

Electronic Spectra and Structure of 2,6-Dimethyl-3-halo-4-nitropyridine *N*-Oxides

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The UV spectra of 2,6-dimethyl-3-halo(F, Cl, Br, I)-4-nitropyridine *N*-oxides in heptane have been examined and compared with the results (transition energies, intensities) of modified INDO calculations in order to make the assignment of some bands. The influence of substituents in the molecule on λ_{\max} and ε_{\max} is discussed. The dipole moments are calculated and compared with experimental values. The effect of steric hindrance on the spectra is interpreted.

This paper is a part of our systematic, spectroscopic investigations on substituted pyridine *N*-oxide derivatives. 4-Nitropyridine *N*-oxide derivatives belong to the most extensively studied compounds because of their interesting properties. It has been suggested that the presence of the nitro group is essential for any significant antifungal activity of these compounds [1]. An electron-donating property of the *N*-oxide group, increased by the NO₂ function, has an essential chemical consequence; it accounts for the easy synthesis of other 4-substituted pyridine *N*-oxides. The nitro derivatives are also prospective crystals for second-harmonic generation [2–6].

The X-ray crystal structure determination and vibrational spectra of 3-chloro- and 3-bromo-2,6-dimethyl-4-nitropyridine *N*-oxides show that the two pyridine derivatives are isomorphic with monoclinic space group P2₁/c and contain four formula units in a cell. The shortest intermolecular contacts form medium strong hydrogen bond of the type C—H···O [7].

In a previous paper the electronic structure and spectra of 2,6-dimethyl-3-halopyridine *N*-oxides were reported [8].

In order to determine the mutual interaction of N⁺—O[−] and NO₂ groups and their modification by the steric effects of the halogen, the absorption spectra of the title compounds were recorded and the charge distribution in the molecule, the dipole moments, and the electronic spectra were calculated by a modified INDO method (GRINDOL) [9].

EXPERIMENTAL

2,6-Dimethyl-3-halo-4-nitropyridine *N*-oxides used in the study were synthesized by the previously described method [11].

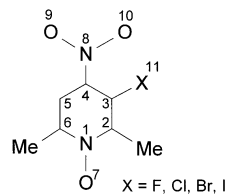
The UV absorption spectra were recorded by means of UV VIS Specord (Zeiss, Jena) spectrometer in heptane solutions (concentration $\approx 10^{-4}$ mol dm^{−3}, cell thickness 0.097 cm). The calculations of the electronic structure and spectra were performed within the framework of the modified all-valence electrons INDO method [12], utilizing some of its modifications [13–15] and including 100 single excited configurations in the configuration procedure. The ground state geometry of the species was optimized using the semiempirical AM₁ method [16], yielding geometries in good agreement with experimental X-ray crystal structure determination [7].

RESULTS AND DISCUSSION

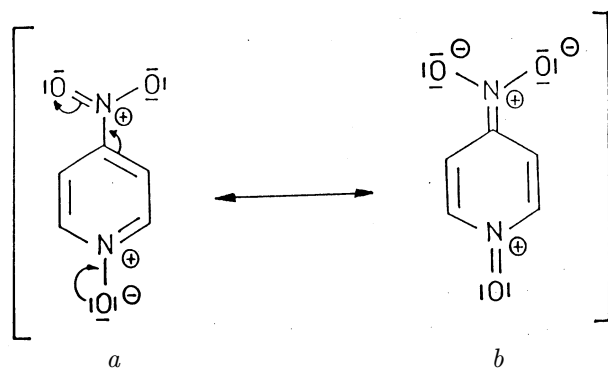
Properties of the Ground State

The nitration of 2,6-dimethyl-3-halopyridine *N*-oxides causes a decrease in HOMO energies from $-(10.05-10.21)$ eV to $-(10.65-10.72)$ eV and LUMO from $-(1.64-1.81)$ eV to $-(2.44-2.89)$ eV (see Table 1 and Ref. [8]). Table 1 summarizes the calculated excessive charge density on the atoms of all studied compounds. Comparison of the excessive charge density on the oxygen atoms of the 2,6-dimethyl-3-halopyridine *N*-oxides [8] and their 4-nitro derivatives points out that the degree of intramolecular charge transfer in the ground state is higher in the 4-nitro compounds. The carbon atom in position 3 of 3-halo-4-nitro derivatives exhibits a large positive charge density which is slightly smaller when compared with unnitrated compounds, and decreases in the analogous sequence: F, I, Cl, Br.

The charge distribution explains the mechanism of methanolysis of 2,6-dimethyl-3-halo-4-nitropyridine *N*-oxides [11]. A large positive charge at position 3

Table 1. The Values of Net Electronic Charges at the Atoms and HOMO, LUMO Energies of 2,6-Dimethyl-4-nitropyridine *N*-Oxide and 2,6-Dimethyl-3-halo(F, Cl, Br, I)-4-nitropyridine *N*-Oxides in the Ground State (S_0) and the First Excited State (S_1)

	2,6-(Me) ₂ -4-NO ₂ -pyridine <i>N</i> -oxide		2,6-(Me) ₂ -3-F-4-NO ₂ -pyridine <i>N</i> -oxide		2,6-(Me) ₂ -3-Cl-4-NO ₂ -pyridine <i>N</i> -oxide		2,6-(Me) ₂ -3-Br-4-NO ₂ -pyridine <i>N</i> -oxide		2,6-(Me) ₂ -3-I-4-NO ₂ -pyridine <i>N</i> -oxide	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
N-1	0.468	0.125	0.457	0.116	0.464	0.122	0.462	0.120	0.460	0.120
C-2	0.126	0.035	0.093	-0.007	0.104	0.009	0.103	0.009	0.114	0.023
C-3	-0.062	-0.070	0.314	0.305	0.145	0.136	0.118	0.110	0.151	0.143
C-4	0.067	-0.054	0.030	-0.087	0.041	-0.079	0.040	-0.080	0.049	-0.073
C-5	-0.062	-0.070	-0.067	-0.074	-0.061	-0.069	-0.061	-0.070	-0.063	-0.071
C-6	0.126	0.035	0.112	0.025	0.121	0.033	0.120	0.031	0.126	0.032
O-7	-0.588	0.085	-0.582	0.091	-0.583	0.087	-0.582	0.087	-0.581	0.089
N-8	0.822	0.822	0.830	0.831	0.826	0.826	0.824	0.824	0.822	0.822
O-9	-0.477	-0.478	-0.472	-0.473	-0.471	-0.473	-0.472	-0.473	-0.469	-0.470
O-10	-0.477	-0.478	-0.472	-0.473	-0.471	-0.472	-0.472	-0.473	-0.469	-0.470
X-11			-0.296	-0.295	-0.162	-0.158	-0.122	-0.118	-0.195	-0.189
C-2'	-0.073	-0.071	-0.072	-0.070	-0.075	-0.073	-0.076	-0.074	-0.078	-0.076
C-6'	-0.073	-0.071	-0.073	-0.071	-0.073	-0.071	-0.073	-0.071	-0.073	-0.072
HOMO eV	-10.52		-10.72		-10.70		-10.67		-10.65	
LUMO eV	-2.27		-2.44		-2.89		-2.57		-2.44	



Scheme 1

in 3-fluoro derivative, higher than that at position 4, results in the replacement of the fluorine atom at first and afterwards the nitro group in reaction with sodium methoxide [11].

The electronic structure of 4-nitropyridine *N*-oxide can be envisaged by the resonance forms *a* and *b* in Scheme 1.

The strong electron-withdrawing nitro group favours the charge-transfer form *b*. For example, the dipole moment value, determined by molecular or-

bital calculations, decreases from 4.41 *D* for 2,6-dimethylpyridine *N*-oxide [8] to 1.08 *D* for its 4-nitro derivative. However, the conjugation (contribution of the resonance form *b* in studied compounds is strongly modified by the *ortho* effect of halogens present in position 3 (the disturbance of the electronic transmission between N^+-O^- and the noncoplanar NO_2 group). For that reason the ground-state dipole moments of title compounds are higher than that of 2,6-dimethyl-4-nitropyridine *N*-oxide and increase from fluoro to the iodo derivative (2.49 *D* → 3.60 *D*). These values are not in agreement with the experimental dipole moments (Table 2). Probably in the solution the association of molecules of examined compounds takes place resulting in the decrease of the dipole moments values. This conclusion is based on the fact that the IR spectrum of the 2,6-dimethyl-3-bromo-4-nitropyridine *N*-oxide in CCl_4 solution consists of one strong band at $\tilde{\nu} = 3084\text{ cm}^{-1}$ and a very weak band at $\tilde{\nu} = 3040\text{ cm}^{-1}$. The former band originates from the free C—H group and, as a result of the C—H...O interaction in the crystal, this band is shifted 27—48 cm^{-1} towards smaller wavenumbers. The appearance of the second, weak band indicates that there still exist some C—H...O interactions in the solution [7].

Table 2. Comparison of the Computed and Experimental Spectra of 2,6-Dimethyl-4-nitropyridine *N*-Oxide and 2,6-Dimethyl-3-halo(F, Cl, Br, I)-4-nitropyridine *N*-Oxides

Compound	State	Sym.	Pol.	Energy	Calculated	Dipole	Energy	Experimental	Dipole
				eV	Oscillator strength	moments	eV	$\varepsilon \cdot 10^{-3}$	moments
						<i>D</i>		$\text{mol}^{-1} \text{cm}^{-1} \text{dm}^3$	<i>D</i>
2,6-Dimethyl-4-nitropyridine <i>N</i> -oxide	S ₀	—	—	—	—	1.08			1.25**
	S ₁ (π, π^*)	A'	<i>x</i>	2.947	0.000	7.46			
	S ₂ (π, π^*)	A'	<i>y</i>	3.351	0.000	0.95			
	S ₃ (π, π^*)	A'	<i>x</i>	3.629	0.000	0.24			
	S ₄ (π, π^*)	A'	<i>y</i>	3.825	0.061	4.97	3.43	17.95	
	S ₅ (π, π^*)	A'	<i>x</i>	3.992	0.337	3.39	3.58	22.51*	
	S ₆ (π, π^*)	A'	<i>x</i>	5.111	0.003				
	S ₇ (σ, π^*)	A''	<i>z</i>	5.175	0.002				
	S ₈ (π, π^*)	A'	<i>y</i>	5.478	0.581		4.99	13.39	
	S ₉ (σ, π^*)	A''	<i>z</i>	5.731	0.100				
S ₁₀ (σ, π^*)	A''	<i>z</i>	6.155	0.449		6.20	29.92		
2,6-Dimethyl-3-fluoro-4-nitropyridine <i>N</i> -oxide	S ₀	—	—	—	—	2.49			0.97***
	S ₁ (n, π^*)	A''	<i>z</i>	2.934	0.000	8.47			
	S ₂ (π, π^*)	A'	<i>y</i>	3.376	0.000	2.46			
	S ₃ (n, π^*)	A''	<i>z</i>	3.639	0.000	1.70			
	S ₄ (π, π^*)	A'	<i>y</i>	3.769	0.041	5.73			
	S ₅ (π, π^*)	A'	<i>x</i>	3.971	0.293	4.35	3.70	14.89	
	S ₆ (σ, π^*)	A''	<i>z</i>	5.149	0.000				
	S ₇ (σ, π^*)	A''	<i>z</i>	5.211	0.002				
	S ₈ (π, π^*)	A'	<i>y</i>	5.299	0.633		4.98	10.81	
	S ₉ (σ, π^*)	A''	<i>z</i>	5.647	0.058		5.14	10.71	
S ₁₀ (π, π^*)	A'	<i>x</i>	6.010	0.401		6.20	19.18		
3-Chloro-2,6-dimethyl-4-nitropyridine <i>N</i> -oxide	S ₀	—	—	—	—	3.08			1.26***
	S ₁ (n, π^*)	A''	<i>z</i>	2.934	0.000	8.93			
	S ₂ (π, π^*)	A'	<i>y</i>	3.386	0.000	3.16			
	S ₃ (π, π^*)	A'	<i>x</i>	3.633	0.000	2.35			
	S ₄ (π, π^*)	A'	<i>y</i>	3.765	0.048	6.22			
	S ₅ (π, π^*)	A'	<i>x</i>	4.016	0.280	4.73	3.66	10.44	
	S ₆ (σ, π^*)	A''	<i>z</i>	5.132	0.000				
	S ₇ (σ, π^*)	A''	<i>z</i>	5.165	0.001				
	S ₈ (π, π^*)	A'	<i>y</i>	5.310	0.631		4.80	10.82	
	S ₉ (σ, π^*)	A''	<i>z</i>	5.645	0.057		5.90	21.51	
S ₁₀ (π, π^*)	A'	<i>x</i>	5.906	0.514					
3-Bromo-2,6-dimethyl-4-nitropyridine <i>N</i> -oxide	S ₀	—	—	—	—	2.89			1.15***
	S ₁ (π, π^*)	A'	<i>x</i>	2.918	0.000	8.73			
	S ₂ (π, π^*)	A'	<i>y</i>	3.379	0.000	2.97			
	S ₃ (π, π^*)	A'	<i>x</i>	3.634	0.000	2.13			
	S ₄ (π, π^*)	A'	<i>y</i>	3.773	0.044	6.02			
	S ₅ (π, π^*)	A'	<i>x</i>	4.026	0.269	4.47	3.66	9.43	
	S ₆ (σ, π^*)	A''	<i>z</i>	5.095	0.000				
	S ₇ (σ, π^*)	A	<i>z</i>	5.154	0.002				
	S ₈ (π, π^*)	A'	<i>y</i>	5.261	0.609		4.73	10.71	
	S ₉ (σ, π^*)	A''	<i>z</i>	5.654	0.059		5.90	20.45	
S ₁₀ (π, π^*)	A'	<i>x</i>	5.791	0.504					
2,6-Dimethyl-3-iodo-4-nitropyridine <i>N</i> -oxide	S ₀	—	—	—	—	3.60			1.10***
	S ₁ (π, π^*)	A'	<i>x</i>	2.916	0.000	9.25			
	S ₂ (π, π^*)	A'	<i>x</i>	3.364	0.000	3.76			
	S ₃ (π, π^*)	A'	<i>x</i>	3.624	0.000	2.93			
	S ₄ (π, π^*)	A'	<i>y</i>	3.767	0.057	7.04			
	S ₅ (π, π^*)	A'	<i>x</i>	4.209	0.251	5.38	3.59	8.04	
	S ₆ (σ, π^*)	A''	<i>z</i>	4.479	0.002				
	S ₇ (σ, π^*)	A''	<i>z</i>	4.756	0.016				
	S ₈ (σ, π^*)	A''	<i>z</i>	5.081	0.001				
	S ₉ (σ, π^*)	A''	<i>z</i>	5.227	0.000				
	S ₁₀ (π, π^*)	A'	<i>x</i>	5.234	0.024		4.52	8.08	
S ₁₁ (π, π^*)	A'	<i>x</i>	5.682	0.296		5.82	21.33		

*See Fig. 3, **Ref. [18], ***Ref. [19].

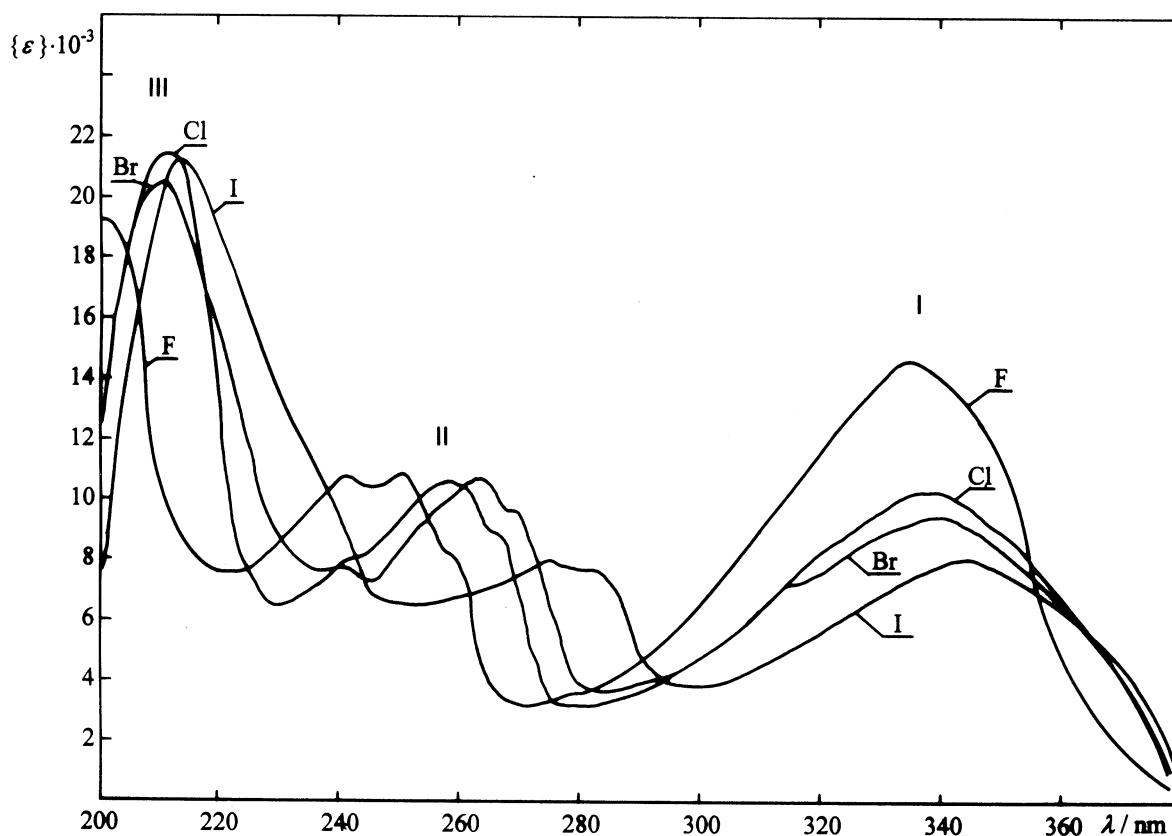


Fig. 1. Absorption spectra of 2,6-dimethyl-3-halo-4-nitropyridine *N*-oxides in heptane.

Spectra and Excited-State Properties

Fig. 1 presents the absorption spectra of 2,6-dimethyl-3-halo-4-nitropyridine *N*-oxides in heptane. The observed and calculated values of the energy of electronic transitions from the ground state to the next excited states, their intensity, symmetry, and orbital nature are summarized in Table 2. The spectra of all compounds exhibit characteristic bands in the regions $\lambda = 200\text{--}213\text{ nm}$ (5.82–6.20 eV) (Band III) and 241–282 nm (4.52–5.14 eV) (Band II). These bands are due to the $\pi^* \leftarrow \pi$ transition of the aromatic pyridine ring and the $\pi_{\text{ring}} \leftarrow \pi_{\text{oxygen}}$ transition and are characteristic of the aromatic amine *N*-oxides in which $\text{N}^+ \text{--} \text{O}^-$ and $\text{C}=\text{C}$ bonds form a conjugated system.

An additional intensive band appears in a longer wavelength region (335–362 nm) (Band I) (3.59–3.70 eV). This so-called CT band contains, like in the spectrum of 4-nitropyridine *N*-oxide [17], a large contribution of electron transition from the highest occupied MO to the lowest vacant MO and brings about a quite large charge transfer from the *N*-oxide group oxygen to the nitro group *via* the pyridine ring.

Comparison of the spectra of 2,6-dimethyl-3-halo-4-nitropyridine *N*-oxides and 2,6-dimethyl-4-nitropyridine *N*-oxide (Figs. 1 and 2) shows that the intensity

of the CT band is decreased by the *ortho* substituent in the following order: H, F, Cl, Br, I.

The calculated oscillator strength corresponding to the intramolecular charge-transfer transition (ICT) is significantly smaller for 3-iodo derivative (0.251) than for parent compound, *i.e.* 2,6-dimethyl-4-nitropyridine *N*-oxide (0.337). The twist angles of the nitro group from the molecular plane θ were estimated from the relation: $\varepsilon/\varepsilon_0 = \cos^2 \theta$ [17], where ε and ε_0 are the respective absorption coefficients of the CT band of investigated compounds and 2,6-dimethyl-4-nitropyridine *N*-oxide and are collected in Table 3.

It is worthwhile to notice that all bands in the spectrum of the 3-iodo derivative are red-shifted in relation

Table 3. The Angles of Twist of the NO_2 Group in 2,6-Dimethyl-3-halo-4-nitropyridine *N*-Oxides

Species of halogen	$\varepsilon/\varepsilon_0^*$ of CT band	$\theta/^\circ$
F	0.6616	35
Cl	0.4640	47
Br	0.4187	49
I	0.3570	53

* $\{\varepsilon_0\} = 22510$ from Fig. 2.

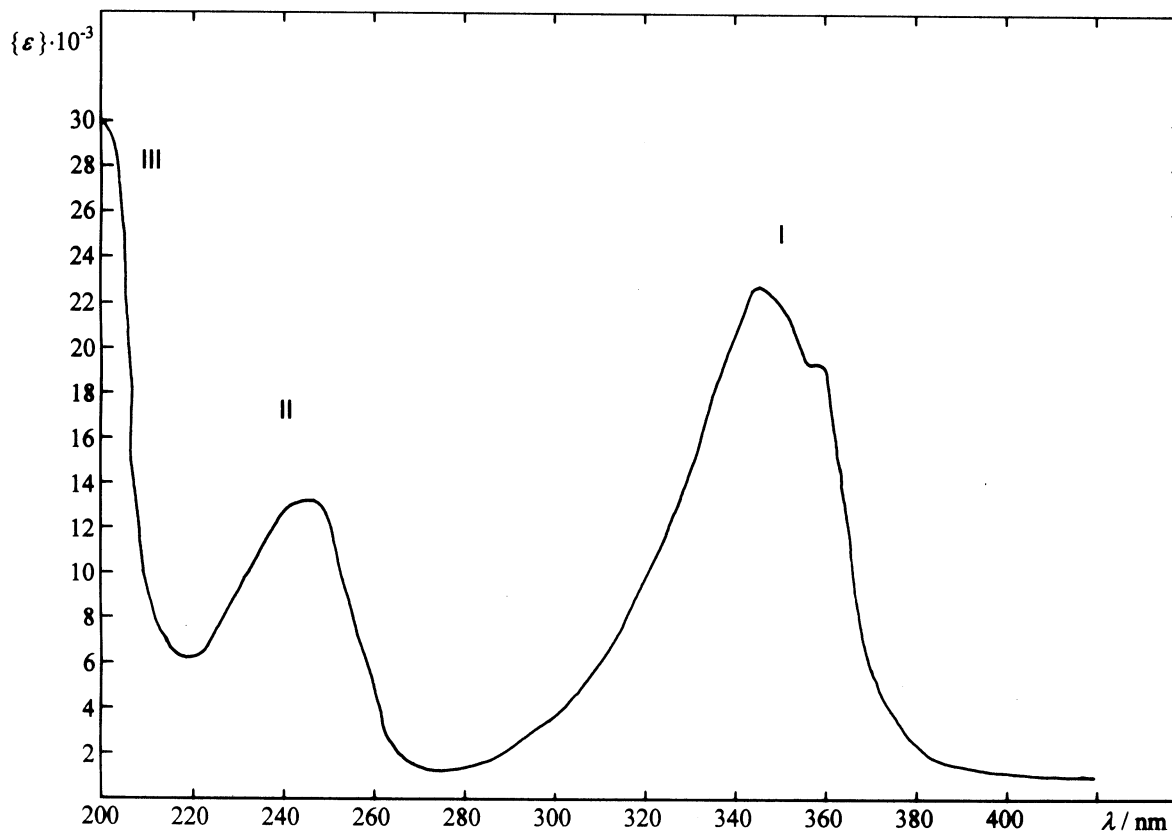


Fig. 2. Absorption spectrum of 2,6-dimethyl-4-nitropyridine *N*-oxide in heptane.

to the other 3-halo derivatives owing to the expansion of valence shell of iodine atom (*d* orbital resonance).

The transition from the ground state to the next excited states is connected with charge density changes in the molecule. 2,6-Dimethyl-3-halo-4-nitropyridine *N*-oxides in the first excited state exhibit a negative charge at position 4 of the pyridine ring contrary to the ground state and the charge at the oxygen atom of the *N*-oxide group changes from negative to positive value. These changes confirm that in the first excited state the intramolecular charge transfer occurs in a higher degree. Similarly the calculated electric dipole moments of the ground and various excited singlet states provide the measure of the electron transfer. In the case of studied compounds significant differences between the ground-state dipole moments and those in the first excited singlet state (6.38–5.65 *D*) are observed. Probably the change of direction of the dipole moment during excitation to the first excited state takes place.

Difference values of the HOMO—LUMO energies oscillate for examined compounds from –7.81 eV to –8.28 eV and are smaller than those for 2,6-dimethyl-3-halopyridine *N*-oxides (–8.41 eV to –8.40 eV). These facts point out a higher susceptibility of their photochemical reactions in comparison with those of 2,6-dimethyl-3-halopyridine *N*-oxides [19].

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