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ELECTRONIC SPECTRA AND STRUCTURE OF 2-BROMOPICOLINES, THEIR N-OXIDES, AND 2-BROMO-4-NITROPICOLINE N-OXIDES

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The UV spectra of 2-bromopicolines, their N-oxides, and 2-bromo-4-nitropicoline N-oxides are presented and the influence of substituents on λ_{max} and ε_{max} of spectral bands are discussed. The electronic spectra were calculated using the modified INDO method. Transition energies, intensities, and assignments were compared with UV spectra. The degree of intramolecular CT in 2-bromopicoline N-oxides is greater than those in 2-bromopicolines and smaller than those in 2-bromo-4-nitropicoline N-oxides. The differences of the HOMO-LUMO energies indicate that the susceptibilities in the photochemical reaction lie in the order: 2-bromo-4-nitropicoline N-oxides > 2-bromopicoline N-oxides > 2-bromopicolines.

1. INTRODUCTION

The chemistry of heterocyclic N-oxides has gained significance owing to the interesting biological activities of these compounds [1]. It has been suggested that the presence of an acceptor group is essential for any significant antifungal activity of these compounds [2].

In the course of physicochemical research carried out in our laboratory on the reactivity of the title compounds it was necessary to measure their UV spectra and electronic structure and compare them with those obtained earlier [3-4]. This comparison provides information on how the presence of both halogen and nitro groups affects the spectral parameters (λ_{max}, ε_{max}) as well as the bond order of the N-oxide group. Moreover, the UV spectra of these compounds give information about the mutual interaction of substituents in the molecule. The position of $\nu_{N\text{-}O}$ in the IR spectra and earlier chemical evidence [3-5] allow the conclusion that the 2-bromine atom provides an electron type conjugation with the N-oxide function with consequent expansion of the valence shell of bromine (π, d coupling).

The ultraviolet spectra of pyridine N-oxides have been investigated by various scientists [1, 2, 6-10] who concentrated on pyridine N-oxide [1, 6-8] and monosubstituted derivatives of pyridine N-oxides, mainly in position 4 [2, 9-10].

The purpose of this paper is to show the influence of the nature of the halogen and its mutual interaction with the 4-nitro substituent on the spectral parameters (λ_{max}, ε_{max}) in the UV spectra of 2-bromopicolines, their N-oxides, and 2-bromo-4-nitropicoline N-oxides. Since in the molecules of these compounds the interaction of substituents (3-, 5- or 6-methyl, 2-halogen, and 4-nitro group) is governed by steric, inductive, and conjugation effects, the analysis of their UV spectra is very interesting.

2. EXPERIMENTAL

The studied compounds were synthesized by the previously described methods [11, 12].

The UV spectra are recorded by means of a Specord UV-vis spectrometer, using a quartz cell of 0.097 cm thickness. Samples were approximately 10^{-4} mole/dm^3 in ethanol.

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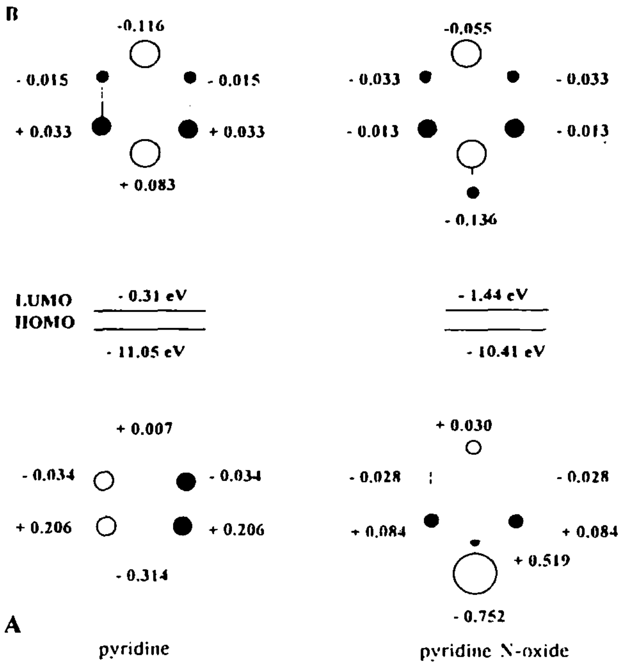


Fig. 1. Charge density of pyridine and pyridine N-oxide.

The calculations of the electronic spectra of the title compounds were performed within the framework of the all-valence electron INDO method [13] utilizing some of its modifications [14, 15] and including 100 single excited configuration interaction procedures. The ground state geometry of the species was optimized using the semiempirical AM1 method [16].

3. RESULTS AND DISCUSSION

3.1. Properties of the Ground State

In Figs. 1-4 the structure of the frontier HOMO and LUMO orbital is shown as well their energies and charge densities for the first excited state of the title compounds.

As known from the literature [3], N-oxidation of pyridine leads to a large energy displacement of the unshared electron (n) pair of the nitrogen atom by about 1 eV toward higher energies, N-oxidation of 2-bromopicolines leads to a significant increase in HOMO from −11.19-11.14 eV to −10.51-10.46 eV, whereas introduction of the nitro group in position 4 of 2-bromopicoline N-oxide results in a decrease of these energies from −10.51-10.46 eV to −11.26-11.22 eV. The methyl group does not significantly influence the level of HOMO energy. The level of HOMO energies and the susceptibility of nucleophilic substitution decrease in the following order: 2-bromo-4-nitropicoline N-oxides > 2-bromopicolines > 2-bromopicoline N-oxide. Comparison of the excess charge density on the oxygen atom of pyridine N-oxide [3] (−0.752), 2-bromopicoline N-oxides (−0.701-0.712 eV), and 2-bromo-4-nitropicoline N-oxides (−0.662-0.672 eV) indicates that the degree of intramolecular charge transfer is the highest in the 4-nitro derivatives. The charge distribution can be helpful when considering the reactivity of the studied compounds. The charge distribution explains the mechanism and kinetics of ethanolysis of 2-bromopicoline N-oxides [17] and 2-bromo-4-nitropicoline N-oxides [16].

The calculated dipole moments of the compounds studied agree satisfactorily with experimental values [14]. The dipole moments of 2-bromopicoline N-oxides are considerably higher than those of their parent bases (the same trend is evident if the dipole moments of 2-chloro- and 2-iodopicolines and their N-oxides are compared) [3, 4, 14]. There is evidence of a great inductive effect of the N-oxide group and as a result susceptibility to nucleophilic substitution of a halogen atom situated in position 2.

It was shown previously that 2-bromopicoline N-oxides are much more reactive in their reactions with sodium alkoxide than 4-nitro derivatives but much less reactive with weak nucleophiles (amines) [15, 16]. Derivatives including the

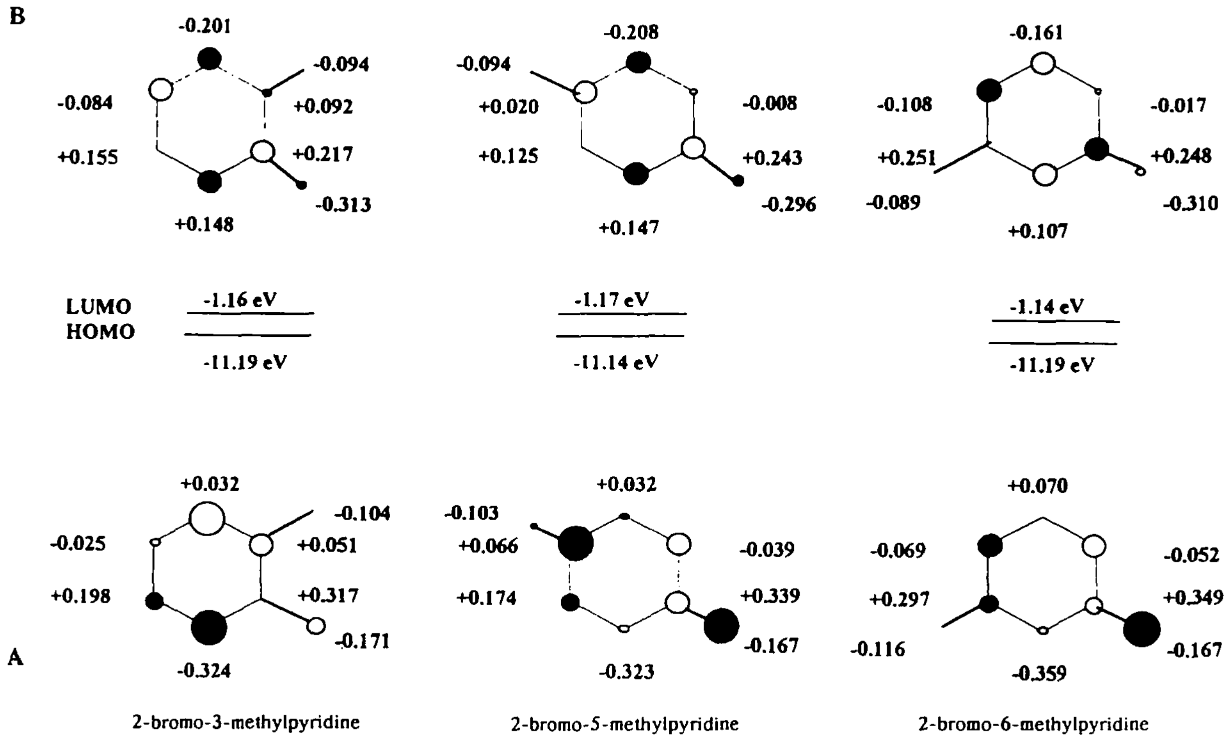


Fig. 2. Charge density diagram of 2-bromopicolines.

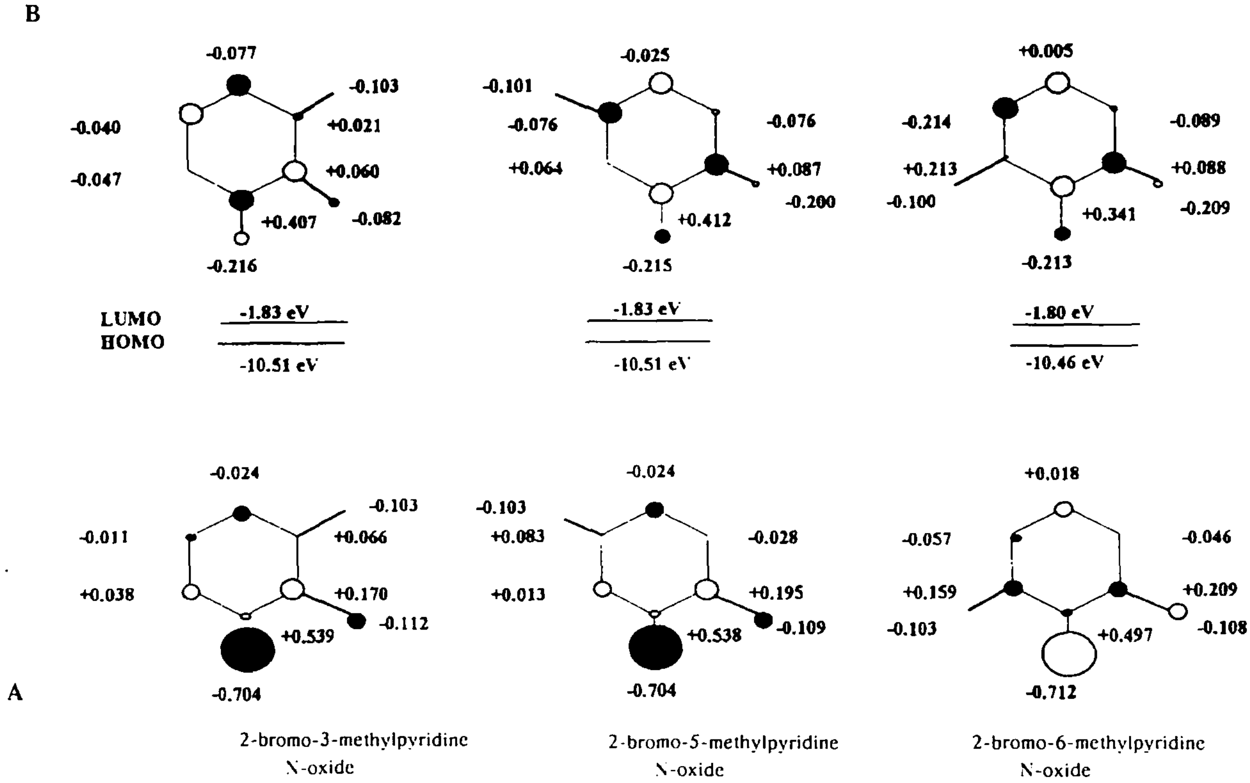


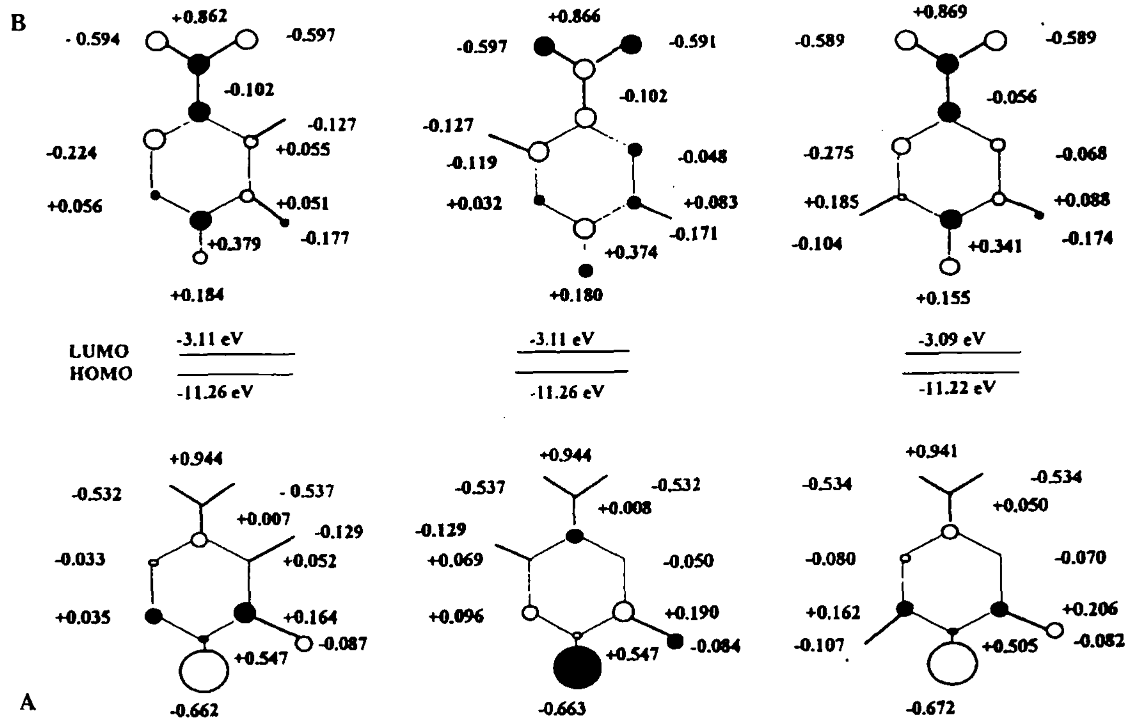
Fig. 3. Charge density diagram of 2-bromopicoline N-oxides.

TABLE 1. Comparison of the Computed and Experimental Spectra of 2-Bromopicolines, 2-Bromopicoline N-Oxides, and 2-Bromo-4-nitropyridine N-Oxides

Compound	State	Sym	Calculated			Experimental		
			Energy eV	Oscillator strength	Dipole moment (D)	Energy	$\varepsilon \times 10^{-3}$	Dipole moment
1	2	3	4	5	6	7	8	9
2-Bromo-3-methyl-pyridine	S_0	—	—	—	3.05			2.87
	S_1 (n,π^*)	A''	3.69	0.003	3.561			
	S_2 (n,π^*)	A''	4.66	0.000	4.188			
	S_3 (π,π^*)	A'	5.22	0.438	5.725	4.43	4.39	
	S_4 (n,π^*)	A''	5.27	0.030	12.689			
	S_5 (π,π^*)	A'	5.41	0.044	6.440	5.40	9.97	
	S_6 (π,π^*)	A'	5.59	0.504	7.210			
	S_7 (π,π^*)	A'	6.19	0.152	5.685			
	S_8 (n,π^*)	A''	6.45	0.007	6.703			
2-Bromo-5-methyl-pyridine	S_0	—	—	—	3.47			3.59
	S_1 (n,π^*)	A''	3.71	0.004	3.78			
	S_2 (n,π^*)	A''	4.65	0.000	4.436			
	S_3 (π,π^*)	A'	5.21	0.459	4.709	4.48	3.58	
	S_4 (n,π^*)	A''	5.34	0.018	14.840	4.56	4.52	
	S_5 (π,π^*)	A'	5.42	0.045	6.556			
	S_6 (π,π^*)	A'	5.63	0.606	10.639	5.71	10.95	
	S_7 (n,π^*)	A''	6.59	0.000	6.692			
2-Bromo-6-methyl-pyridine	S_0	—	—	—	1.82			2.03
	S_1 (n,π^*)	A''	3.77	0.004	4.115	3.97	0.19	
	S_2 (n,π^*)	A''	4.68	0.000	4.290			
	S_3 (π,π^*)	A'	5.27	0.478	5.173	4.48	2.72	
	S_4 (n,π^*)	A''	5.34	0.020	13.956			
	S_5 (π,π^*)	A'	5.44	0.028	6.915			
	S_6 (π,π^*)	A'	5.64	0.529	8.571	5.52	5.29	
	S_7 (π,π^*)	A'	6.24	0.129	5.607			
	S_8 (n,π^*)	A''	6.54	0.000	6.329			
2-Bromo-3-methyl-pyridine N-oxide	S_0	—	—	—	4.91			4.67
	S_1 (n,π^*)	A''	3.35	0.000	3.351			
	S_2 (π,π^*)	A'	3.93	0.211	3.336	4.56	16.54	
	S_3 (π,π^*)	A'	4.29	0.061	0.736			
	S_4 (n,π^*)	A''	4.46	0.010	13.990			
	S_5 (n,π^*)	A''	5.11	0.000	5.754			
	S_6 (π,π^*)	A'	5.55	0.031	1.633	5.19	11.11	
	S_7 (π,π^*)	A'	5.69	1.144	6.125	5.44	34.57	
	S_8 (π,π^*)	A'	6.04	0.013	8.655	5.82	18.76	
	S_9 (π,π^*)	A'	6.13	0.649	5.302			
	S_{10} (π,π^*)	A'	6.18	0.087	15.950			
2-Bromo-5-methyl-pyridine N-oxide	S_0	—	—	—	5.02			5.44
	S_1 (n,π^*)	A''	3.36	0.000	3.597			
	S_2 (π,π^*)	A'	3.93	0.219	3.480	4.59	11.37	
	S_3 (π,π^*)	A'	4.29	0.079	0.680			
	S_4 (n,π^*)	A''	4.46	0.009	14.728			
	S_5 (n,π^*)	A''	5.09	0.000	5.770			
	S_6 (π,π^*)	A'	5.55	0.027	14.145			
	S_7 (π,π^*)	A'	5.70	1.160	5.964	5.44	28.91	
	S_8 (π,π^*)	A'	6.14	0.718	4.492	5.82	13.98	
	S_9 (n,π^*)	A''	6.15	0.000	8.419			
	S_{10} (n,π^*)	A''	6.28	0.018	17.824			

TABLE 1 (continued)

Compound	State	Sym.	Calculated			Experimental		
			Energy eV	Oscillator strength	Dipole moment (D)	Energy	$\varepsilon \times 10^{-3}$	Dipole moment
1	2	3	4	5	6	7	8	9
2-Bromo-6-methyl-pyridine N-oxide	S_0	—	—	—	3.61			3.32
	S_1 (n,π^*)	A''	3.36	0.000	3.894			
	S_2 (π,π^*)	A'	3.90	0.203	3.752			
	S_3 (π,π^*)	A'	4.27	0.062	0.580	4.56	7.96	
	S_4 (n,π^*)	A''	4.45	0.008	14.535			
	S_5 (n,π^*)	A''	5.03	0.000	5.735			
	S_6 (π,π^*)	A'	5.51	0.025	14.198			
	S_7 (π,π^*)	A'	5.67	1.135	5.838	5.19	22.47	
	S_8 (n,π^*)	A''	6.11	0.000	7.954			
	S_9 (π,π^*)	A'	6.16	0.752	4.483	5.83	10.69	
	S_{10} (n,π^*)	A''	6.22	0.019	17.799			
2-Bromo-3-methyl-4-nitro-pyridine N-oxide	S_0	—	—	—	2.45			2.38
	S_1 (n,π^*)	A''	3.88	0.000	12.453			
	S_2 (π,π^*)	A'	4.00	0.320	5.519	3.85	11.68	
	S_3 (π,π^*)	A'	4.27	0.319	6.651	4.94	13.75	
	S_4 (n,π^*)	A'	4.73	0.013	11.994			
	S_5 (n,π^*)	A''	4.85	0.006	13.297			
	S_6 (π,π^*)	A'	5.39	0.007	14.136			
	S_7 (π,π^*)	A'	5.43	0.779	5.678	5.90	26.29	
	S_8 (n,π^*)	A'	5.75	0.002	6.380			
	S_9 (π,π^*)	A'	6.05	0.020	15.493			
2-Bromo-5-methyl-4-nitro-pyridine N-oxide	S_0	—	—	—	2.54			2.43
	S_1 (n,π^*)	A''	3.90	0.001	12.517			
	S_2 (π,π^*)	A'	3.94	0.328	4.607	3.84	12.25	
	S_3 (π,π^*)	A'	4.13	0.086	6.251			
	S_4 (π,π^*)	A'	4.74	0.010	10.489			
	S_5 (n,π^*)	A''	4.81	0.006	13.684			
	S_6 (n,π^*)	A''	5.34	0.000	14.298			
	S_7 (π,π^*)	A'	5.46	0.676	5.757	4.90	13.05	
	S_8 (π,π^*)	A'	5.88	0.592	10.740	5.83	29.30	
	S_9 (π,π^*)	A'	6.09	0.385	12.381			
	S_{10} (π,π^*)	A'	6.16	0.323	9.833			
2-Bromo-6-methyl-4-nitro-pyridine N-oxide	S_0	—	—	—	1.17			1.01
	S_1 (n,π^*)	A''	3.87	0.014	12.522			
	S_2 (π,π^*)	A'	3.88	0.294	5.768	3.75	7.44	
	S_3 (π,π^*)	A'	4.11	0.075	6.708			
	S_4 (n,π^*)	A''	4.83	0.005	14.168			
	S_5 (n,π^*)	A''	5.05	0.000	7.019			
	S_6 (n,π^*)	A''	5.28	0.002	14.564			
	S_7 (π,π^*)	A'	5.42	0.627	5.728	4.80	9.92	
	S_8 (π,π^*)	A'	5.90	0.673	9.981	5.49	19.53	
	S_9 (n,π^*)	A''	6.14	0.409	11.098	5.73	21.53	
	S_{10} (π,π^*)	A'	6.18	0.269	10.850			



2-bromo-3-methyl-4-nitropyridine N-oxide

2-bromo-5-methyl-4-nitropyridine N-oxide

2-bromo-6-methyl-4-nitropyridine N-oxide

Fig. 4. Charge density diagram of 2-bromo-4-nitropicoline N-oxides.

methyl group in position 5 have the highest dipole moments, because the methyl group in position 5 coupled with a halogen in position 2 increases the electron density at C-2, decreasing the halogen reactivity with a nucleophilic reagent [17]. A considerable decrease of the dipole moments is observed after introduction of the nitro group into position 4 of 2-bromopicoline N-oxides. The nitro group having a strong mesomeric M-effect and a strong inductive I-effect exerts in position 4 such a great influence that the N-oxide group becomes an electron-donating group. In 2-halo-4-nitropicoline N-oxide the influence of the quinoid structure becomes significant. The calculated dipole moments of the compounds studied (Table 1) agree satisfactorily with experimental values [14].

This agreement proves the accuracy of geometry of the studied molecules. The INDO method gives better agreement than vector calculation, as was shown earlier [3, 4, 14]. Determination of the experimental dipole moment values of 2-bromo-4-nitropicoline N-oxides made it possible to conclude that the nitro group situated in position 4 decreases the semipolar bond contribution of the N-oxide group, resulting in a decrease in polarity of the above-mentioned compounds [14] as compared with 2-chloropicoline and 2-iodopicoline N-oxides [4, 14].

Vector calculation of dipole moments of 2-bromopicolines, their N-oxides, and 2-bromo-4-nitropicoline N-oxides does not take into account the strong influence of the halogen atom in position 2 and the nitro group in position 4, various mesomeric interactions of the N-oxide group and methyl group with the ring, as well as the effect of solvent and the ability of the mentioned compounds to form self-complexes.

3.2. Spectra and Excited State Properties

In Figs. 5-7 the absorption spectra of 2-bromopicolines, their N-oxides, and 2-bromo-4-nitropicoline N-oxides are presented. The spectra of these compounds manifest characteristic bands in the regions 200-250 nm and 250-300 nm. These bands are ascribed to $\pi^* - \pi$ or $\pi_{oxygen} - \pi_{ring}$ excitations and are typical for N-oxides of aromatic amines, in which the N–O

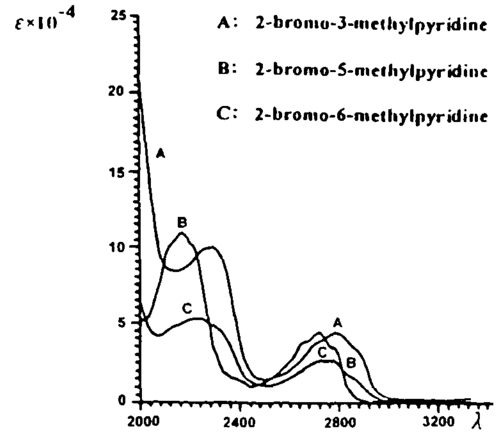


Fig. 5. Absorption spectra of 2-bromopicolines in ethyl alcohol.

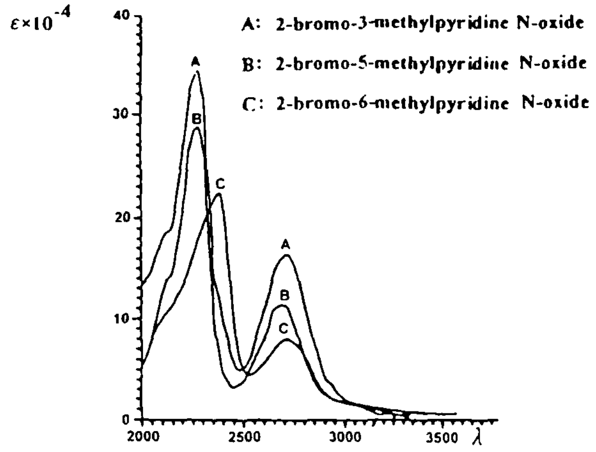


Fig. 6. Absorption spectra of 2-bromopicoline N-oxides in ethyl alcohol.

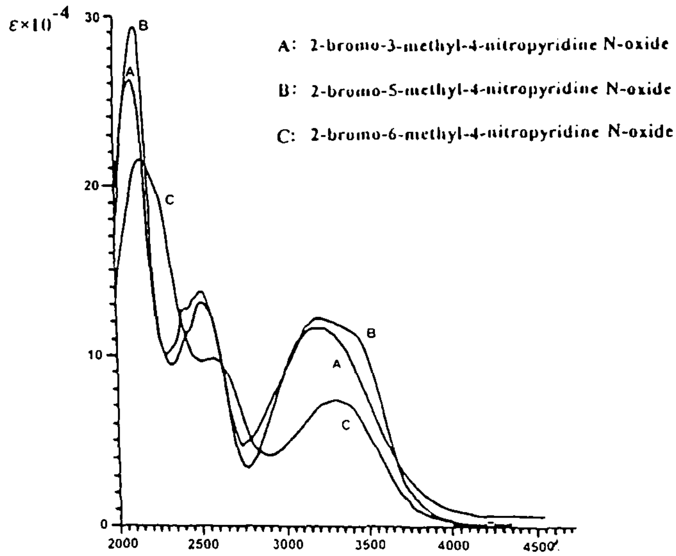


Fig. 7. Absorption spectra of 2-bromo-4-nitropicoline N-oxides in ethyl alcohol.

and C=C groups form a conjugated system. Intensification of the band in the 200-240 nm interval of all the compounds tested is caused by expansion of the valence shells of halogen (d orbital resonance).

In comparison with the spectra of 2-chloropicolines, those of 2-bromopicolines are characterized by higher intensity in the region of 200-250 and are shifted towards red. The intensities of bands I are comparable and have a marked oscillatory structure.

The N-oxidation of 2-bromopicolines is manifested in a significant change in the intensity of bands I and II, due to enlargement of the coupling system.The appearance of an additional separate band in the case of 2-bromo-4-nitropicoline N-oxides leads to the conclusion that this band contributes (as in the spectrum of 4-nitropyridine N-oxide) a large share of the electron transition from the highest occupied MO and brings about a large charge transfer from the N-oxide group to the nitro group via the pyridine nucleus.

The spectral parameters are summarized in Table 1. In this study the nature and importance of intramolecular charge transfer in excited states was examined. The calculated dipole moments of the ground and various excited states provide the measure for the electron transfer. The change in dipole moment during excitation to the first excited singlet state is calculated to be about 0.4 D for 2-bromopicolines, 0.15 for 2-bromopicoline N-oxides, and 0.7 D for 2-bromo-4-nitropicoline N-oxides.

It is interesting to note that, among the singlet states, S_3 and S_6 for 2-bromopicolines, S_4, S_6, and S_{10} for 2-bromopicoline N-oxide, and S_4, S_7, and S_9 for 2-bromo-4-nitropicoline N-oxides correspond to high transfer bands; this agrees with Kubota's conclusion [6]. The distribution of charge in the ground and excited states provide the measure for the electron transfer. On transition from the ground state to the first excited state in 2-bromopicoline N-oxides (Figs. 1-4) the value of the negative charge at the oxygen atom of N-oxide group is lowered but at the 3 and 5 position as well as at the 4-nitro group it is increased. The above observations as well as the lowering of positive charge at the carbon in 4-position in the first excited state appear to indicate that the intramolecular charge transition occurs not only from the oxygen atom of the N-oxide group to the ring but also from the nitro group in position 4 to the ring.

Summarizing the results of this paper and comparing them with those obtained earlier, we arrive at an important conclusion. Among all the 2-halopicolines tested, 2-iodopicolines, and in each group of methyl derivatives, the 5-methyl derivatives are characterized by the highest intensities in the UV spectra. This results from participation of the d electrons in conjugation as well as from interaction between the halogen in position 2 and the methyl group in position 5. The spectra of 2-bromopicoline N-oxides compared to those of 2-bromopicolines are characterized by not only higher intensity, but also by considerably increased intensity of the π band in the region of 200-250 nm, particularly in relation to chloro derivatives. This band may be largely ascribed to excitation of the electrons of substituents and that is why the spectra of bromo derivatives are characterized by such a high intensity (π, δ coupling). Though the intensity of bands in the UV spectrum of 2-bromo-5-methyl-4-nitropyridine N-oxide is the highest, it differs not as markedly as in the case of 2-bromopicolines because of the predominant part played by the coupling between substituents in positions 2 and 4 and the nitrogen atom of the pyridine ring, as well as between the halogen in position 2 and the 4-nitro group. The spectra of these compounds have triband structure, typical of pyridine N-oxide derivatives. Based on the calculated and experimental data for 2-bromo-4-nitropicoline N-oxides these compounds should demonstrate higher susceptibility to photochemical reactions than 2-bromopicoline N-oxides.

The values of HOMO energy allow one to predict the reactivities: 2-bromo-4-nitropicoline N-oxide > 2-bromopicoline N-oxides > 2-bromopicolines.

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