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ELECTRONIC SPECTRA AND STRUCTURE OF 2,4-DIHALOPICOLINES AND THEIR N-OXIDES

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UV spectra of 2,4-dihalopicolines and their N-oxides are presented, and the influence of substituents on spectral parameters is discussed. The electronic spectra were calculated by a modified INDO method. Transition energies, intensities, and assignments were compared with UV spectra. The degree of intramolecular charge transfer in 2,4-dihalopicolines is greater than in 2-halopicoline N-oxides and smaller than in 2-halo-4-nitropicoline N-oxides. Difference values of HOMO–LUMO energies point out that the susceptibility on photochemical reaction lies in the order: 2-halo-4-nitropicoline N-oxides > 2,4-dihalopicoline N-oxides > 2-halopicoline N-oxides > pyridine N-oxide.

The ultraviolet spectra of pyridine N-oxides have been investigated by various scientists [1-5] who concentrated on monosubstituted derivatives of pyridine N-oxide, mainly in position 4 [3, 5-7].

The chemistry of heterocyclic N-oxides has gained significance owing to the interesting biological activities of these compounds [2]. It has been suggested that the presence of an acceptor group is essential for any significant antifungal activity of these compounds [3].

In the physicochemical research project 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 with those obtained earlier [8-19]. This comparison provides information on how the presence of both halogen atoms affects spectral parameters (λ_{max}, ε_{max}) as well as variation in bond order of the N-oxide group. Moreover, this comparison gives information about the mutual interaction of the substituents in the molecule. The position of $\nu_{N\rightarrow O}$ in IR spectra and earlier chemical evidence [8, 9, 11] lead to the conclusion that the 4-bromine atom displays an electron type conjugation with N-oxide function with consequent expansion of the valence shell of bromine (π, d coupling).

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

The calculated electric dipole moment of the ground and various excited states provides a measure of the electron transfer. The properties of methyl derivatives of pyridine N-oxides are especially interesting because of their antifungal activity [3, 20, 21] and optical nonlinearity on the molecular as well as on the macroscopic level [22, 23]. An indispensable prerequisite for achieving large second-order nonlinear optical response in organic molecule is the existence of a strong intramolecular charge transfer, resulting from electron-donor and -acceptor groups communicating through a π-conjugated molecular framework.

EXPERIMENTAL

The 2,4-dihalopicolines and their N-oxides were synthesized by previously described methods [18, 19].

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.

The calculations of the electronic spectra of the titled compounds were performed within the framework of the all-valence electrons INDO method [24] utilizing some of its modifications [25-27] and including 100 single excited configurations in the configuration interaction procedure. The ground state geometry of the species was optimized using the semiempirical AM1 method [28].

RESULTS AND DISCUSSION

Properties of the Ground State

In Table 1 and Fig. 1 the structure of the limiting HOMO, LUMO orbital is shown as well as their energies, charge densities for the ground state, and charge densities for the first excited state of the title compounds. As is

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TABLE 1. The Values of Net Electronic Charges at the Atoms and HOMO, LUMO Energies of 2,4-Dihalopicolines and Their N-Oxides

Atom[a]	2,4-dichloro-3-methylpyridine		2,4-dichloro-5-methylpyridine		2,4-dichloro-6-methylpyridine		2,4-dibromo-3-methylpyridine		2,4-dibromo-5-methylpyridine		2,4-dibromo-6-methylpyridine	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
1N	-0,293	0,104	-0,293	0,118	-0,321	0,086	-0,283	0,097	-0,283	0,097	-0,311	0,078
2C	0,354	0,175	0,375	0,222	0,383	0,226	0,328	0,149	0,350	0,189	0,357	0,201
3C	0,024	0,051	-0,071	-0,051	-0,076	-0,055	0,038	0,064	-0,056	-0,032	-0,061	-0,042
4C	0,239	0,059	0,239	0,060	0,270	0,092	0,210	0,027	0,211	0,027	0,242	0,062
5C	-0,051	-0,032	0,041	0,064	-0,086	-0,051	-0,041	-0,025	0,049	0,070	-0,076	-0,044
6C	0,163	0,006	0,145	-0,042	0,251	0,070	0,162	0,007	0,143	-0,031	0,250	0,072
7X	-0,210	-0,187	-0,211	-0,189	-0,216	-0,192	-0,202	-0,163	-0,203	-0,163	-0,208	-0,168
8X	-0,194	-0,195	-0,193	-0,193	-0,197	-0,197	-0,179	-0,174	-0,178	-0,174	-0,184	-0,177
9H	0,008	0,015	0,015	0,022	0,017	0,028	0,007	0,014	0,013	0,023	0,016	0,025
10H	-0,018	0,016	-0,019	0,012	0,010	0,018	-0,017	0,017	-0,017	0,015	0,009	0,018
11C	-0,070	-0,064	-0,070	-0,066	-0,078	-0,062	-0,072	-0,066	-0,069	-0,064	-0,078	-0,062
12H	0,015	0,019	0,016	0,018	0,018	0,020	0,015	0,019	0,016	0,017	0,018	0,021
13H	0,017	0,016	0,013	0,012	0,013	0,008	0,017	0,017	0,016	0,017	0,013	0,008
14H	0,017	0,016	0,012	0,012	0,012	0,008	0,017	0,017	0,009	0,009	0,013	0,008
HOMO	-11,1558		-11,0979		-11,1713		-11,1540		-11,1052		-11,1608	
LUMO	-1,3638		-1,3820		-1,3609		-1,3920		-1,4123		-1,3933	

TABLE 1. (Continued)

Atom[a]	2,4-dichloro-3-methylpyridine N-oxide		2,4-dichloro-5-methylpyridine N-oxide		2,4-dichloro-6-methylpyridine N-oxide		2,4-dibromo-3-methylpyridine N-oxide		2,4-dibromo-5-methylpyridine N-oxide	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
1N	0,495	0,151	0,497	0,152	0,464	0,126	0,505	0,157	0,506	0,158
2C	0,210	0,087	0,237	0,128	0,244	0,133	0,172	0,046	0,198	0,081
3C	0,028	0,025	-0,065	-0,069	-0,072	-0,076	0,043	0,039	-0,049	-0,053
4C	0,165	0,042	0,166	0,043	0,199	0,076	0,134	0,012	0,135	0,012
5C	-0,038	-0,041	0,052	0,049	-0,075	-0,078	-0,027	-0,031	0,061	0,058
6C	0,025	-0,074	0,000	-0,114	0,127	0,019	0,023	-0,069	-0,000	-0,101
7X	-0,144	-0,148	-0,145	-0,148	-0,148	-0,151	-0,125	-0,126	-0,126	-0,127
8X	-0,170	-0,176	-0,169	-0,176	-0,172	-0,178	-0,154	-0,159	-0,154	-0,159
9H	0,018	0,022	0,024	0,027	0,027	0,030	0,017	0,020	0,021	0,024
10H	0,026	0,027	0,025	0,026	0,020	0,024	0,027	0,028	0,026	0,027
11C	-0,073	-0,071	-0,072	-0,071	-0,075	-0,072	-0,074	-0,073	-0,071	-0,070
12H	0,022	0,022	0,021	0,022	0,043	0,043	0,022	0,022	0,023	0,023
13H	0,022	0,022	0,020	0,019	0,016	0,013	0,022	0,022	0,023	0,023
14H	0,022	0,022	0,019	0,019	0,016	0,013	0,022	0,022	0,014	0,014
15O	-0,609	0,090	-0,610	0,090	-0,614	0,081	-0,605	0,090	-0,606	0,089
HOMO	-10,1748		-10,1789		-10,1260		-10,2024		-10,1978	
LUMO	-1,8170		-1,8216		-1,8112		-1,8191		-1,8291	

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[a] Numbering of atoms in Fig. 10.

TABLE 2. Comparison of the Computed and Experimental Spectra of 2,4-Dihalopicolines and Their N-Oxides

Compound	State	Sym.	Calculated			Experimental			
			Energy (eV)	Oscillator strength	Dipole moment (D)	Energy		$\varepsilon \times 10^{-3}$	Dipole moment (D)
						(nm)	(eV)		
1	2	3	4	5	6	7	8	9	10
2,4-Dichloro-3-methylpyridine	S_0	—	0	—	2,23	—	—	—	2,47
	S_1 (n,π^*)	A''	3,48	0,003	3,58	276	4,49	4,11	
	S_2 (n,π^*)	A''	4,39	0,000	5,43	268	4,62	5,29	
	S_3 (π,π^*)	A'	4,42	0,050	1,51	230	5,38	11,42	
	S_4 (π,π^*)	A'	5,07	0,027	1,61	230	5,38	11,42	
	S_5 (π,π^*)	A'	5,97	0,589	2,57				
	S_6 (n,π^*)	A''	6,07	0,714					
2,4-Dichloro-5-methylpyridine	S_0	—	0	—	2,82	—	—	—	2,41
	S_1 (n,π^*)	A''	3,49	0,003	3,95				
	S_2 (n,π^*)	A''	4,40	0,000	5,67				
	S_3 (π,π^*)	A'	4,42	0,056	2,55	278	4,46	3,78	
	S_4 (π,π^*)	A'	5,06	0,091	2,60	270	4,59	4,50	
	S_5 (π,π^*)	A'	6,08	0,770	4,27	216	5,73	12,64	
	S_6 (π,π^*)	A'	6,10	0,482		216	5,73	12,64	
2,4-Dichloro-6-methylpyridine	S_0	—	0	—	2,79	—	—	—	2,26
	S_1 (n,π^*)	A''	3,52	0,003	3,84				
	S_2 (n,π^*)	A''	4,43	0,000	5,64				
	S_3 (π,π^*)	A'	4,43	0,056	2,40	276	4,49	3,94	
	S_4 (π,π^*)	A'	5,14	0,032	2,17	269	4,60	4,22	
	S_5 (π,π^*)	A'	6,01	0,552	2,26	217	5,70	9,29	
	S_6 (π,π^*)	A'	6,11	0,770		217	5,70	9,29	
	S_7 (σ,π)	A''	6,22	0,024					
2,4-Dibromo-3-methylpyridine	S_0	—	0	—	2,29	—	—		2,59
	S_1 (n,π^*)	A''	3,45	0,003	3,39				
	S_2 (n,π^*)	A''	4,34	0,000	5,22				
	S_3 (π,π^*)	A'	4,44	0,052	1,48	277	4,48	3,20	
	S_4 (π,π^*)	A'	5,05	0,019	1,78	271	4,57	3,49	
	S_5 (n,π^*)	A''	5,21	0,018	1,37				
	S_6 (n,π^*)	A''	5,24	0,009					
	S_7 (π,π^*)	A'	5,54	0,011		223	5,55	7,94	
	S_8 (π,π^*)	A'	5,55	0,023					
	S_9 (π,π^*)	A'	5,72	0,137		202	6,07	25,29	
	S_{10} (σ,π^*)	A''	5,85	0,000					
2,4-Dibromo-5-methylpyridine	S_0	—	0	-	2,89	—	—	—	2,80
	S_1 (n,π^*)	A''	3,46	0,003	3,67				
	S_2 (n,π^*)	A''	4,37	0,000	5,37				
	S_3 (π,π^*)	A'	4,44	0,058	2,47	280	4,43	4,89	
	S_4 (π,π^*)	A'	5,05	0,063	2,05	272	4,56	14,95	
	S_5 (n,π^*)	A''	5,23	0,006	2,44				
	S_6 (n,π^*)	A''	5,27	0,024		223	5,55	39,67	

TABLE 2. (Continued)

1	2	3	4	5	6	7	8	9	10
	S_7 (π,π^*)	A'	5,58	0,010					
	S_8 (π,π^*)	A'	5,60	0,024					
	S_9 (π,π^*)	A'							
2,4-Dibromo-6-methylpyridine	S_0	—	0	—	2,89	—	—	—	2,02
	S_1 (n,π^*)	A''	3,49	0,003	3,70				
	S_2 (n,π^*)	A''	4,39	0,000	5,42				
	S_3 (π,π^*)	A'	4,45	0,059	2,35	279	4,46	3,58	
	S_4 (π,π^*)	A'	5,11	0,023	1,64	270	4,59	3,93	
	S_5 (n,π^*)	A''	5,26	0,016	1,82	224	5,52	7,86	
	S_6 (n,π^*)	A''	5,30	0,015					
	S_7 (π,π^*)	A'	5,58	0,011					
	S_8 (π,π^*)	A'	5,59	0,024					
	S_9 (π,π^*)	A'	5,78	0,148		203	6,10	27,74	
	S_{10} (π,π^*)	A'	5,89	0.000					
2,4-Dichloro-3-methylpyridine N-oxide	S_0	—	0	—	3,74	—	—	—	4,39
	S_1 (n,π^*)	A''	3,07	0,000	3,95				
	S_2 (π,π^*)	A'	3,80	0,057	1,52				
	S_3 (π,π^*)	A'	4,02	0,341	1,85	278	4,46	20,65	
	S_4 (n,π^*)	A''	5,23	0,002	8,03				
	S_5 (π,π^*)	A'	5,43	0,564	3,89	229	5,41	33,17	
	S_6 (n,π^*)	A''	5,83	0,013					
	S_7 (π,π^*)	A'	5,99	0,438					
	S_8 (π,π^*)	A'	6,29	0,406					
	S_9 (π,π^*)	A'	6,31	0,019					
2,4-Dichloro-5-methylpyridine N-oxide	S_0	—	0	—	4,07	—	—	—	3,57
	S_1 (n,π^*)	A''	3,08	0,000	4,32				
	S_2 (π,π^*)	A'	3,81	0,059	2,21				
	S_3 (π,π^*)	A'	4,03	0,353	2,20	276	4,49	17,22	
	S_4 (n,π^*)	A''	5,22	0,002	8,18				
	S_5 (π,π^*)	A'	5,45	0,575	3,64	229	5,41	28,13	
	S_6 (n,π^*)	A''	5,81	0,011					
	S_7 (π,π^*)	A'	6,03	0,354					
	S_8 (π,π^*)	A'	6,29	0,534					
2,4-Dichloro-6-methylpyridine N-oxide	S_0	—	0	—	3,92	—	—	—	4,11
	S_1 (n,π^*)	A''	3,07	0,000	4,44				
	S_2 (π,π^*)	A'	3,79	0,068	2,02				
	S_3 (π,π^*)	A'	3,97	0.320	2,65	274	4,52	16,64	
	S_4 (n,π^*)	A''	5,18	0,001	8,17				
	S_5 (π,π^*)	A'	5,42	0,583	3,53	228	5,44	31,32	
	S_6 (n,π^*)	A''	5,80	0,008					
	S_7 (π,π^*)	A'	6,07	0,378					
	S_8 (π,π^*)	A'	6,30	0,514					

TABLE 2. (Continued)

1	2	3	4	5	6	7	8	9	10
2,4-Dibromo-3-methylpyridine N-oxide	S_0	—	0	—	3,64				4,09
	S_1 (n,π^*)	A''	3,07	0,000	3,92				
	S_2 (π,π^*)	A'	3,84	0,057	1,44				
	S_3 (π,π^*)	A'	4,07	0,357	1,76	282	4,40	21,14	
	S_4 (n,π^*)	A''	4,91	0,010	6,56				
	S_5 (n,π^*)	A''	5,26	0,002	8,01				
	S_6 (π,π^*)	A'	5,39	0,021					
	S_7 (π,π^*)	A'	5,40	0,521		234	5,30	32,72	
	S_8 (π,π^*)	A'	5,91	0,020					
	S_9 (π,π^*)	A'	5,91	0,027					
	S_{10} (π,π^*)	A'	5,97	0,414		208	5,95	18,,97	
2,4-Dibromo-5-methylpyridine N-oxide	S_0	—	0	—	4,01	—	—	—	3,87
	S_1 (n,π^*)	A''	3,07	0,000	4,30				
	S_2 (π,π^*)	A'	3,85	0,057	1,82				
	S_3 (π,π^*)	A'	4,07	0,369	2,21	280	4,43	19,95	
	S_4 (n,π^*)	A''	4,93	0,009	7,25				
	S_5 (n,π^*)	A''	5,28	0,002	8,14				
	S_6 (π,π^*)	A'	5,41	0,542		234	5,30	31,41	
	S_7 (n,π^*)	A''	5,43	0,027					
	S_8 (π,π^*)	A'	5,95	0,002					
	S_9 (π,π^*)	A'	5,95	0,031					
	S_{10} (π,π^*)	A'	6,03	0,186		210	5,89	20,64	

2,4-Dibromo-6-methylpyridine N-oxide was not isolated in analytical purity [19].

known from literature [13] N-oxidation of pyridine brings a large energy displacement of pyridine's unshared electron pair (n) by about 1 eV toward higher energies. N-oxidation of 2,4-dihalopicolines brings a significant increase in HOMO from -11.15-11.09 eV to -10.20-10.13 eV, whereas introduction of the second halogen to 2-chloropicoline N-oxides in position 4 results in a slight decrease of these energies from -10.49--10.455 eV [13] to -10.18--10.13 eV. The methyl group does not significantly influence the level of HOMO energy. The level of HOMO energies and the susceptibility on electrophilic substitution decreased in the same order: 2,4-dibromopicolines > 2,4-dichloropicolines > 2,4-dichloropicoline N-oxides > 2,4-dibromopicoline N-oxides. Comparison of the excessive charge density on the oxygen atom of pyridine N-oxide [13] (-0.752), 2-chloropicoline N-oxides [13] (-0.730--0,738), 2-bromopicoline N-oxides (-0.701--0.712 eV), 2,4-dichloropicoline N-oxides (-0.609--0.614 eV, Table 1, Fig. 1) and 2,4-dibromopicoline N-oxides (-0.605--0.606 eV) points out that the degree of intramolecular charge transfer in the ground state is the highest in 2,4-dibromo derivatives. The charge distribution can be helpful when considering the reactivity of the studied compounds. Positive extensive charge densities on carbon 2 and 4 in 2,4-dichloropicoline N-oxide result in replacement of halogen-2 and halogen-4 in reaction with thioacetamide [19].

The calculated dipole moments of the compounds studied agree satisfactorily with experimental values [9] (Table 2). The dipole moments of 2,4-dihalopicoline N-oxides are considerably higher than those of their parent base (it is analogous if the dipole moments of 2-halopicolines and their N-oxides are compared [8, 9, 17]). There is evidence of great inductive effect of the N-oxide group, and susceptibility to nucleophilic substitution of a halogen situated in position 2 confirms this effect. The dipole moments of 2,4-dihalo-5-methylpyridine N-oxides are the lowest because the close neighborhood of methyl group (having positive inductive effect on halogen in position 4) increases the dipole moment of this halogen. This fact causes a decrease in the dipole moment of 2,4-dihalo derivatives because dipole moments of the halogen 4 and N-oxide group are oppositely directed. The methyl group in position 3 influenced by a halogen in positions 2 and 4 exerts a smaller influence on the dipole moment of the molecule. The calculated dipole moments of the studied compounds agree satisfactorily with the experimental values [9] (Table 2). This agreement proves the accuracy of the geometry of the studied molecules. Using INDO method gives better agreement than vector calculus as is shown earlier [9, 13, 17]. Determination of the experimental dipole moment values of 2,4-dihalopicoline N-oxides enabled us to state that the halogen in position 4 decreased a similar bond contribution of N-oxide group, resulting in polarity decrease of the above-mentioned compounds [9] compared with 2-halopicoline N-oxides [8]. Calculation of dipole moments by vector calculus and their N-oxides does not take into account the strong influence of halogen atoms situated in positions 2 and 4, various mesomeric interactions with the N-oxide group and methyl group and with the ring as well as the effect of solvent and ability of the mentioned compounds to form *self*-complexes.

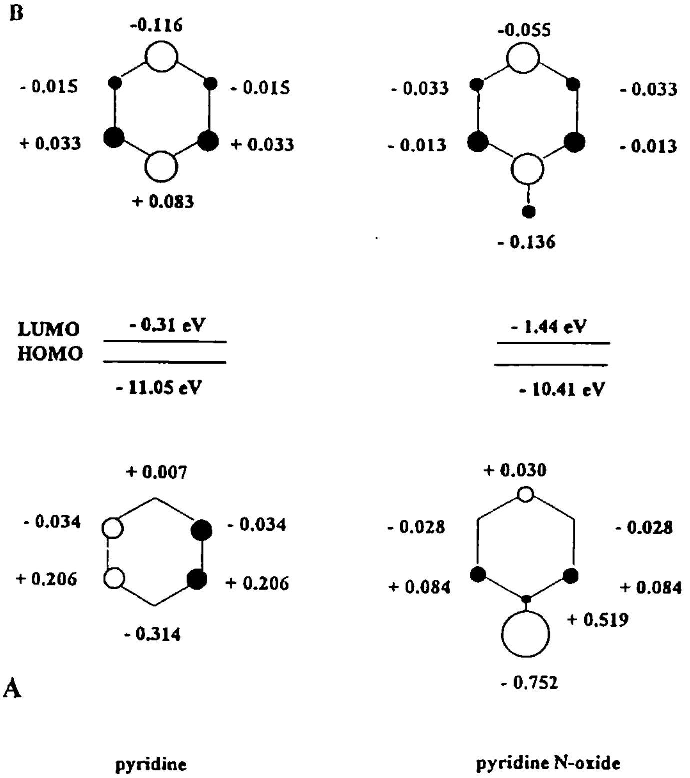


Fig. 1. Charge density of pyridine and pyridine N-oxide.

Spectra and Excited State Properties

In Figs. 6-9 the absorption spectra of 2,4-dihalopicolines and 2,4-dihalopicoline N-oxides are presented. Spectra of these compounds manifest their characteristic bands in the regions 200-240 nm and 240-300 nm. These bands are ascribed to excitations $\pi^* \leftarrow \pi$ or π_{ring} and are typical for N-oxides of aromatic amines, in which groups N—O and C=C 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).

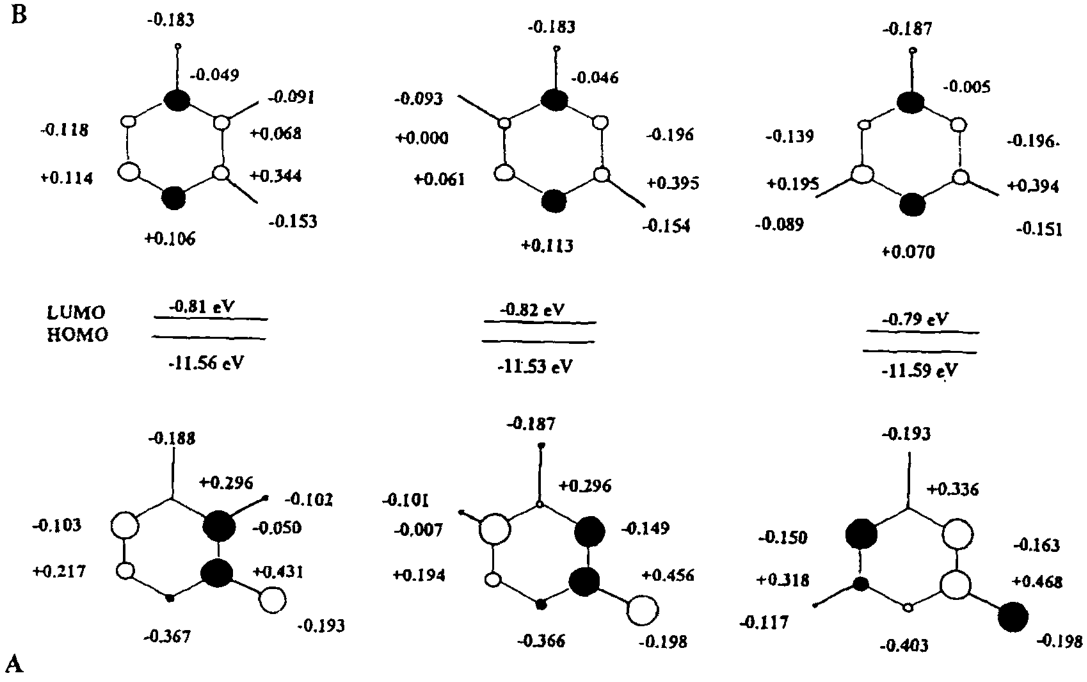
In comparison to the spectra of 2,4-dichloropicolines, those of 2,4-dibromopicolines are characterized by higher intensity in the region of 200-240 nm and are shifted towards red. The intensities of bands I are comparable and have a marked oscillatory structure.

N-oxidation of 2,4-dihalo derivatives manifests itself with a considerable change in the intensity of band I, whereas the intensities of the remaining bands are close to each other irrespective of the kind of halogen (Figs. 6-9). The spectral parameters are summarized in Table 2.

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 calculated change in dipole moment during electron excitation to the first excited singlet state is about 1.05-1.35 D for 2,4-dichloropicolines, 0.79-1.1 D for 2,4-dibromopicolines, 0.21-0.52 D for 2,4-dichloropicoline N-oxides and 0.28-0.29 D for 2,4-dibromopicoline N-oxides.

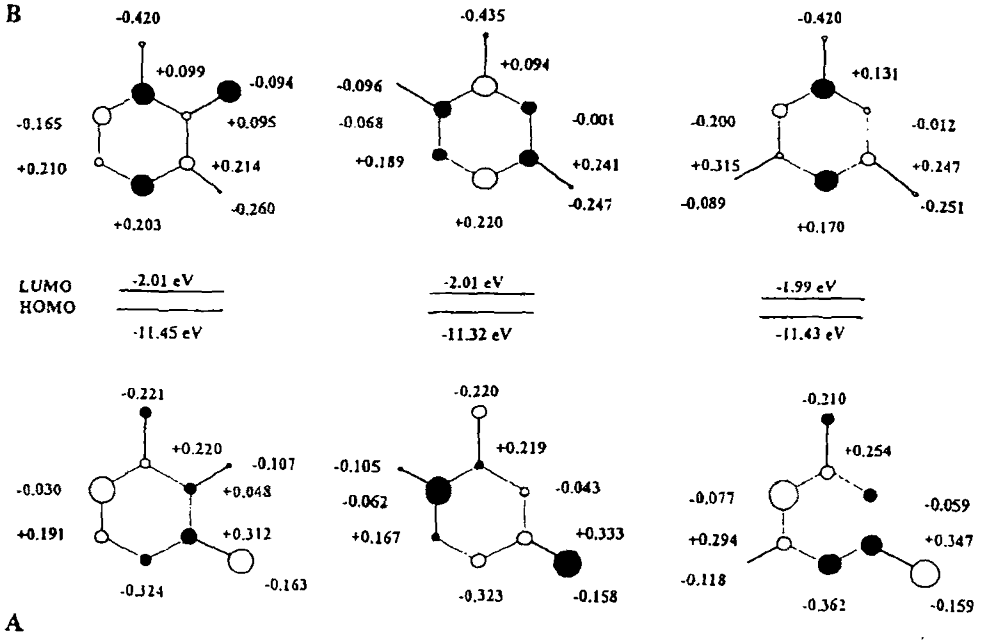
It is interesting to note that among the $\pi^* \leftarrow \pi$ singlet states, S_1 and S_2 states for dihalopicolines and S_1 and S_4 states for dihalopicoline N-oxides correspond to high transfer bands; this agrees with Kubota's experimental conclusions [1]. The distribution of charge in the ground and excited states provides the measure for the electron transfer. On transition from the ground state to the first excited state in 2,4-dichloropicoline N-oxides (Table 1) the value of the negative charge at the oxygen atom of N-oxide group is lowered but it is increased at positions 3 and 5 as well as at the halogen-4 atom. The above observations, as well as the positive charge lowering 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 halogen atom in position 4 to the ring.

Summing up the results of this paper and comparing them with those obtained earlier leads to an important conclusion. Among all the 2-halopicolines tested, the UV spectra of 2-iodopicolines, and in each group of methyl derivatives the 5-methyl derivatives, distinguished themselves by highest intensity. This fact results from participation



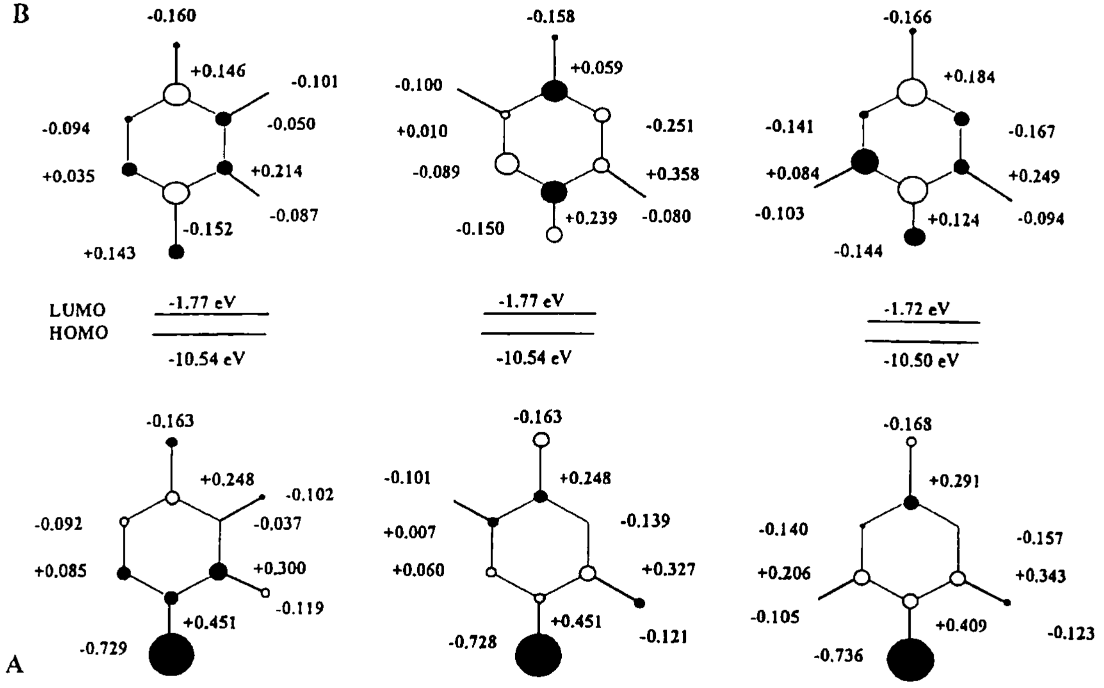
2,4-di-Cl-3-CH$_3$-pyridine 2,4-di-Cl-5-CH$_3$-pyridine 2,4-di-Cl-6-CH$_3$-pyridine

Fig. 2. Charge density diagram of 2,4-dichloropicolines.



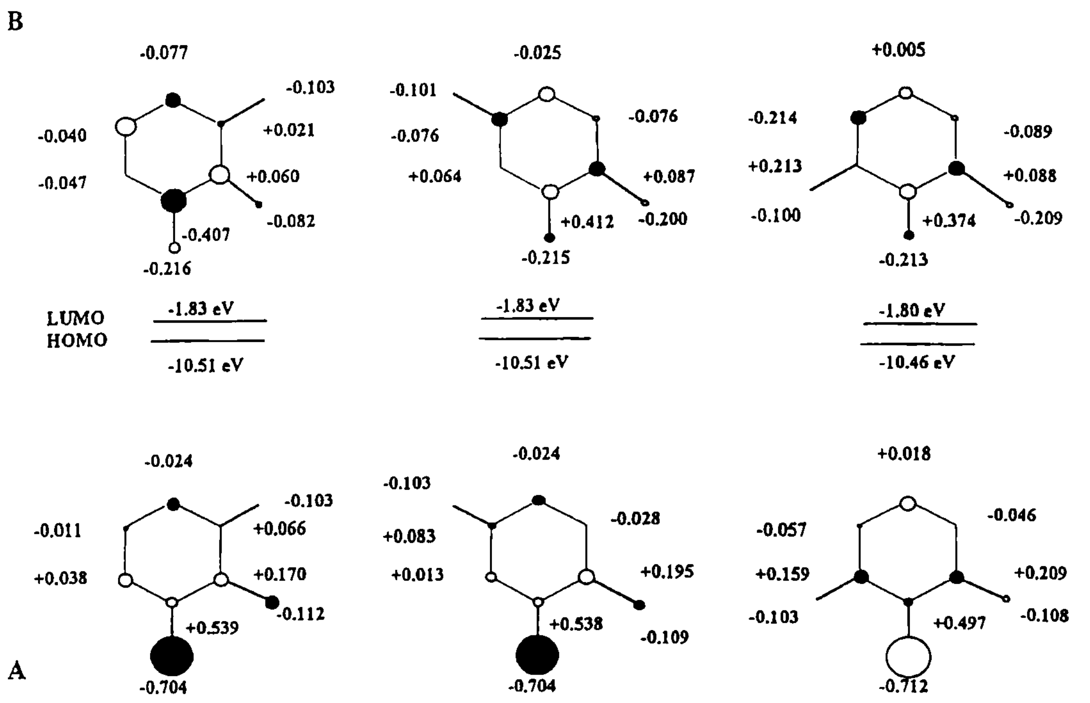
2,4-di-Br-3-CH$_3$-pyridine 2,4-di-Br-5-CH$_3$-pyridine 2,4-di-Br-6-CH$_3$-pyridine

Fig. 3. Change density diagram of 2,4-dibromopicolines.



2,4-di-Cl-3-CH_3-pyridine N-oxide   2,4-di-Cl-5-CH_3-pyridine N-oxide   2,4-di-Cl-6-CH_3-pyridine N-oxide

Fig. 4. Charge density diagram of 2,4-dichloropicoline N-oxides.



2,4-di-Br-3-CH$_3$-pyridine N-oxide   2,4-di-Br-5-CH$_3$-pyridine N-oxide   2,4-di-Br-6-CH$_3$-pyridine N-oxide

Fig. 5. Charge density diagram of 2,4-dibromopicoline N-oxides.

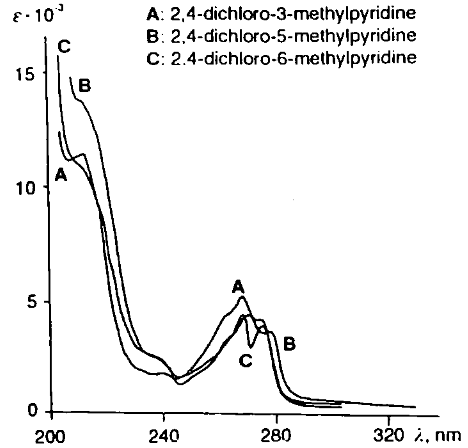


Fig. 6. Absorption spectra of 2,4-dichloropicolines in ethyl alcohol.

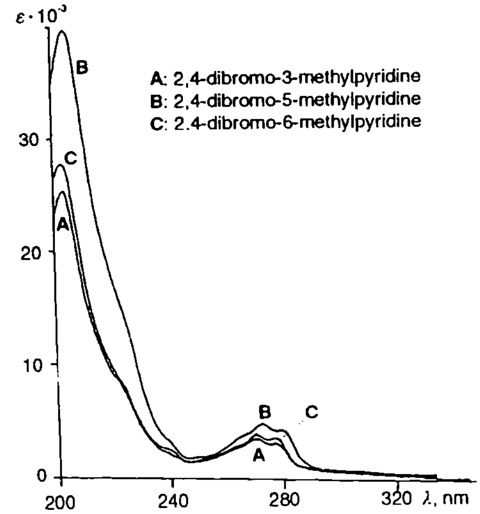


Fig. 7. Absorption spectra of 2,4-dibromopicolines in ethyl alcohol.

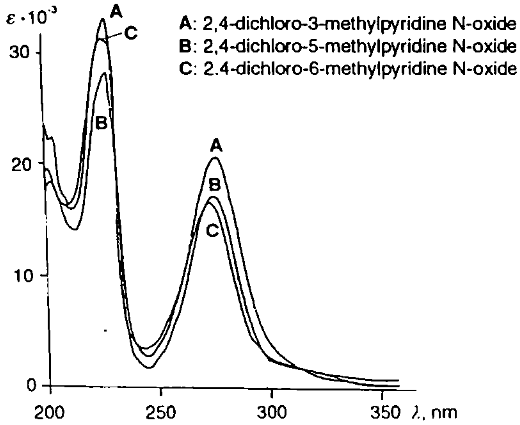


Fig. 8. Absorption spectra of 2,4-dichloropicoline N-oxides in ethyl alcohol.

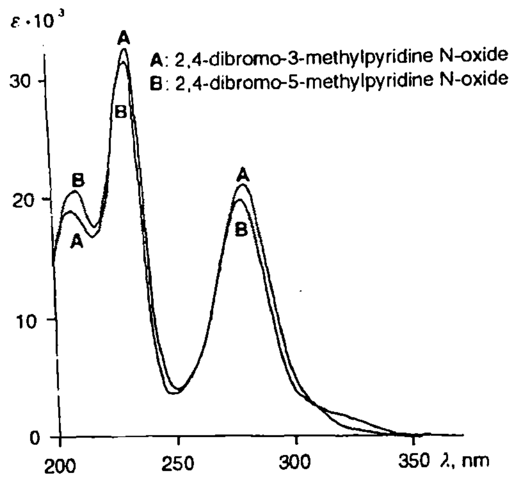


Fig. 9. Absorption spectra of 2,4-dibromopicoline N-oxides in ethyl alcohol.

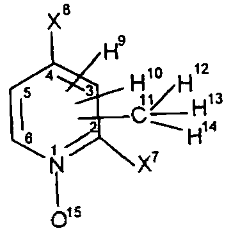


Fig. 10. Enumeration of atoms in examined molecules.

of d electrons in conjugation as well as from complementary interaction between halogen in position 2 and methyl group in position 5. The spectra of 2,4-dihalopicoline N-oxides, compared to those of 2,4-dihalopicolines, are characterized not only by higher intensity, but also by considerably increased intensity of band II in the region of 200-240 nm, particularly in relation to bromo derivatives. That 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, d coupling). Though the intensity of 5-methyl derivatives is high, it is not marked as well as in the case of 2-halopicolines because of the predominant part played by the coupling between halogen in positions 2 and 4 and nitrogen of the pyridine ring, as well as between halogens in positions 2 and 4. The dependence under discussion is still more weakly marked in the spectra of 2,4-dihalopicoline N-oxides. The spectra of these compounds hardly attain triband structure (typical of pyridine N-oxide derivatives) because the band in the region of 200-250 nm is composed of two bands (one of which is weakly developed, particularly in the case of chloro derivatives).

The spectra of 2,4-dihalopicoline N-oxides are shifted towards red (200-350 nm), as in relation to parent bases (200-300 nm), whereas band I (in the region 250-350 nm) considerably increases its intensity (about four times); band II (in the region 200-250 nm) in the case of chloro derivatives increases its intensity almost twice.

As can be stated on the backgrounds of calculated and experimental data concerning of 2,4-dihalopicoline N-oxides, these compounds should demonstrate higher susceptibility to photochemical reactions than 2-halopicoline N-oxide and lower than that of 2-halo-4-nitropicoline N-oxides. The value of the HOMO—LUMO energy difference changes in a similar way. The values of HOMO energy allow us to foresee a series of reactivities: 2,4-dihalopyridine N-oxide (-10.12-10.20 eV) < 2-halopyridine N-oxide (-10.50--10.45 eV) < 2-halo-4-nitropyridine N-oxides (-11.29--11.22 eV).

The values of LUMO energies (E) and susceptibility on electrophilic substitution change in following way:

$E_{\text{pyridine N-oxide}}$ (-1.44 eV) > $E_{\text{2-halopyridine N-oxide}}$ (-1.83—1.55 eV) > $E_{\text{2,4-dihalopyridine N-oxide}}$ (-2.60—1.72 eV) > $E_{\text{2-halo-4-nitropyridine N-oxide}}$ (-3.01--3.11 eV).

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