ELECTRONIC SPECTRA OF QUINOXALINE 1-N-OXIDES

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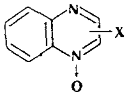
The nature of the $\pi \rightarrow \pi^*$ transitions in the spectra of quinoxaline 1-N-oxides as compared with unoxidized quinoxalines was examined on the basis of an experimental study and calculation by the Pariser–Parr–Pople configurational interaction method.

We have measured the UV spectra of quinoxaline 1-N-oxides (I-IX) in n-heptane, ethanol, and water. The electronic structures and spectra were calculated for I-V by the Pariser–Parr–Pople method with allowance for interaction of nine singly excited configurations.



I-IX

I X=H; II X=2-Cl; III X=3-Cl; IV X=2-OCH_3; V X=3-OCH_3; VI X=2-$COOCH_3$;
VII X=3-$COOC_2H_5$; VIII X=2-NH_2; IX X=3-NH_2

Three $\pi \rightarrow \pi^*$ transitions at 316 nm (ε=5840), 280 nm (ε=2600), and 232 nm (ε=26,700), which are of the ^1L_b, ^1L_a, and ^1B_b types, respectively, according to the Platte classification [1-3], were isolated in the electronic spectrum of quinoxaline in nonpolar media at > 210 nm. The ^1L_b and ^1L_a bands are overlapped to a considerable degree. In addition to the absorption regions characteristic for quinoxaline, the spectrum of quinoxaline 1-N-oxide (I) in heptane (see Fig. 1 and Table 1) contain bands at 248-254 nm (ε=13,200-16,000) and 347 nm (ε=9100). Their high intensities make it possible to assign these bands to $\pi \rightarrow \pi^*$ transitions. As the polarity of the solvent increases, both bands undergo a hypsochromic shift and are not observed in the spectrum of an aqueous solution. It is known [4] that a hypsochromic shift as the polarity of the medium increases is a characteristic property of the $\pi \rightarrow \pi^*$ bands of aromatic N-oxides. This is associated with charge transfer from the oxygen atom of the N→O group to the heteroring on passing from the ground state to the excited states. When heptane is replaced by water, a band appears at 290 nm (ε=5000) in the spectrum of I, whereas the absorption at 320-337 nm is retained and undergoes only a certain decrease in the intensity and weakening of the vibrational structure. It might be assumed that the absorption at 300-337 nm in heptane is due to two overlapped bands. Thus the spectrum of quinoxaline 1-N-oxide in the investigated region consists of five $\pi \rightarrow \pi^*$ bands, which are numbered in Table 1 in order of increasing energy. The assignment of the bands in the spectra of 1-N-oxides of monosubstituted quinoxalines (II-VII) were sim-

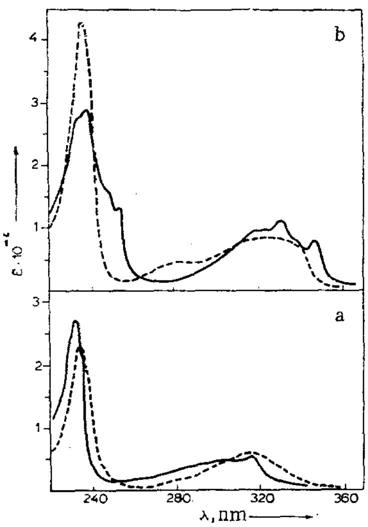


Fig. 1. UV Spectra of quinoxaline (A) and its 1-N-oxide (B) in n-heptane (——) and water (---).

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TABLE 1. UV Spectra of Quinoxaline 1-N-Oxide in n-Heptane

Compound	$\pi \to \pi^*$ bands, λ_{max}, nm (log ε)			
	1	2, 3	4	5
I	347 (3,96)	337 (3,88) 331 (4,04) 324 (3,99) 318 (3,98) 312 (3,89)	254 (4,12) 248 (4,20)	238 (4,46) 236 (4,45)
II		338 (3,89) 323 (3,96) 311 (3,83)	255 (4,46)	247 (4,49) 242 (4,49)
III		351 (3,77) 335 (3,82) 321 (3,99) 310 (3,90)	255 (4,34)	244 (4,60)
IV	367 (3,14)	346 (3,75) 331 (3,87)	252 (4,49)	240 (4,34)
V		354 (3,69) 338 (3,73) 324 (3,60) 311 (3,99) 299 (3,88) 290 (3,72) 280 (3,56)	247 (4,54)	242 (4,47) 221 (4,21)
VI	357 (3,49)	340 (3,64) 325 (3,85) 315 (3,81)	258 (4,37)	242 (4,51)
VII	365 (3,59)	345 (3,94) 331 (3,97) 320 (3,84)	264 (4,30) 257 (4,39)	242 (4,41) 237 (4,32)

TABLE 2. Vibrational Structure of the Overlapped Bands in the Spectra of Quinoxaline and Its 1-N-Oxide (cm^{-1})

Transitions	Quinoxaline [3]			Quinoxaline 1-N-oxide		
	ν	Δ′ν	Δ″ν	ν	Δ′ν	Δ″ν
0—0	31600			29670		
0—1	32150 32900	1300	750	30210 30860	1190	650
0—2	33500 34200	1300	700	31480 32050	1190	570

TABLE 3. Calculated and Experimentally Observed Spectra of Quinoxaline 1-N-oxides

Compound	$\pi \to \pi^*$ transitions	Exptl.		Calc.	
		ΔE, eV	ε	ΔE, eV	f
I	1	3,58	9100	3,55	0,33
	2	3,70	9800	3,79	0,07
	3*			4,29	0,28
	4	5,00	16000	4,98	0,75
	5	5,26	29000	5,26	0,81
II	1*			3,61	0,20
	2	3,83	9100	3,76	0,08
	3*			4,26	0,23
	4	4,80	29000	4,87	0,72
	5	5,13	31000	5,20	0,74
III	1*			3,60	0,16
	2	3,53	9800	3,81	0,06
	3*			4,36	0,34
	4	4,81	22000	4,99	0,80
	5	5,09	40000	5,29	0,88
IV	1	3,38	1460	3,61	0,21
	2	3,58	7400	3,76	0,08
	3*			4,26	0,23
	4	4,93	31000	4,86	0,82
	5	5,17	22000	5,20	0,76
V	1*			3,60	0,16
	2	3,50	4000	3,81	0,06
	3	4,29	5200	4,36	0,33
	4	5,03	35000	4,99	0,71
	5	5,13	26000	5,28	0,67

* The 2 band is overlapped in the experimental spectrum.

ilarly assigned. The spectra of 2- and 3-aminoquinoxaline 1-N-oxides (VIII and IX) in heptane were not measured because of their exceptionally low solubilities.

The overlapped 2 and 3 bands in the spectra of the N-oxides are similar to the ^1L_b and ^1L_a bands in the spectra of the corresponding unoxidized quinoxalines [3] with respect to their position, intensity, character of their vibrational structure, and substitution effects. Thus two vibrations with $\Delta'\nu = 1190$ cm^{-1} and $\Delta''\nu = 570$–650 cm^{-1}, which are close to the two vibrational quanta in the spectrum of quinoxaline ($\Delta'\nu = 1300$ cm^{-1} and $\Delta''\nu = 700$–750 cm^{-1}), appear in the spectrum of I (see Table 2). Inasmuch as the vibrational structure of the overlapped bands of quinoxaline are related to the long-wave ^1L_b band [3], the fine structure of the overlapped 2 and 3 bands in the spectrum of I can be assigned to the 2 band. Overlapping of the ^1L_b and ^1L_a bands is weakened in the spectrum of 2-methoxy-quinoxaline [3] as compared with quinoxaline.

TABLE 4. Contributions of the AO of the Oxygen Atom of the N→O Group to the MO of Quinoxaline 1-N-Oxide*

Compound	$m-2$	$m-1$	m	$m+1$	$m+3$
I	0,012	0,155	0,432	0,185	0,016
II	0,104	0,039	0,476	0,170	0,018
III	0,110	0,079	0,415	0,185	0,018
IV	0,108	0,036	0,476	0,169	0,018
V	0,109	0,081	0,415	0,185	0,018

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* For I-V, the contribution of the AO of the oxygen atom to the MO is $\Psi_{m+2}^{NO} \approx 0$.

TABLE 5. Contributions of the AO of the Heteroring (φ_i) to the MO of Quinoxaline, 2-Chloroquinoxaline (Ψ_j), and Their 1-N-Oxides (Ψ_j^{NO})

X	AO	Quinoxalines		Quinoxaline N-oxides	
		MO	Σc^2	MO	Σc^2
H	5,6,7,8	m	0,650	m−1	0,647
	2,3,6,7,9,10	m−1	0,996	m−2	0,965
	1,2,3,4	m+1	0,746	m+1	0,586
	5,6,7,8,9,10	m+2	0,998	m+2	0,996
	2,3,6,7,9,10	m+3	0,892	m+3	0,887
2-Cl	5,6,7,8	m	0,710	m−2	0,726
	2,3,6,7,9,10	m−1	0,990	m−1	0,867
	1,2,3,4,5,8	m+1	0,870	m+1	0,713
	2,3,6,7,9,10	m+2	0,988	m+2	0,985
	5,6,7,8,9,10	m+3	0,826	m+3	0,882

TABLE 6. Predominant Configurations in the π→π* Transitions of Quinoxaline 1-N-Oxides

Configuration	Quinoxaline N-oxide		Monosubstituted quinoxaline 1-N-oxide				
	transitions	T^2	transitions	T^2			
				II	III	IV	V
$\Psi_m^{NO} \rightarrow \Psi_{m+1}^{NO}$	1	0,720	1	0,804	0,689	0,804	0,692
$\Psi_{m-1}^{NO} \rightarrow \Psi_{m+1}^{NO}$	3	0,674	2	0,483	0,263	0,500	0,260
$\Psi_{m-2}^{NO} \rightarrow \Psi_{m+1}^{NO}$	2	0,556	3	0,608	0,537	0,629	0,524
$\Psi_m^{NO} \rightarrow \Psi_{m+2}^{NO}$	4	0,487	4	0,585	0,523	0,585	0,511
$\Psi_m^{NO} \rightarrow \Psi_{m+3}^{NO}$	5	0,592	5	0,771	0,610	0,774	0,599

The introduction of a methoxy group into the 3 position of quinoxaline 1-N-oxide has a similar effect on the relative position of the 2 and 3 bands. Absorption maxima at 280-300 nm, which can be assigned to the 3 band, appear in the spectrum of V. Like the ^1L_b band of the unoxidized base [3], the 2 band of quinoxaline 1-N-oxide is shifted to the long-wave region under the influence of substitution in the pyrazine ring, and the magnitude of the bathochromic shift in both series of compounds increases as the electron-donor properties of the substituent increase. The 5 band of quinoxaline 1-N-oxide is only slightly sensitive to the effects of the medium and substitution. With respect to these features and also with respect to its intensity and position in the spectrum, it displays a similarity to the ^1B_b band of quinoxaline. The 1 and 4 bands do not have analogies in unoxidized quinoxalines. They are easily identified from the characteristic hypsochromic shift as the polarity of the solvent increases. A 4 band is observed in the spectra of all of the investigated compounds in heptane. The intensity of the 1 band in the spectra of 1-N-oxides of substituted quinoxalines decreases, and it is probably overlapped by the 2 band in the spectra of II, III, and V.

In agreement with the experimental observations, the calculation reveals five π→π* transitions > 210 nm (see Table 3). The calculated energies of the transitions in all of the compounds are in satisfactory agreement with the observed values. The ΔE_{exp} value of the 3 band (4.29 eV) found from the spectrum of 3-methoxyquinoxaline 1-N-oxide (V) is in satisfactory agreement with the calculated energy of the third electronic transition (ΔE_{th} = 4.36 eV). A comparison of the results of the calculation of the electronic structures and spectra of quinoxaline and its monosubstituted derivatives [5] with the values for the corresponding N-oxides showed that 1-N-oxidation leads to the appearance of an additional bonding molecular orbital (MO), whereas the number of antibonding MO does not change. From an analysis of the coefficients

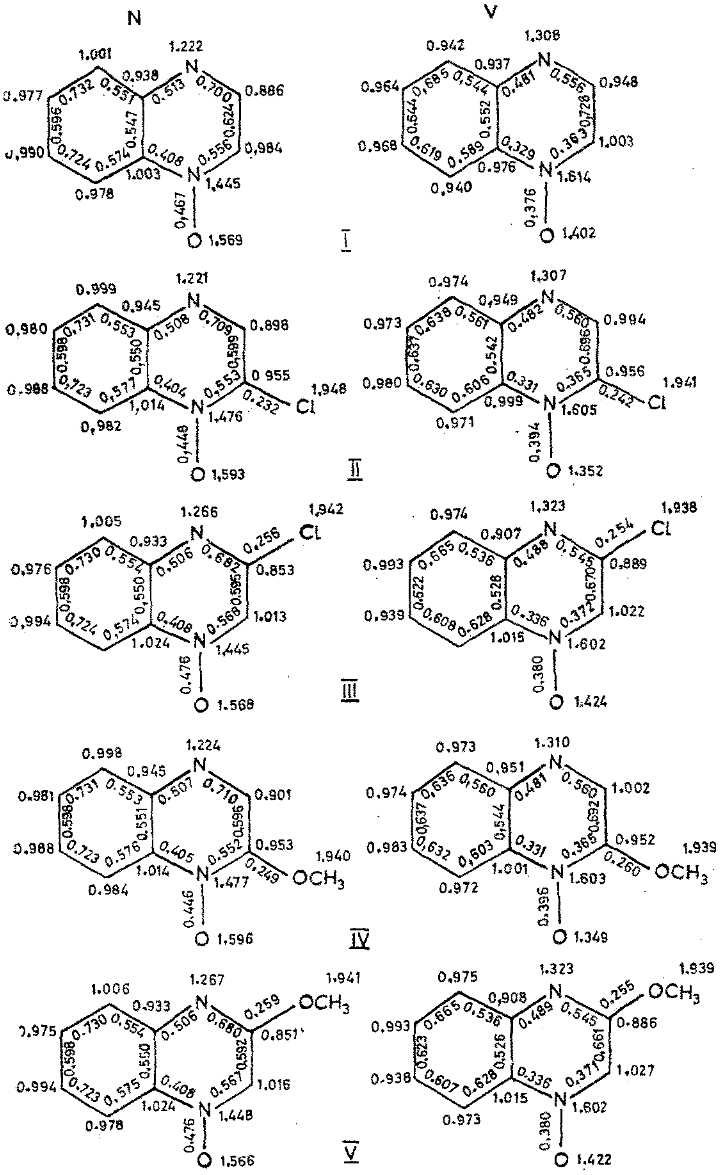

Fig. 2. Molecular diagrams of the ground (N) and first excited (V) states of quinoxaline 1-N-oxides (I-V).

of the atomic orbital (AO) of the oxygen atom of the N→O group to the MO of quinoxaline 1-N-oxides (Table 4) it follows that ~80% of its contribution is distributed among three higher occupied and three lower vacant MO. The contribution of the AO of the oxygen atom to the higher occupied MO of the investigated N-oxides ($\Psi_m{}^{NO}$) is 40-50%, and this MO consequently cannot have an analog in the unoxidized systems. The AO of the quinoxaline two-membered ring that make the maximum contributions to the MO of quinoxalines and their 1-N-oxides are presented in Table 5. It is apparent from these data that the bonding MO of quinoxaline 1-N-oxide ($\Psi_{m-1}{}^{NO}$ and $\Psi_{m-2}{}^{NO}$) display a similarity to the bonding MO of quinoxaline (Ψ_m and Ψ_{m-1}, respectively). Thus the composition of the $\Psi_{m-1}{}^{NO}$ and Ψ_m MO includes a 65% contribution from the AO of the benzene ring. The AO of the carbon bridge (C_9, C_{10}) and the carbon atoms in the 2, 3, 6 and 7 positions of the two-ring system make the predominant contribution to the $\Psi_{m-2}{}^{NO}$ and Ψ_{m-1} MO (96.5 and 99.6%). With respect to the AO contributions, there is an analogy between the three lower vacant MO of quinoxaline (Ψ_{m+1}, Ψ_{m+2}, and Ψ_{m+3}) and its 1-N-oxide ($\Psi_{m+1}{}^{NO}$, $\Psi_{m+2}{}^{NO}$, and $\Psi_{m+3}{}^{NO}$). The parallelism in the MO is retained for monosubstituted quinoxalines and their 1-N-oxides, but the sequence of the corresponding (with respect to the AO contributions) bonding MO of the N-oxides and the unoxidized bases changes. In the case of the chloro derivatives it was shown that the Ψ_m and Ψ_{m-1} MO of 2-substituted quinoxalines are similar to the $\Psi_{m-2}{}^{NO}$ and $\Psi_{m-1}{}^{NO}$ MO of the 1-N-oxides, respectively.

TABLE 7. Coulombic and Resonance Parameters

Atom	γ_{qq}, eV	Bond	l (Å)	β_{qp}, eV
C	11,13	(C—C) ring	1,39	−2,39
N	12,34	(C—N) ring	1,36	−2,30
N→(O)	16,76	N→O	1,27	−2,60
O←(N)	18,08			
O(CH_3)	14,38	C—O(CH_3)	1,50	−2,24
Cl	11,25	C—Cl	1,70	−2,27

TABLE 8. UV Spectra of Quinoxaline 1-N-Oxides in Ethanol and Water*

Compound	λ_{max}, nm (log ε)
I	341 (3,84), 324 (3,93), 238 (4,53)
	339 (3,88), 325 (3,92), 290 (3,70), 236 (4,62)
II	341 (3,77), 322 (3,95), 246 (4,66)
	343 (3,88), 328—322 (3,98), ~298, 244 (4,76)
III	350 (3,77), 334 (3,82), 321 (3,98), 310 (3,87), 296 (3,73), 246 (4,66), 244 (4,64)
	349 (3,92), 335 (3,84), 321 (3,87), 310 (3,82), 290 (3,77), 244 (4,68)
IV	355 (3,81), 341 (3,83), 325 (3,94), 245 (4,69)
	352 (3,82), 340 (3,86), 322 (3,95), ~290, 243 (4,71)
V	354 (3,72), 340 (3,74), 306 (3,80), 296 (3,84), 288 (3,78), 246 (4,47), 222 (4,33)
	354 (3,70), 343 (3,73), 303 (3,72), 294 (3,75), 281—275 (3,77), 245 (4,40), 222 (4,38)
VI	342 (3,71), 325 (3,84), 315 (3,82), 246 (4,53)
	341 (3,76), 327 (3,81), ~300, 275 (3,77), 245 (4,40), 222 (4,38)
VII	344 (3,94), 332 (3,98), 250 (4,49)
	344 (3,94), 333 (3,98), 250 (4,63)
VIII	379 (3,77), 315—307 (3,55), 252 (4,62)
	369 (3,77), 313—304 (3,60), 248 (4,64)
IX	370 (3,68), 312 (3,72), 301 (3,79), 256 (4,34), 234 (4,41)
	371 (3,76), 311 (3,64), 300 (3,68), 256 (4,31), 232 (4,10)

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* The upper line pertains to spectra of 96% ethanol solutions, and the lower line pertains to water solutions.

It is known [5] that configurations corresponding to the one-electron transitions $\Psi_{m-1} \to \Psi_{m+1}$, $\Psi_m \to \Psi_{m+1}$, and $\Psi_m \to \Psi_{m+2}$, respectively, predominate in the ^1L_b, ^1L_a, and ^1B_b transitions of quinoxaline. The configurations that make the maximum contributions to the first five excited states of quinoxaline 1-N-oxides are presented in Table 6. It follows from the calculations that the second and third electron transitions in quinoxaline 1-N-oxide are due mainly to the $\Psi_{m-2}^{NO} \to \Psi_{m+1}^{NO}$ and $\Psi_{m-1}^{NO} \to \Psi_{m+1}^{NO}$ configurations, respectively. Taking into account the analogy in the MO, one may conclude that the $\Psi_{m-1} \to \Psi_{m+1}$ and $\Psi_m \to \Psi_{m+1}$ configurations responsible for the ^1L_b and ^1L_a bands correspond to these two configurations in the spectrum of quinoxaline. A comparative examination of the data on the configurational interaction with allowance for the analogy in the corresponding MO for chloro- and methoxy-quinoxalines and their 1-N-oxides leads to a similar conclusion. Thus it follows from both the theoretical analysis and from the experimental data that two transitions (2 and 3) in the spectra of quinoxaline 1-N-oxides are similar in nature to the ^1L_b and ^1L_a transitions in unoxidized quinoxalines. The predominant configurations of the three remaining transitions in the investigated compounds are associated with Ψ_m^{NO} MO, which does not have an analogy in the unoxidized molecules. In the experiments, these data correspond to the fact that the 1 and 4 bands of the N-oxides do not have analogies in the spectra of quinoxalines. In addition, it follows from the calculations that the 5 band in the spectrum of quinoxaline 1-N-oxide is located in the same energy range as the ^1B_b band of quinoxaline.

A calculation of the molecular diagrams of the ground state and the first excited state (Fig. 2) showed that in all of the examined compounds the low-energy transition is accompanied by considerable transfer of π-electron charge from the oxygen atom of the N→O group to the heteroring. This effect corresponds to the experimentally observed hysochromic shift of the 1 band as the polarity of the solvent increases.

EXPERIMENTAL

The electronic spectra were calculated by Pariser–Parr–Pople configurational interaction method with a program composed in conformity with the data in [6]. The coulombic and resonance parameters used in these calculations are presented in Table 7. The one-center integrals for the atoms making up the

N→O bond were close to those described in [4]. The two-center integrals were calculated from the Mataga–Nishimoto formula [7]. The methyl group in IV and V was examined with respect to an inductive model, according to which it lowers the potential of the atom bonded to it [8].

The UV spectra were measured with an EPS-3 spectrophotometer. The authors sincerely thank A. S. Elina for kindly providing us with the compounds.

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