b, curves *2* and *3*). This fact implies that the lower S_1 and T_1 states of compound **V** are mostly contributed by CT-2 rather than CT-3, like in 1-nitro-2-naphthylamine [10]. With X = EtO (compound **IV**), the contribution of CT-3 is small, and the long-wave band is likely to be a superposition of CT-1 and CT-2 $\pi\pi^*$ bands, as well as the $n\pi^*$ band. In polar solvents, the $n\pi^*$ contribution decreases, as evidenced by the appearance of a fluorescence band of model **VII** (vide supra).

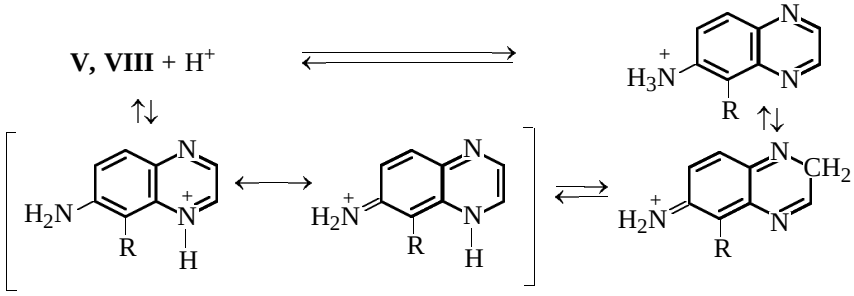
The effect of the nitro group on the photophysical properties of **I**–**V** manifests itself in a blue shift of the phosphoresce band, decrease of τ_{ph} (Table 1) [2], and, as with compound **V**, increase of the φ_{ph}/φ_f ratio (Figs. 1a and 1b, curve *2*) as a result of enhanced spin–orbit coupling. The stronger structured phosphoresce spectrum of nitro compound **V** and its slight red shift with respect to that of amine **VIII** (Figs. 1a and 1b, curve *3*) suggest perturbing effect of CT-2 on the T_1 state. Our present results together with published data [7, 11], allow the latter state of nitro derivatives **I**–**V** to be represented as a mixed $T(\pi\pi^*)$

state contributed by CT-1, CT-2, and T_1–T_2 vibronic transition. The effect of vibronic transition arises as a result of the possible additional configuration of the $T_2(n\pi^*)$ state in the presence of the nitro group [12].

Acid–base properties. The fact that the acidity of the medium affects the rate of photolysis of 5-nitroquinoxalines we revealed in [1, 2] suggests protonation of pyrazine nitrogen atoms in **I**–**VIII** and amino nitrogen in **V** and **VIII**. Table 1 presents the electronic absorption spectra of bases **I**–**VIII** and their conjugate acids in water (pH 7) and sulfuric acid. Protonation of the pyrazine ring [scheme (1)] is accompanied by disappearance of the $n\pi^*$ band of compound **I** and red shifting of $\pi\pi^*$ bands (500–2900 cm^{-1}), except for the short-wave (220–230 nm) band which preserves its position in the case of compounds **I**–**III**. The spectra of cations **IV**H^+ and **VII**H^+ acquire a new band at λ 375–380 nm, formed by the $X \rightarrow N^+$ charge transfer (CT-4) [scheme (1)].

$$\textbf{I–VIII} + H^+ \rightleftharpoons (\textbf{I–VIII})H^+. \quad (1)$$

The pK_a values [scheme (1), Table 1] show that 5-nitro substitution decreases the basicity of the pyrazine ring by 1.7–2.2 pK_a units [pK_a of quinoxaline is 0.56 [13]). Electron-donor substituents X wipe out the effect of the nitro group and enhance basicity in the series X = H < CH_3 < OC_2H_5. Protonation of amines **V** and **VIII** gives rise to a new strong absorption band at λ 460–465 nm, that is lacking in the spectrum of the 2-naphthylammonium cation (λ 275, 302 nm, sh [14]) and can be assigned to formation of quinoid structures [scheme (2)].



(2)

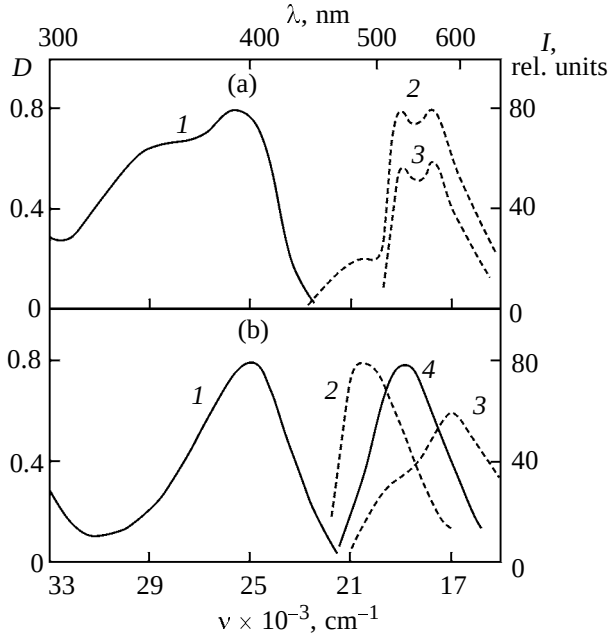
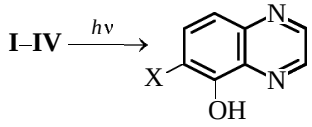


Fig. 1. Spectral characteristics of ethanolic solutions of (a) 5-nitro-6-quinoxalylamine (**V**) and (b) 6-quinoxalylamine (**VIII**) at (solid line) 295 and (dotted line) 77 K. (*1*) Long-wave absorption band, (*2*) summary luminescence spectrum, (*3*) phosphorescence, and (*4*) fluorescence (λ_{exc} 366 nm).

6-Quinoxalylamine (**VIII**) is protonated in a weakly acidic medium (pK_a 2.8) (Table 1), whereas nitro derivative **V** can only be protonated in concentrated (>90%) sulfuric acid, which can be explained by insufficient electron density on the amino and is consistent with data for the 2-naphthylamine–1-nitro-2-naphthylamine pair (pK_a 4.1 and –0.85 [15]).

Rate of photochemical reaction. The major products of the preparative photolysis of nitro compounds **I**–**IV** in acid media (see [1] and Experimental), irrespective of the nature of substituent X, are the corresponding phenols [scheme (3)].



(3)

IX–**XII**

X = H (**IX**), CH_3 (**X**), Cl (**XI**), OC_2H_5 (**XII**).

The IR spectra of hydroxyquinoxalines **IX**–**XII** contain a strong band at 3100–3300 cm^{-1} due to O–H stretching vibrations. The C^2–H, C^3–H, C^7–H, and C^8–H proton signals in the ^{1}H NMR spectra are

Table 2. Absorption and luminescence of hydroxyquinoxalines **IX**–**XII**, 295 K

Solvent	Measured value	**IX**	**X**	**XI**	**XII**
Heptane	λ_a ($\varepsilon \times 10^{-3}$)	247 (38.1), 252 (43.9), 255 (36.8), 305 sh, 318 (2.87), 325 sh	251 sh, 255 (53.3), 259 (49.3), 320 sh, 327 (4.07), 350 sh	251 sh, 255 (45.5), 259 (44.0), 315 sh, 324 (4.02), 350 sh	260 (35.4), 318 sh, 330 (2.24), 360 sh
	λ_f (φ_f)		490 ($<10^{-4}$)	490 (10^{-4})	475 (0.02)
95% ethanol	λ_a ($\varepsilon \times 10^{-3}$)	252 (37.7), 317 (2.10), 350 sh	256 (43.7), 328 (2.64), 362 sh	256 (34.4), 320 (3.27), 350 sh (1.58)	261 (32.9), 330 (2.07), 365 (1.55)
	λ_f (λ_f)			415 ($<10^{-4}$)	414 (0.04),[b] 414, 500 sh (0.01)[c]
Water	λ_a ($\varepsilon \times 10^{-3}$)	250 (35.7)	254 (40.7)	254 (29.2)	258 (31.9)
pH 7	λ_f (φ_f)	316 (3.54)	328 (3.61)	323 (4.38)	328 (2.74), 470 (0.004)
10 N H_2SO_4	λ_a ($\varepsilon \times 10^{-3}$)	262 (34.9), 338 (5.76), 415 (0.91)	267 (38.2), 343 (7.41), 425 (1.07)	267 (32.8), 343 (6.84), 425 (1.04)	273 (28.2), 348 (5.02), 445 (1.61)

[a] (φ_f) Fluorescence quantum yield; for the other denotations, see Table 1. [b] λ_{exc} 313 m. [c] λ_{exc} 366 nm.

shifted downfield from those of the parent nitro compounds (see Experiemntal).

The optical properties of hydroxyquinoxalines **IX**–**XII** are presented in Table 2. A strong (ε 3×10^4–5×10^4 l mol^{-1} cm^{-1}) characteristic absorption band is observed at 250–270 nm, as well as a luminescence band. Fluorescence, while fairly weak ($\lambda_f \le 0.02$), is characteristic of only two compounds, chloro- and ethoxy-substituted phenols **XI** and **XII**. Therewith, a two-band fluorescence is observed, containing a violet (415 nm) and a bluish-green (460–490 nm) components whose ratio is dependent on the medium and excitation energy (Table 2). A probable reason of such a behavior, along with those discussed previously [2], can be hydrolysis (solvolysis), which requires separate investigation.

Photolysis of compounds **I**–**IV** in other solvents, too, follows scheme (3). This is evidenced by the enhanced intensity of the characteristic absorption and fluorescence excitation of the corresponding phenols (Figs. 2a and 2b). Prolonged irradiation, especially at λ_{exc} 253.7 nm, produces photolysis of the phenol itself (Figs. 2a and 2b, curve *4*).

The results of photokinetic measurements [scheme (3)] are listed in Table 3. From the data for compounds **I**–**IV** we can draw the following important conclusions.

Irrespective of irradition conditions and medium, the quantum yield of quinoxalinol formation (Φ_2) most commonly increases in the series X = H < CH_3, Cl < OC_2H_5, i.e. with increasing size of the substituent (from covalent radii [16]). For the extreme members of this series (compounds **I** and **IV**), a 15-fold increase is observed (hexane, 10 N H_2SO_4). This finding provides evidence for the classical mechanism of nitro-nitrite rearrangement, according to which orthogonal location of the nitro group with respect to the aromatic ring plane in the excited state favors oxaziridine ring (transition state) formation [3]. Whether the $T_2(n\pi^*)$ state formed by p–π interaction between the nitro oxygen and aromatic system depends on the molecular geometry in the excited state. This state is unlikely if the molecule is planar.

The efficiency of photolysis on excitation into the S_4 state (λ_{exc} 253.7 nm) is higher 1.4–14-fold than on irradiation in the long-wave range (S_1 and S_2 states), implying that there are at least two mechanisms of phenol formation [2].

The efficiency of nitroquinoxaline consumption Φ_1 is higher that the efficiency of phenol formation Φ_2, except for sulfuric acid solutions of compounds **III** and **IV**. Therewith, Φ_1 only slightly depends on solvent, suggesting that the destruction processes are largely intramolecular in nature (Figs. 2a and 2b).

The Φ_2 values for conjugate acids **I**H$^+$–**IV**H$^+$ are 3–30 higher than those for bases **I**–**IV**. This effect can be explained by two reasons. The first is that protonation of the pyrazine nucleus radically changes the arrangement of energy levels of the parent nitro derivative and its photophysical characteristics [2]. Protonation renders the nitroquinoxaline similar to the corresponding monoprotonated quinoline [scheme (1)] or diporotonated naphthalene [scheme (4)].

$$(\mathbf{I}\text{–}\mathbf{IV})H^+(S_1) + H^+ \rightleftarrows (\mathbf{I}\text{–}\mathbf{IV})H_2^{2+}(S_1). \qquad (4)$$

Evidence for this assumption comes from the fact

Table 3. Quantum yields of quinoxaline consumption (Φ_1) and hydroxyquinoxaline formation (Φ_2)[a]

Comp. no.	E_T	λ_{exc}	Heptane		95% ethanol		Water, pH 7		10 N H_2SO_4	
			Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2
I	21.2	253.7	11	10	11	5.1	11	5.9	60	37
		313	1.0	0.7	1.7	2.2	1.5	0.7	70	24
II	21.1	253.7	26	12	30	12	28	23	150	88
		313	5.8	1.4	8.8	6.8	7.5	3.7	113	62
III	20.8	253.7	31	14	27	20	28	23	85	95
		313	7.3	0.7	24	17	7.6	5.1	100	96
IV	20.5	253.7	54	23	66	35	14[b]	19	660	570
		334	17	9.3	25	12	7.2[b]	8.5	160	190
V	19.0	253.7			9.4	3.5			21	
		406			1.6	0.7			11	

[a] (E_T) Energy of the T_1 state ($\times 10^{-3}$), cm^{-1} (from phosphorescence spectra); (λ_{exc}) excitation wavelength; Φ_1, Φ_2 ($\times 10^4$).
[b] The Φ_1 values are underestimated because of the strong overlap of absorption bands of compounds **IV** and **XII**.

that the basicity of quinoxaline is strongly enhanced by photoexcitation [$\Delta pK_a(S_1)$ 7.7] [17]. The second reason is that protonation [schemes (1) and (4)] enhances the photochemical activity of the nitro group. As known [18], increased contribution of the charge-transfer configuration involving the latter inhibits its photoreactions by attenuating electrophilic properties of photoexcited states. Protonation of the pyrazine ring generates a new strong electron-acceptor center, which cancels the electronic effect of the nitro group (in our case, CT-2 and CT-3) and enhances its reactivity. Therefore, the *ortho*-effect on Φ_2 in 10 N H_2SO_4 is most pronounced: H < CH_3 < Cl < OC_2H_5 (Table 3).

The photolysis rate is inversely related to E_T at the latter spanning the range 21000–20500 cm^{-1}, even

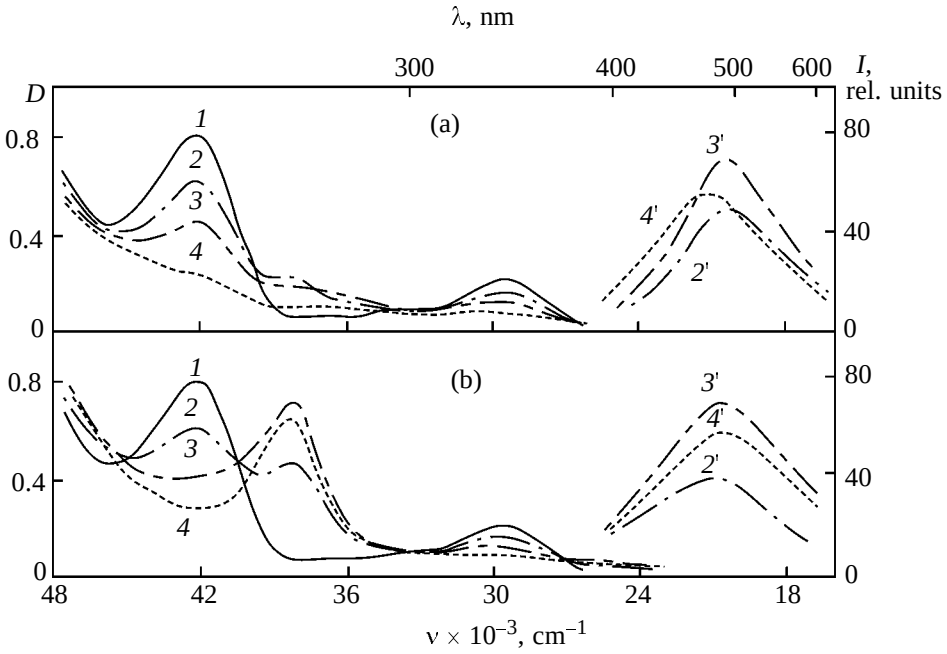


Fig. 2. Spectrochemical changes in the course of photolysis of alcoholic 6-ethoxy-5-nitroquinoxaline (**IV**) under irradiation at (a) λ_{exc} 253.7 and (b) 330–380 nm (BS6 + UFS6). (*1*) Absorption spectra of the initial solution, (*2*–*4*) absorption spectra of photolysates, and (*2*′–*4*′) luminescence spectra of photolysates.

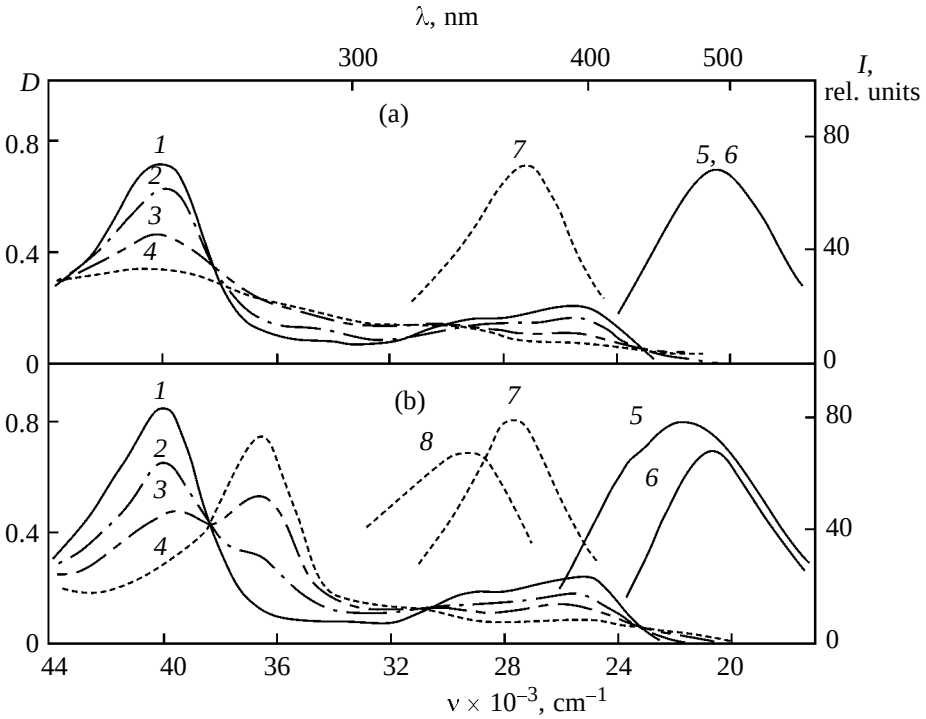


Fig. 3. Spectrochemical changes in the course of photolysis of alcohol solutions of 6-amino-5-nitroquinoxaline (**V**) under irradiation at (a) 253.7 and (b) 360–430 nm (CC8). (*1*) Absorption spectrum of the initial solution, (*2–4*) current spectra of photolysates, (*5*, *6*) fluorescence spectrum of photolysate no. 4 at λ_{exc} 366 and 406 nm, respectively, and (*7*, *8*) fluorescence excitation spectrum of λ_{sound} 500 and 400 nm, respectively.

though this is not a key factor [cf. Φ_1 and Φ_2 for compounds **I** and **II**).

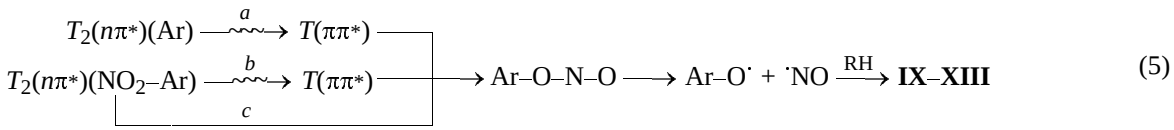
It follows from the aforesaid that the photochemical activity of compounds **I**–**V** is affected, along with the size of substituent X, by the CT-2 and CT-3 processes. Indirect evidence for this conclusion is provided by the fact that compound **IV** has lower Φ_2 values in ethanol (λ_{exc} 313 and 334 nm) and water (λ_{exc} 253.7 nm) than compound **III** (Table 3), on account of stabilization of photoexcited states involing the CT-3 configuration in polar media and enhances coplanarity of the NO_2–Ar system in **IV**.

An especially strong effect of electronic interactions on photochemical properties in observed in amine **V** (Table 3, Figs. 3a and 3b). This compound has the lowest E_S and E_T (23000 and 19000 cm^{-1}, respectively), the red absorption boundary near 440 nm, and the lowest photochemical activity comparing with that of 5-nitroquinoxaline (**I**). Since 6-amino-5-hydroxyquinoxaline proved difficult to isolate, its optical parameters were obtained by spectral luminescent measurements in an irradiated solution. The spectrochemical changes were generally similar to those observed with the other nitro derivatives, i.e. decreased intensity of the short-wave ππ* band (250 nm), characteristic absorption near 274 nm (36500 cm^{-1}), and fluorescence excitation at 380–600 nm with its maximum at 490 nm (~20400 cm^{-1}). The observation of similar fluorescence bands and fluorescence excitation spectra (λ_a 370 nm) in various photolysis conditions suggests similar final products (Figs. 3a and 3b, curves *6* and *7*). However, under short-wave UV irradiation the aminohydroxyquinoxaline gradually decomposed to form colorless bloomless products. The hyprochromic and hypsofluoric shifts of the $S_0 \rightleftarrows S_1$ transition compared with 5-aminoquinoxaline (**VIII**) ($\Delta\lambda_a$ –24 nm and $\Delta\lambda_f$ –34 nm) are consistent with unidirectional moments of transitions involving amino and hydroxy groups. The ε values for the phenol were determined upon limiting exposure of nitro compound **V** to the long-wave absorption wavelengths at which the most "pure" photolysis occurred (Fig. 3b). The spectral luminescent analysis of the final reaction product revealed a side reaction involving no nitro–nitrite rearrangement (Fig. 3b, curves *5* and *8*). However, this reaction contributes little into the overall photoreaction result, as evidenced by the appearance of three isosbestic points (260, 326, and 421 nm) (Fig 3b, curves *1–4*). The

concentration of the final reaction product was determined as a difference between the initial and final concentrations of the starting compound **V**, phenol absorption being neglected. The resulting ε value of 4.16×10^4 l mol^{-1} cm^{-1} is consistent with those for the other hydroxyquinoxalines (Table 2).

The Φ_1 and Φ_2 values (Table 3) proved the lowest, providing evidence for the second and third conclusions (vide supra) but contradicting the first in view of the substituent size (H < CH_3, Cl, NH_2 < OC_2H_5) and photochemical activity (H, NH_2 < CH_3, Cl < OC_2H_5) series. This contradiction can be explained by electronic effects associated with the CT-2 and CT-3 processes in nitramine **V**. As a result, (a) the lifetime of the reactive state gets shorter, (b) the tendency for planarization of the NO_2–Ar system enhances, thus decreasing the probability of population of the $T(n\pi^*)$ level, and (c) the molecular level diagram changes, in particular, the T level gets lower.

In view of the aforesaid and data in [19], scheme (3) in [2] (λ_{exc} > 300 nm) can be complemented and represented as scheme (5).



(5)

The nitro–nitrite rearrangement may involve two alternative $T(n\pi^*)$ levels, depending on the size and electron-donor properties of substituent X and on the medium. Paths *a* and *b* are radiationless transitions of the same type, whereas path *c* is a photochemical process associated with oxaziridine ring cleavage. The limiting case (path *a*) is realized primarily with compounds **I** and **V**, as well as ethoxy derivative **IV** in polar solvents.

At λ_{exc} 253.7 nm scheme (5) is augmented with homolytic NO_2–Ar bond rupture with the participation of locally excited $S(n\pi^*)$ and $T(n\pi^*)$ states of the nitro group {see scheme (4) in [2]}.

EXPERIMENTAL

The IR spectra of compounds **III**, **IX**, **XI**, and **XII** were measured on a UR-20 instrument in KBr. The ^{1}H NMR spectra of compound **IV** were obtained on a Tesla BS-497 (100 MHz) instrument, and the ^{1}H NMR spectra of compounds **XI** and **XII**, on a Bruker AM-500 (500 MHz) instrument. The electronic absorption spectra were obtained on a Specord M-40 instrument in quartz cells (layer length 1 or 0.1 cm).

The equipment and procedures for liminescence and photochemical measurements were described previously [2]. The light sorce was a mercury lamp from which the 406-nm line was isolated using a combination of the PS13 and ZhS10 filters, isolation purity 99.5%.

The melting points were measured in capillaries, no corrections were applied. Elemental analysis was performed on a Hewlett–Packard C, H, N analyzer. Thin-layer chromatography was performed on Silufol UV-254 plates (development in UV light or iodine vapor), eluent ethyl acetate. The pK_a values were determined by spectrophotometry [20].

Preparative photolyses of quinoxaline and compounds **II**–**IV** was performed as described in [1, 2].

Analytical grade 2,4-dinitroaniline, 4-chloro-2-nitroaniline (Azoamine red 2C), 4-ethoxyacetanilide (phenacetin), and glyoxal bisulfite were used as starting materials.

5-Nitroquinoxaline (**I**) and 6-methyl-5-nitroquinoxaline (**II**) were synthesized as described in [1].

4-Chloro-3-nitro-1,2-phenylenediamine. 4-Chloro-2-nitroaniline was hydrogenated on Raney nickel in 2-propanol by the procedure described in [21]. The resulting diamine was brought *in situ* into condensation with SeO_2. The subsequent workup, sublimation at atmospheric pressure, and crystallization from 2-propanol gave a pure 5-chlorobenzo[2.1.3]selenadiazole, yield 66%, mp 119–121°C [22]. The product was nitrated with a mixture of $NaNO_3$ and conc. H_2SO_4 at 100°C by the procedure in [23] to obtain 5-chloro-4-nitrobenzo[2.1.3]selenadiazole as yellow crystals, yield 90%, mp 222–225°C. The nitro derivative was reduced with a mixture of 50% HI and 35% HCl by the procedure in [24] to obtain the diamine, yield 52% (total yield 31%), R_f 0.75.

6-Chloro-5-nitroquioxaline (III). A hot solution of 5.7 g of glyoxal bisulfite in 50 ml of water was added to a boiling solution of 3.5 g of 4-chloro-3-nitro-1,2-phenylenediamine in 50 ml of ethanol. The reaction mixture was heated for 2 h on a boiling water

bath, after which 2.5 g of glyoxal bisulfite was added and heating was continued for an additional 1 h. After cooling, the red solution was evaporated to dryness, the residue was ground and sublimed in a vacuum to obtain 2.52 g (64%) of the reaction product as light crystals, mp 120–132°C. It was crystallized from 100 ml of 50% aqueous ethanol with charcoal to obtain 1.86 g (48%) of a pure compound **III**, mp 134–136°C [24], R_f 0.8–0.9. IR spectrum, ν, cm^{-1}: 1555 s, 1375 s (NO_2). Found, %: C 45.90; H 2.09; N 20.22. $C_8H_4ClN_3O_2$. Calculated, %: C 45.82; H 1.91; N 20.05.

6-Chloroquinoxaline (VI). 4-Chloro-1,2-phenylenediamine obtained by hydrogenation of 4-chloro-2-nitroaniline was brought into condensation with glyoxal bisulfite (see synthesis of 4-chloro-3-nitro-1,2-phenylenediamine). Crystallization from ethanol followed by sublimation gave compound **VI**, yield 55%, mp 63–64°C [25].

6-Ethoxyquinoxaline (VII). 4-Ethoxy-2-nitroaniline was prepared (yield 92%) by nitration of 4-ethoxyacetanilide with fuming HNO_3 (d 1.5 g/cm^3) in AcOH at 5–20°C, followed by hydrolysis of the resulting acetyl derivative with 50% H_2SO_4 at 70–80°C, mp 108–112°C [26].

4-Ethoxy-2-nitroaniline, 15.1 g, suspended in 100 ml of 2-propanol was hydrogenated on Raney nickel by the procedure described in [21]. The reaction mixture was then filtered to remove the catalyst, diluted with a hot solution of 23.4 g of glyoxal bisulfite in 100 ml of water, refluxed for 1 h, and subjected to a water-jet-pump vacuum to remove 50 ml of the solvent. The residue was cooled, diluted with water to 2 l, and treated with $CHCl_3$ (8 × 80 ml). The aqueous phase was distilled at atmospheric pressure, and the distillate was treated with $CHCl_3$ (4 × 80 ml). The combined extracts were dried with Na_2SO_4, the solvent was removed by distillation, and the dry black residue was sublimed in a vacuum to obtain 11.4 g (79%) of a yellowish brown material. Crystallization from 2-propanol (35 ml) gave 9.7 g (68%) of a yellowish material, mp 78–81°C. Successive crystallizations from 2-propanol and hexane gave a pure 6-ethoxyquinoxaline (**VII**) as colorless needles, mp 80–81°C [25], R_f 0.45–0.55.

6-Ethoxy-5-nitroquinoxaline (IV) was prepared by nitration of 6-ethoxyquinoxaline by a procedure similar to that described for its 6-methoxy analog [27]. Ground KNO_3, 1.92 g, was added in small portions to a stirred solution of 3 g of 6-ethoxyquinoxaline in 20 ml of conc. H_2SO_4. The mixture was stirred until KNO_3 had dissolved completely, allowed to stand for 4 h at room temperature, and then poured into 300 ml of water with ice. The white crystals that formed were filtered off, washed in succession with water (5–6 times), aqueous $NaHCO_3$, and water (3–4 times), and then dried at 60°C to obtain 3.02 g (80%) of a crude reaction product, mp 142–145°C. Double crystallization from 2-propanol (150 ml) gave 2.21 g (58%) of the nitro derivative, mp 150–152°C. A pure compound **IV** was obtained by crystallization of the latter sample from hexane, mp 151–152°C, R_f 0.4–0.6. ^1H NMR spectrum (acetone-d_6, internal reference HMSO, δ 0.05 ppm), δ, ppm: 1.43 t and 4.49 q (3H and 2H, 6-OC_2H_5, J 7 Hz), 8.93 s (2H, 2-H and 3-H), 8.26 and 7.94 (2H, 7-H and 8-H, *AB*, J 9.5 Hz). Found, %: C 54.85; H 4.29; N 19.21. $C_{10}H_9N_3O_3$. Calculated, %: C 54.79; H 4.11; N 19.18.

6-Quinoxalylamine (VIII). 2,4-Dinitroaniline, 17 g, suspended in 100 ml of 2-propanol was hydrogenated on Raney nickel by the procedure described in [21]. The reaction mixture was then diluted with a solution of 22 g of glyoxal bisulfite in 100 ml of water, heated for 2 h at 50–60°C, and slowly evaporated to dryness. The residue was treated with hexane in a Soxhlet apparatus. Evaporation of the extracts gave 2.51 g (19%) of the product as yellow needles, mp 152–156°C. Successive crystallizations from ethanol and hexane gave a pure compound **VIII**, mp 157–158°C [25].

5-Nitro-6-quinoxalylamine (V). Amine **VIII**, 1.36 g, was nitrated by the procedure described in [28] with a mixture of 14 ml of conc. H_2SO_4 and 0.43 ml of HNO_3 (d 1.5 g/cm^3) for 1 day. The reaction mixture was poured into 60 ml of water, neutralized with 25% ammonia, and the reaction product (dark orange precipitate) was filtered off, dried, and sublimed in a vacuum to obtain 0.33 g (25%) of a crude compound **V**, mp 213–221°C. Successive crystallizations from ethanol (two times) and ethyl acetate gave a pure compound **V** as yellow crystals, mp 224–228°C [28].

5-Hydroxyquinoxaline (IX) was prepared by photochemical hydroxylation of quinoxaline by a procedure similar to that described for 5-hydroxy-2,3,6-trimethylquinoxaline [2]. The combined photolysates were neutralized with 17.5 N NaOH, after which 1 g of $NaHCO_3$ was added, and the mixture was treated with $CHCl_3$ (6 × 50 ml), the extract was dried with Na_2SO_4, the solvent was removed by vacuum distillation, and the dark residue was dried in a dessicator over P_2O_5. The dry residue was sublimed in a vacuum, recrystallized from ethanol, and repeatedly sublimed in a vacuum to obtain a pure alcohol **IX** as colorless needles, yield 15%, mp 101–102°C [29]. IR spectrum, ν, cm^{-1}: 3340 s (assoc. OH). Found, %: C 65.67; H 4.31; N 19.20. $C_8H_6N_2O$. Calculated, %: C 65.76; H 4.11; N 19.18.

Photolysis of nitroquinoxalines II–IV. Nitro compound, 0.20 g, was dissolved in 8.4 ml of conc. H_2SO_4, water and ethanol (150 ml each) were added, and the mixture was stirred until the precipitate that formed dissolved completely. The solution was irradiated until the new absorption band no longer grew (λ_a 250–265 nm). The protoreaction progress was followed by the absorption spectra of samples of the reaction mixture, duluted 100 times with 0.2 N H_2SO_4. The photolysate was neutralized with a solution of 12 g of NaOH in 50 ml of water and 0.5 g of $NaHCO_3$ and treated with chloroform (5×30 ml). The extract was washed with water (5×30 ml) and dried with Na_2SO_4. The solvent was removed in a water-jet-pump vacuum, and the residue was dried in a dessicator over P_2O_5. The dried residues were treated by procedures specific for each compound.

5-Hydroxy-6-methylquinoxaline (X). A brown tarry dry residue, 0.17 g, resulting from the photolysis of nitro compound **II** was sublimed in a vacuum to obtain 0.11 g (65%) of the reaction product as yellow crystals, mp 80–91°C. Recrystallization of a 0.10-g portion of the product from 5 ml of 50% aqueous ethanol gave 0.04 g of compound **X** as colorless needles, mp 91–93°C [1]. The melting point did not change after vacuum sublimation, R_f 0.65–0.75.

6-Chloro-5-hydroxyquinoxaline (XI). A greenish-brown dry residue, 0.16 g, resulting from the photolysis of nitro compound **III**, was sublimed in a vacuum to obtain 0.11 g (64%) of the reaction product as green crystals, mp 129–137°C. Crystallization from 50% aqueous ethanol gave a brown material with a lower melting point. Repeated vacuum sublimation gave 0.09 g of compound **XI** as colorless neediles, mp 135–137°C, R_f 0.55–0.65. IR spectrum, ν, cm^{-1}: 3075 s., br. (assoc. OH). ^1H NMR spectrum [CF_3COO–$CDCl_3$, 1 : 1 (v/v), external reference TMS), δ, ppm: 9.37 and 9.48 (2H, 2-H and 3-H, *AB*, *J* 3 Hz), 8.03 and 8.26 (2H, 7-H and 8-H, AB, *J* 9 Hz). Found, %: C 53.11; H 2.80; N 15.65. $C_8H_5ClN_2O$. Calculated, %: C 53.19; H 2.77; N 15.51.

6-Ethoxy-5-hydroxyquinoxaline (XII). A greenish brown tarry dry residue, 0.16 g, resulting from the photolysis of nitro compound **IV**, that had crystallized in part within several days, was sublimed in a vacuum to obtain 0.08 g (46%) of the reaction product as a yellow semicrystalline material which melted completely at 94°C and got orange when handled in air. Repeated vacuum sublimation gave compound **XII** as yellow crystals, mp 100–106°C, R_f 0.5–0.6. IR spectrum, ν, cm^{-1}: 3320 s (assoc.OH). ^1H NMR spectrum [CF_3COOH–$CDCl_3$ (1 : 1 (v/v), xternal reference TMS), δ, ppm: 1.63 t and 4.55 q (3H and 2H, 6-OC_2H_5, *J* 7.5 Hz), 9.25 and 9.31 (2H, 2-H and 3-H, *AB*, *J* 3 Hz), 8.12 and 8.20 (2H, 7-H and 8-H, *AB*, *J* 9 Hz).

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