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INVESTIGATION OF THE TAUTOMERISM AND THE INTRAMOLECULAR CHARGE TRANSFER IN THE SERIES OF AROMATIC N-OXIDES BY ELECTRON SPECTROSCOPY

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The electron spectra of functionally substituted N-oxides of pyridine and quinoline in different solvents have been analyzed. It is shown that the long-wave region of the spectra can be used to investigate the tautomeric forms and the resonance structures of these compounds with substituents which are directly conjugated with the N-oxide group.

Electron spectroscopy is one of the methods used to study the structure of aromatic N-oxides. For instance, the electron spectra of the pyridine N-oxide and of its simplest derivatives in different solvents are quite informative [1]. On the other hand, the spectra of the polynuclear aromatic N-oxides have been described in the literature to a much lesser degree. This is probably because they are more difficult to interpret (due to the appearance of additional absorption bands) and particularly because they are difficult to isolate in pure form.

We have investigated the rules, governing the changes in the electron spectra of some known N-oxides, of compounds, which have not been described earlier, and of functionally substituted derivatives of N-oxides of pyridine and quinoline, synthesized in our laboratory, with oxygen-, sulfur-, and nitrogen-containing substituents, most of which are directly conjugated with the N-oxide group.

Pyridine N-Oxides. The electron spectrum of the pyridine N-oxide (Ia) in ethanol has only two maxima, caused by $\pi \rightarrow \pi^*$ transitions (Table 1). A further absorption maximum appears at 330 nm in the gaseous phase, which is assigned to the $n \rightarrow \pi^*$ transition on account of the 2p electrons of the oxygen atom [2]; this band is relatively weak and possesses a fine vibration structure. Similar $n \rightarrow p^*$ transitions are also observed in the electron spectra of the N-oxides of 2- and 3-picolines in the gaseous phase. They are recorded when the spectra are taken in nonpolar solvents and disappear completely in protonic solvents [3, 4]. The data presented in Table 1 for the N-oxides of 4-methyl, 4-chloro-, and 4-methoxypyridine, prepared in our laboratory (Ib-d), agree with these results.

However, in many N-oxides (for instance, Ie-k) intensive absorption bands appear in the long-wave region of the spectrum, which cannot be explained solely by the chromophore properties of the substituents in the heterocycle. In order to simplify the interpretation of the spectra, we have separated them into three absorption regions: 1, 2, and 3 (Table 1).

The first region of $\pi \rightarrow \pi^*$ transitions (201-216 nm) offers little information for the identification of the compounds, except for those containing a nitro group, which causes a hypsochromic shift and a hypochromic effect; the latter is strongly weakened in the presence of methyl groups, particularly in the position 3 (N-oxides Ih, i, k).

An analysis of the second region of $\pi \rightarrow \pi^*$ transitions (228-299 nm) shows that the introduction of most substituents into the pyridine ring shifts the absorption band to the long-wave region of the spectrum. This holds particularly for the functional groups, in which the heteroatom with an unshared electron pair is directly linked to the heterocycle. On the other hand the nitro group causes, as in the first spectral region, a strong hypsochromic shift and hypochromic effect. It must be pointed out that in all compounds, listed in Table 1 (Ib, h-k), methyl groups cause a shift of the absorption maximum to the long-wave region with a simultaneous hyperchromic effect, which is usually attributed to hyperconjugation [5].

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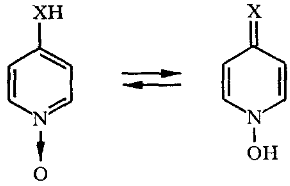
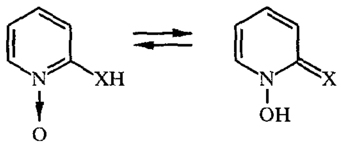
In the third wavelength interval (305-333 nm) absorption bands appear when S–H and OH groups with acid properties or a nitrogroup, which is a strong electron acceptor, are present in position 4. However, in our opinion the causes for the appearance of the above absorption bands are different for S–H and OH acids and nitro compounds. In the first instance a tautomerism of the type III ⇄ IV is possible.

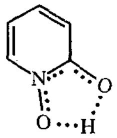




III IV V VI

X = O, S

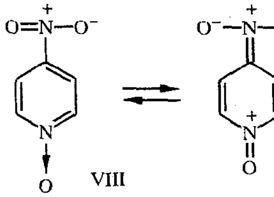
The occurrence of form IV must lead to the appearance of an absorption band in the long-wave region. This conclusion conforms with literature data for the N-oxides of 2-hydroxy- and 2-mercaptopyridine (Il, m), which exist in the tautomeric forms V and VI and absorb at 305 and 322 nm respectively. The lower long-wave shift for the hydroxy derivative Il can be related to an intramolecular proton transfer with the formation of a structure of type VII; the probability of such a shift is low for the mercapto compound.



VII

In compounds, in which at the oxygen and sulfur atoms in position 4 hydrogen is replaced by substituents, for instance Id, n, o, the above tautomerism is not possible; regularly they have absorption bands only in the interval 200-300 nm (Table 1).

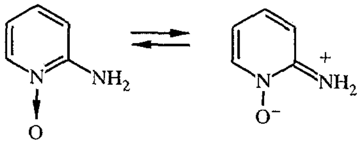
For the 4-nitro derivatives Ig-k the appearance of absorption bands in the long-wave region (323-330 nm) is related to the direct conjugation between the N-oxide and nitro groups and to the possible existence of the resonance structure IX [6]:



VIII IX

As in the case of the N-oxides Ie, f, l, m, existing in "quinoid" tautomeric forms, the formation of the resonance structure IX in the nitro derivatives leads to a decrease in the intensity of $\pi \rightarrow \pi^*$ absorption bands in the spectral regions 1 and 2. The formation of type IX resonance structures is frequently used to explain a similar red shift, for instance, for p-nitrophenol in comparison with phenol and for amino-acetophenones in comparison with acetophenone [5, 7].

In compounds Ig-k the N-oxide group acts as an electron donor; however, it can also act as an acceptor when the corresponding substituent is present in the ring. This is attributed to the easy polarizability of the N–O bond. For instance, the N-oxide of 2-aminopyridine Ip, which has a donor amino group, can exist in the form of the resonance structures X and XI; as in the case of the nitro compounds, this explains the absorption in the long-wave region of the spectrum.



X XI

For other N-oxides, for instance Ic, which cannot form "quinoid" structures, neither by tautomerism nor by resonance conjugation, absorption bands in the long-wave region of the spectrum are missing.

TABLE 1. Electron Spectra of Pyridine N-Oxides

Compound	Substituent	Solvent	λ_{max}, nm (log ε)			Literature
			1	2	3	
Ia	H	96-% ethanol	212(4,24)	263,5(4,09)		[1]
	H	Heptane	214(4,20) 281,5(4,16)	216,5(4,25) 312,5(3,44)	220,8(4,16)	[1]
Ib	4-CH_3	96-% ethanol	212(4,23)	267(4,15)		
Ic	4-Cl	96-% ethanol	214(4,22)	275(4,19)		
Id	4-OCH_3	Diethyl ether	208	286		
		96-% ethanol	208(4,09)	268(4,14)		
		Water		261(4,21)		[12]
		0.1 N HCl	203(4,10)	246(3,95)		
		Conc. HCl	208(3,96)	248(3,96)		
Ie	4-OH	96-% ethanol	207(4,00)	270(3,88)	327(3,42)	
		Conc. HCl	208(3,74)	244(3,94)		
If	4-SH	Water	214(3,90)	233(3,66), 285(3,93), 326(4,00)		[10]
Ig	4-NO_2	Diethyl ether	203 sh	239(3,89)	347(4,20)	
		96-% ethanol	201(3,38)	236(3,69)	330(3,91)	
		Water	206 sh	227(3,89)	314(4,05)	
		0.1 N HCl	206(3,66)	227(3,93)	313(4,07)	
		Conc. HCl	211(3,70)	247(3,78), 290 sh		
		Acetonitrile	204(3,60)	238(3,93)	345(4,20)	
Ih	4-NO_2, 2-CH_3	96-% ethanol	203(3,79)	237(3,72)	333(3,91)	
Ii	4-NO_2, 2,6-CH_3	96-% ethanol	203(4,08)	240(3,76)	330(3,98	
Ik	4-NO_2, 3-CH_3	96-% ethanol	202(4,11)	242(3,82)	323(3,96)	
I*l*	2-OH	96-% ethanol		228(3,86)	305(3,66)	[12]
Im	2-SH	Water		235(4,00), 261,5(3,85), 322(3,57		[10]
In	4-$OCH_2C \equiv CH$	96-% ethanol	207(4,13)	270(4,08)		
Io	4-$SCH_2C_6H_5$	Water	205(4,48)	299(4,47)		[10]
Ip	2-NH_2	96-% ethanol	227(4,40)	251(3,76)	321(3,66)	
Ir	4-COOH	Water	216(4,05)	280(4,23)		[11]
Is	2-(2′-pyridyl) N-oxide	96-% ethanol	206 sh 222(4,34), 243(4,04), 270(4,08)			

Quinoline N-Oxides. In accordance with a structure which is more complicated than the structure of the N-oxide of pyridine, the spectrum of the quinoline N-oxide (IIa) in ethanol contains four absorption bands and becomes even more complicated when the spectrum is taken in heptane. The absorption intervals of Ia, Ib, 2, and 3 are presented in Table 2; the first three correspond to $\pi \rightarrow \pi^*$ as well as to $n \rightarrow p^*$ transitions, depending on the structure of the compound. However, some of our data cannot be described only in this way. The phenomenon will be explained below.

The interval 202-238 nm includes bands Ia and Ib, the first of which frequently appears as a shoulder on the second band. Both offer only little information; however, the band at the longer wavelength can be used to identify the hydrazine derivatives (short-wave shift, 219-222 nm), for N-oxides with substituents, conjugated with the heterocycle through a sulfur atom (long-wave shift, 236-238 nm), and for nitro derivatives (absorption in missing).

The interval 238-277 nm can be used for detection of thio derivatives: the absence of absorption in the presence of a conjugation between the quinoline ring and the substituent, linked to sulfur, and absorption in the region 250-277 nm in its absence. In distinction from the other compounds, the nitro derivatives absorb in a very narrow wave-length interval (254-257 nm).

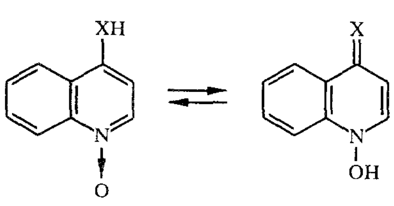
As in the case of the pyridine N-oxides, the third absorption interval (λ > 320 nm) is the most informative. The presence of sulfur- or nitrogn-containing substituents, conjugated with the heterocycle, causes a bathochromic shift of the absorption band at the highest wavelength and, in most instances, its hyperchromic effect.

These phenomena can be explained also from the standpoint of the "quinoid" structures, used for the pyridine N-oxides. Nevertheless, the contribution of such structures in the quinoline N-oxides must be weaker, since the adjacent aromatic ring

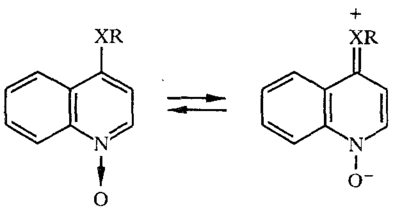
TABLE 2. Electron Spectra of Quinoline and quinoxaline N-Oxides

Compound	Substituent	Solvent	λ_{max}, nm (log ε)			
			1a	1б	2	3
IIa	H	96-% ethanol	210sh	231(4,60)		325(3,84) 340sh(3,79)
	H [1]	Heptane			247(4,21) 257(4,06)	335(3,92) 350(3,98) 360(3,87)
IIb	4-SH	96-% ethanol	201(3,96)	228(4,06)	243sh	363(3,56) 409sh
IIc	4-NO_2	96-% ethanol	207(4,51)		254(4,35)	375(4,09)
IId	4-NO_2, 2-CH_3	96-% ethanol	210(4,40)		257(4,08)	379(3,83)
IIe	4-SCH_3	96-% ethanol	208sh(3,74)	228(4,02)		360(3,59)
		0.1 N HCl	210sh(4,04)	234(4,28)	250sh	350(4,03)
IIf	4-$SCH_2C_6H_5$	96-% ethanol	210sh(4,20)	229(4,48)	277sh	362(4,00)
IIg	4-SCH_2CH_2OH	96-% ethanol	209sh(3,89)	228(4,43)	273sh(3,64)	362(4,00)
IIh	4-$SCH_2C \equiv CH$	96-% ethanol	210sh(4,12)	230(4,42)	250sh	360(3,93)
IIi	4-SC_6H_4(4-NO_2)	96-% ethanol	203(4,15)	236(4,28)		338(4,08)
IIk	4-SC_6H_3(2,4-NO_2)	96-% ethanol	211(4,34)	238(4,56)		377(4,36)
IIl	4-$SC(NH_2){=}NH^{+}{}_2Cl^{-}$	96-% ethanol	208(4,20)	238(4,39)		338(4,00) 352(4,00)
IIm	4-$NHNH_2$	96-% ethanol	202sh	220(4,40)	243(3,91) 260(3,88)	370(3,87)
IIn	4-$NHNHCOC_6H_5$	96-% ethanol	203sh	222(4,62)		364(4,00)
IIo	4-$NHNHCOC_6H_4$ 4(chloro-)	96-% ethanol	202(4,48)	220(4,38)	238sh(4,37)	368пл(3,67)
IIp	4-$NHN{=}CHC_6H_5$	96-% ethanol	204sh	220(4,30)	245sh(4,06)	370(3,84)
IIr	4-$NHN{=}CHC_6H_4$ (3-NO_2)	96-% ethanol	203sh	219(4,71)	244(4,28) 261(4,26)	371(4,23)
IIs	4-$NHNHC_6H_3$ (2,4-NO_2)	96-% ethanol	209sh	222(4,22)	270sh(3,86) 331(3,46)	349(3,44) 474(3,19)
IIt	4-$NHN{=}CHC_6H_4$ (4-NO_2)	96-% ethanol	206(4,14)		270(3,84)	455(3,54)
IIu	4-OCH_3	Diethyl ether	204	221	247	362
		96-% ethanol	210sh	223(4,52)	249(4,06)	341(3,86)
		Water	207sh	223(4,44)	243(4,18)	331(3,88)
		0.1 N HCl	208(4,00)	233(4,48)	250sh	310(3,71)
		Conc. HCl	212sh(3,94)	235(4,50)	255sh(3,64)	314(3,72)
		Acetonitrile	203sh	220(4,56)	258(4,06)	360(3,89)
IIv	4-OC_6H_5	96-% ethanol	208sh(4,26)	224(4,54)	247(3,75)	342(3,89)
IIw	4-OC_6H_4(3-NO_2)	96-% ethanol	207sh	226(4,74)	247(4,39)	340(4,08)
IIt	4-Cl	96-% ethanol	208(3,98)	230(4,53)	246sh	333(3,89)
IIy	2-CH_3	96-% ethanol	213sh	230sh	237(4,60)	319(3,79) 328sh
IIz	4-O-β-naphthyl	96-% ethanol	211sh	226(4,84)	251(4,35), 275(3,96), 287(3,99), 295(4,04), 307(4,04), 321(3,99), 336(4,01)	
	N,N-quinoxaline dioxide	96-% ethanol	207sh	235(4,48)	258(4,28)	372sh 385(4,23)

levels out this effect on account of the conjugation of the N-oxide group with the substituent in the heterocycle through the benzene ring. All the same, the effect appears in most cases.



XII XIII

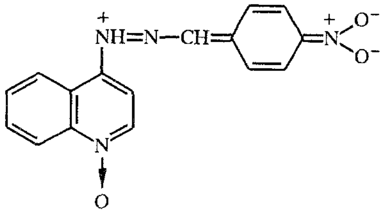


XIV XV

In fact, the red shift of the long-wave absorption band for the sulfur-containing N-oxide IIb in comparison with the unsubstituted N-oxide IIa can be explained, based on the tautomeric equilibrium XII ⇄ XIII. The bathochromic shift is even better noticed for the nitro compounds IIc, d, in which the bipolar structure of type XV arises due to a charge transfer from the N-oxide to the nitro group. For the sulfur-containing quinoline N-oxides IIe-h (and for the pyridine N-oxide Io) with the substituent instead of the hydrogen atom at the sulfur, a tautomerism is not possible. However, the "quinoid" resonance structures exist and consequently the bathochromic shift is characteristic for the absorption maxima in the long-wave region. When the sulfur atom is linked with a saturated carbon atom of the substituent (N-oxides IIe-h), the absorption occurs in the narrow interval 360-362 nm.

As mentioned above, the sulfur-containing N-oxides in which the sulfur atom is linked to an unsaturated carbon atom IIi-l, are more readily identified, based on the region 2 of the spectrum. Among the investigated compounds the N-oxide of 4-mercaptoquinoline (IIb) is unique in that tautomerism as well as resonance are possible; this explains the appearance of an additional maximum in the region 2. From this point of view the appearance of analogous bands in the spectra of N-oxides of the pyridine series If, m also becomes plausible.

As expected, a large long-wave shift in comparison with the sulfur-containing compounds is observed for N-oxides with a nitrogen atom in position 4. The unshared electron pair of the nitrogen atom is conjugated with the N-oxide group; this leads to the stabilization of the "quinoid" structure XV. This case was studied on the example of the little-investigated hydrazine derivatives. Thus, for instance, the compounds IIm-r absorb in the region 364-370 nm and the position of the maximum is virtually independent on the structure of the substituent at the β-nitrogen atom. Exceptions are the compounds IIs, t, in which one or two nitrogroups are directly conjugated with the N-oxide group; this leads to the formation of structures of type XVI (for the N-oxide IIt) with a relatively long conjugation chain.



XVI

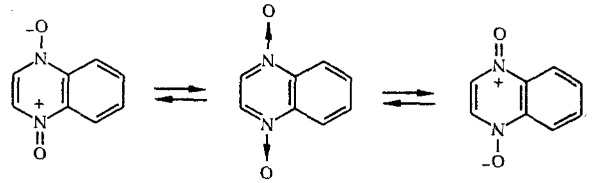
For such compounds the long-wave band is located already in the visible region of the spectrum (455-474 nm). Besides this, a significant bathochromic shift is also observed in the preceding wavelength interval. When the nitro group is in the m-position (N-oxide IIr), this direct conjugation is not possible and has no influence on the position of the maximum.

In the case of oxygen-, chlorine-, and methyl-substituted N-oxides IIu-y, for which the formation of "quinoid" structures as a result of tautomerism or resonance is not probable, no bathochromic shift of the long-wave absorption band is observed in ethanol in comparison with the unsubstituted quinoline N-oxide (IIa). The fact attracts our attention that a fine structure of the absorption bands (251-336 nm) appears in the spectrum of the N-oxide IIz; this could be expected in the conjugation between two polynuclear aromatic fragments: quinoline and naphthaline.

We have found that the long-wave region of the spectra of the majority of N-oxides was susceptible not only to the structural peculiarities of the substituents but also to a change of solvent (Tables 1 and 2).

For the investigated compounds of the pyridine as well as the quinoline series, a clear bathochromic shift is observed of the absorption bands, shifted most into the long-wave region when the polarity of the solvent is increased. The particular behavior of the N-oxides Ig and IIu in acetonitrile indicates that not the polarity of the solvent but the specific interaction, which does not occur in acetonitrile, is the determining factor; the absorption maxima in acetonitrile in region 3 virtually coincide with the maxima in the low-polarity diethyl ether. These interactions comprise either the formation of a hydrogen bond of the solvent with the N-oxide, or even salt formation of the latter with HCl, which influences the degree of $p \rightleftarrows \pi^*$ conjugation in the above-mentioned compounds.

When the absorption bands correlate, a similar bathochromic shift must be attributed to $n \rightarrow \pi^*$ transitions, which are characterized by low ε values and disappear completely when the atom with the unshared electron pair is protonized [7, 8]. In fact, the protonation of the N-oxide group of compounds Ie, g with conc. HCl prevents the formation of "quinoid" structures, due to tautomerism or resonance. As a result of this, their spectra become similar to the spectrum of the N-oxide Id, in which the above-mentioned processes cannot take place in any of the solvents. However, the unusually high intensity of the long-wave absorption bands lead to the assumption that these transitions are caused by an intramolecular charge transfer (ICT) thanks to the presence of electron donor and electron acceptor groups in conjugation with each other. For instance, such an explanation can be used successfully to interpret the spectra of p-nitroaniline [9]. In our compounds the N-oxide group can act as donor (with respect to the nitrogroup) as well as acceptor of electrons (with respect to most other substituents). Its ambidentate character manifests itself clearly in the spectra of the N,N-dioxide of quinoxaline, which shows strong absorption in the long-wave region, caused in our opinion by ICT processes:



For the N,N-dioxide of 2,2′-dipyridyl Is, in which the intramolecular charge transfer is difficult, no absorption is noticed in the considered region of the spectrum. Thus, the observed regularities lead to the conclusion that electron spectroscopy is a highly informative method for the investigation of the structure of functionally substituted heteroatomic N-oxides, particularly of those, in which tautomeric and charge transfer processes are taking place.

EXPERIMENTAL

The electron spectra of solutions of the substances were recorded on a Specord UV-VIS spectrometer. The N-oxides were synthesized by using procedures, described in the literature [1]. Their structure was confirmed by elemental analysis and IR spectra.

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