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ELECTRONIC SPECTRA AND STRUCTURE OF METHYL DERIVATIVES OF 4-NITROPYRIDINE N-OXIDE

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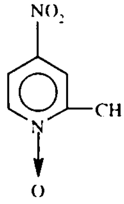
The UV spectra of seven methyl derivatives of 4-nitropyridine N-oxide in ethanol have been examined. The electronic spectra were calculated by a modified INDO method. Transition energies, intensities and assignments were compared with UV spectra. Spectroscopic manifestations of intramolecular interaction indicate that methyl groups modify the electronic interaction between the N-oxide and NO$_2$ groups mainly through a steric strain.

Keywords: methyl-4-nitropyridine N-oxides, UV spectra, INDO calculations.

A four-band system at the lowest energy is known to exhibit vibrational structure under low resolution and was extensively investigated experimentally [1-6] and theoretically [7-10]. The first transition at 3.81 eV is assigned to the lowest $^1B_2$ ($\pi\pi^*$) excitation, which agrees well with some recent theoretical and experimental data on pyridine N-oxide [4, 5, 7, 10]. The electronic spectra of pyridine N-oxide were analyzed and it was indicated, in particular, that the strong band appearing near 280 nm in aprotic solvents has $^1A_1$ symmetry and is characterized by the largest contribution of intramolecular charge transfer conjugation (HOMO-LUMO) from the N-oxide group oxygen atom to a ring π-system [11]. Molecules with high molecular β-hyperpolarizability possess a highly delocalized π-electron system bearing an electron-donor (push) and electron-acceptor (pull) groups in such positions that there occurs an intramolecular charge transfer.

Among the many organic molecules meeting the above molecular requirements, in recent years attention was attracted to 3-methyl-4-nitropyridine N-oxide because it has high nonlinear optical coefficients, high optical damage threshold, and excellent phase matching properties [12].

In this paper we have concentrated on the influence of methyl substituents on polarity and intramolecular charge transfer in seven methyl derivatives of 4-nitro-pyridine N-oxide **1-7**:



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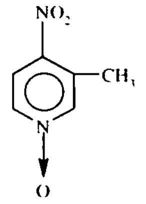

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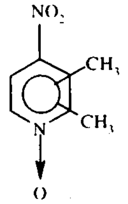

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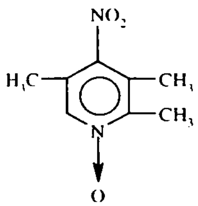

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3 [2CH$_3$, 3CH$_3$]; **4** [2CH$_3$, 5CH$_3$];
5 [2CH$_3$, 6CH$_3$]; **6** [3CH$_3$, 5CH$_3$]

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The influence of methyl groups on charge transfer, which is rarely explained in the literature, was discussed in terms of μ_{int} and the spectral characteristics of low-energy $\pi \rightarrow \pi^*$ transitions.

EXPERIMENTAL

The methyl derivatives of 4-nitropyridine N-oxide used in the study were synthesized using previously described methods [13-17].

The UV absorption spectra were recorded on a UV-Vis (Zeiss, Jena) spectrometer (alcohol solutions, concentration ~10^{-4} M, cell thickness 0.097 cm); calculations of electronic spectra and electronic structure of the studied compounds were performed within the framework of the modified all-valence electrons INDO method [18] utilizing some of its modifications [19-21] and including 100 single excited configurations in the configuration interaction procedure. The ground state geometry of the species was optimized using the *ab initio* method in the 3-21 G HF basis.

RESULTS AND DISCUSSION

Properties of the Ground State

As can be seen in Table 1, the HOMO energies depend significantly on the positions of methyl groups in the range of -11.049 to -11.228 eV. Table 1 summarizes the calculated excess charge density on the atoms of pyridine N-oxide [22], and the studied compounds point out that the degree of intramolecular charge transfer in the ground state is the highest in 3-methyl-4-nitropyridine N-oxide. For example, a discussion of excess charge distribution can be helpful considering the reactivity of the studied compounds. The charge distribution explains the mechanism and kinetics of ethanolysis of methyl derivatives of 4-nitropyridine N-oxides [23]. The latter, like pyridine N-oxide [22], exhibit the highest negative charge at the oxygen atom of the N-oxide group. The highest positive charge on C-4 (0.079) in 3,5-dimethyl-4-nitropyridine N-oxide predicts the highest nucleophilic susceptibility among the compounds studied. The susceptibility to nucleophilic substitution in relation to the positions of methyl groups is as follow: 2,6- > 2,3,6- > 2- > 2,3- > 2,5- > 2,6- > 3,5-. A detailed discussion of dipole moments of the studied compounds has been reported previously [24]. The paper [24] contains the correlation between the interaction dipole moments and the wave number of the intramolecular charge-transfer transition of methyl-4-nitropyridine N-oxides and 4-nitropyridine N-oxide and the correlation between the interaction dipole moments and the $^{13}C_{(4)}$ chemical shifts of methyl-4-nitropyridine N-oxides. While the linear relation $\mu_{int} - \nu_{ICT}$ with $\mu = 14.01 - 4.7 \times 10^{-4} \nu$ is very poor (correlation coefficient $r = 0.74$), the best correlation between μ_{int} and $\delta^{13}C$ ($r = 0.97$) was obtained by the polynominal $\mu = 7.11 - 9.84\ \delta + 0.03\delta^2$. It can be stated that introduction of methyl groups into the 4-nitropyridine N-oxide molecule modifies the charge transfer mainly by means of steric interaction. The simultaneous introduction of two methyl groups in positions 3 and 5 weakens the electron-acceptor properties of the 4-nitro group significantly. On the basis of the value μ_{int} one can expect that the contribution of the resonance from abquinoid structure would be highest in the resonance hybrid of 3,5-dimethyl-4-nitropyridine N-oxide [24].

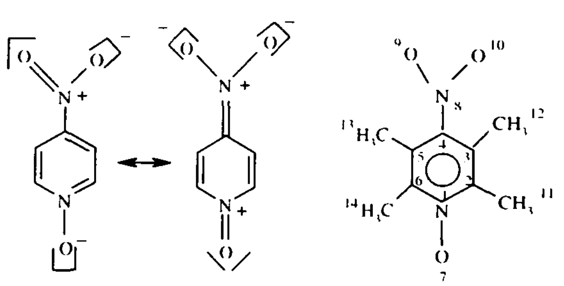

Fig. 1. Enumeration of atoms.

TABLE 1. The Values of Net Electronic Charges at the Atoms and HOMO-LUMO Energies of Methyl-4-nitropyridine N-oxides in the Ground State (S_0) and in the First Excited State (S_1)

Atom*	2-Methyl-4-nitropyridine N-oxide		3-Methyl-4-nitropyridine N-oxide		2,3-Dimethyl-4-nitropyridine N-oxide		2,5-Dimethyl-4-nitropyridine N-oxide		2,6-Dimethyl-4-nitropyridine N-oxide		3,5-Dimethyl-4-nitropyridine N-oxide		2,3,5-Trimethyl-4-nitropyridine N-oxide	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
N-1	0.486	0.213	0.548	0.269	0.484	0.214	0.498	0.228	0.436	0.172	0.549	0.279	0.486	0.225
C-2	0.194	0.121	0.025	-0.048	0.154	0.058	0.183	0.129	0.207	0.136	0.023	-0.034	0.152	0.071
C-3	-0.087	-0.164	0.080	0.008	0.031	-0.038	-0.082	-0.168	-0.103	-0.177	0.079	-0.004	0.030	-0.049
C-4	0.056	-0.205	0.001	-0.255	0.017	-0.244	0.013	-0.247	0.068	-0.197	-0.032	-0.300	-0.015	-0.292
C-5	-0.052	-0.125	-0.031	-0.115	-0.048	-0.136	0.066	-0.005	-0.103	-0.178	0.079	-0.004	0.048	-0.001
C-6	0.084	0.021	0.059	0.010	0.084	0.042	0.040	-0.032	0.207	0.136	0.023	-0.034	0.062	-0.025
O-7	-0.710	0.154	-0.697	0.157	-0.713	0.155	-0.708	0.152	-0.719	0.148	-0.702	0.159	-0.717	0.157
N-8	0.950	0.942	0.951	0.944	0.949	0.942	0.950	0.943	0.949	0.941	0.953	0.947	0.952	0.946
O-9	-0.539	-0.556	-0.541	-0.557	-0.542	-0.557	-0.542	-0.558	-0.540	-0.556	-0.541	-0.555	-0.538	-0.551
O-10	-0.539	-0.556	-0.543	-0.558	-0.538	-0.553	-0.541	-0.558	-0.540	-0.556	-0.541	-0.555	-0.539	-0.551
C-11	-0.1038	-0.103			-0.114	-0.107	-0.102	-0.101	-0.103	-0.102			-0.112	-0.107
C-12			-0.106	-0.105	-0.108	-0.107					-0.108	-0.107	-0.110	-0.109
C-13							-0.104	-0.103			-0.108	-0.107		
C-14									-0.103	-0.102			-0.108	-0.107
HOMO [eV]	-11.143		-11.228		-11.109		-11.117		-11.049		-11.175		-11.060	
LUMO [eV]		-3.097		-3.135		-3.051		-3.067		-3.021		-2.996		-2.891
HOMO-LUMO [eV]	-8.046		-8.093		-8.058		-8.050		-8.028		-8.179		-8.169	

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* Enumeration of atoms in Fig. 1.

Spectra and Excited State Properties

Figures 2 and 3 show the absorption spectra of methyl-4-nitropyridine N-oxides. The observed and calculated energies of electron transitions and their intensities are given in Table 2. The spectra of all compounds exhibit characteristic bands in the regions 196-242 and 242-333 nm. These bands are due to the $\pi^*\leftarrow\pi$ transition of the aromatic pyridine ring or $\pi_{oxygen}\leftarrow\pi_{ring}$ and are common to the $\pi^*\leftarrow\pi$ band of aromatic amine N-oxides in which

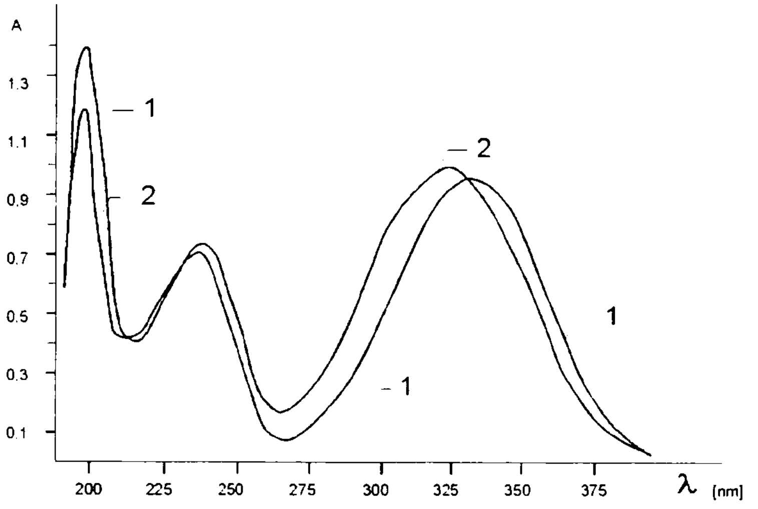

Fig. 2. UV spectra of derivatives of 4-nitropyridine N-oxide:
1 2-methyl-4-nitropyridine N-oxide, $c = 9.99 \times 10^{-4}$ mol / dm^3
2 3-methyl-4-nitropyridine N-oxide, $c = 9.99 \times 10^{-4}$ mol / dm^3.

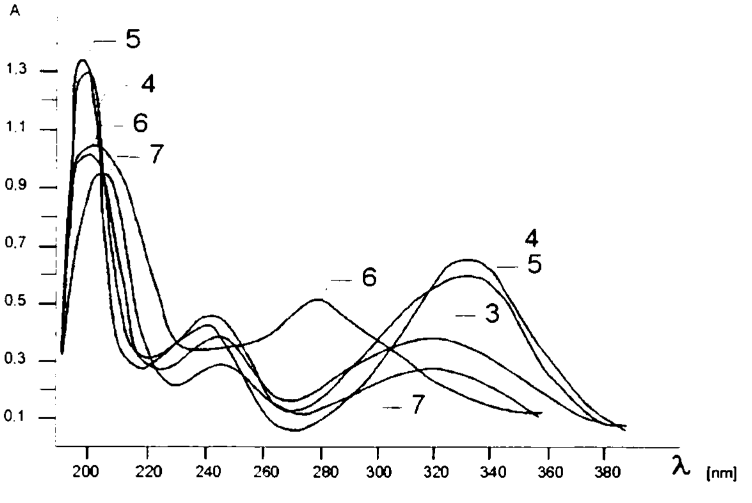

Fig. 3. UV spectra of methyl derivatives of 4-nitropyridine N-oxide:
3 2,3-dimethyl-4-nitropyridine N-oxide, $c = 5.10 \times 10^{-4}$ mol / dm^3;
4 2,5-dimethyl-4-nitropyridine N-oxide, $c = 5.55 \times 10^{-4}$ mol / dm^3;
5 2,6-dimethyl-4-nitropyridine N-oxide, $c = 5.42 \times 10^{-4}$ mol / dm^3;
6 3,5-dimethyl-4-nitropyridine N-oxide, $c = 6.66 \times 10^{-4}$ mol / dm^3;
7 2,3,6-trimethyl-4-nitropyridine N-oxide, $c = 4.41 \times 10^{-4}$ mol / dm^3.

the N–O and C=C groups form a conjugated system. All spectra of the compounds studied are characterized by a three-band structure. The band in the region 242-333 nm contributes a large share of the electron transmission 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, i.e., a CT band. All spectra of methyl-4-nitropyridine N-oxides are shifted in comparison to 4-nitropyridine N-oxide (196, 233, 329 nm) to longer wavelengths, but the intensity in particular bands in the longest wavelengths decreased (13487, 12422, 20231, Table 2).

TABLE 2. Comparison of the Computed and Experimental Spectra of Methyl-4-nitropyridine N-Oxides

Compound	State	Sym.	Calculated			Experimental			
			Energy (eV)	Oscillator strength	Dipole moment (D)	Energy (nm)	Energy (eV)	$\varepsilon \times 10^{3}$	Dipole moment (D)
1	2	3	4	5	6	7	8	9	10
2-Methyl-4-nitropyridine N-oxide	S_0				0.638				1.06
	$S_1(\pi,\pi^*)$	A'	3.234	0.000	11.389				
	$S_2(\pi,\pi^*)$	A'	4.102	0.637	8.828	331	3.77	10.53	
	$S_3(\pi,\pi^*)$	A'	4.250	0.000	9.472				
	$S_4(\pi,\pi^*)$	A'	4.293	0.035	7.815				
	$S_5(\pi,\pi^*)$	A'	4.736	0.000	10.860				
	$S_6(\pi,\pi^*)$	A'	5.039	0.000		236	5.31	7.43	
	$S_7(n,\pi^*)$	A"	5.608	0.057		196	6.32	13.72	
	$S_8(n,\pi^*)$	A"	6.073	0.702					
	$S_9(\pi,\pi^*)$	A'	6.118	0.035					
	$S_{10}(\pi,\pi^*)$	A'	7.210	0.000					
3-Methyl-4-nitropyridine N-oxide	S_0				1.005				1.01
	$S_1(\pi,\pi^*)$	A'	3.235	0.000	11.077				
	$S_2(\pi,\pi^*)$	A'	4.178	0.720	8.152	323	3.74	10.32	
	$S_3(\pi,\pi^*)$	A'	4.321	0.000	10.151				
	$S_4(n,\pi^*)$	A"	4.335	0.021	7.345				
	$S_5(\pi,\pi^*)$	A'	4.758	0.000	11.459				
	$S_6(\pi,\pi^*)$	A'	5.177	0.001					
	$S_7(n,\pi^*)$	A"	5.606	0.088					
	$S_8(n,\pi^*)$	A"	5.999	0.589		239	5.25	7.79	
	$S_9(n,\pi^*)$	A"	6.180	0.107		198	6.32	14.65	
	$S_{10}(\pi,\pi^*)$	A'	7.326	0.000					
2,3-Dimethyl-4-nitropyridine N-oxide	S_0				1.547				1.60
	$S_1(\pi,\pi^*)$	A'	3.240	0.000	11.305				
	$S_2(\pi,\pi^*)$	A'	4.080	0.604	8.693	319	3.88	7.28	
	$S_3(n,\pi^*)$	A"	4.270	0.022	7.613				
	$S_4(n,\pi^*)$	A"	4.329	0.001	9.271				
	$S_5(n,\pi^*)$	A"	4.787	0.000	11.164				
	$S_6(\pi,\pi^*)$	A'	5.000	0.001					
	$S_7(n,\pi^*)$	A"	5.507	0.220		244	5.08	7.28	
	$S_8(n,\pi^*)$	A"	5.993	0.552		200	6.19	20.23	
	$S_9(\pi,\pi^*)$	A'	6.151	0.045					
	$S_{10}(n,\pi^*)$	A"	7.160	0.000					
2,5-Dimethyl-4-nitropyridine N-oxide	S_0				0.555				0.72
	$S_1(\pi,\pi^*)$	A'	3.248	0.000	11.415				
	$S_2(\pi,\pi^*)$	A'	4.125	0.659	8.697	333	3.72	10.77	
	$S_3(\pi,\pi^*)$	A'	4.293	0.021	7.379				
	$S_4(\pi,\pi^*)$	A'	4.296	0.001	9.352				
	$S_5(\pi,\pi^*)$	A'	4.735	0.000	11.042				
	$S_6(\pi,\pi^*)$	A'	5.086	0.001					
	$S_7(n,\pi^*)$	A"	5.482	0.173		242	5.12	8.36	
	$S_8(n,\pi^*)$	A"	5.975	0.551		199	6.23	23.40	
	$S_9(n,\pi^*)$	A"	6.147	0.087					
	$S_{10}(\pi,\pi^*)$	A'	7.250	0.000					

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10
2,6-Dimethyl-4-nitropyridine N-oxide	S_0				0.193				1.25
	$S_1(\pi,\pi^*)$	A'	3.254	0.008	11.724				
	$S_2(\pi,\pi^*)$	A'	4.068	0.590	9.360	333	3.72	12.08	
	$S_3(\pi,\pi^*)$	A'	4.229	0.000	8.837				
	$S_4(n,\pi^*)$	A"	4.259	0.027	8.072				
	$S_5(\pi,\pi^*)$	A'	4.719	0.000	10.417				
	$S_6(n,\pi^*)$	A"	4.965	0.001					
	$S_7(\pi,\pi^*)$	A'	5.481	0.138		241	5.14	7.80	
	$S_8(n,\pi^*)$	A"	6.035	0.676		199	6.23	25.11	
	$S_9(\pi,\pi^*)$	A'	6.111	0.006					
	$S_{10}(\pi,\pi^*)$	A'	7.148	0.000	1.021				1.20
3,5-Dimethyl-4-nitropyridine N-oxide	S_0								
	$S_1(\pi,\pi^*)$	A'	3.327	0.000	11.053				
	$S_2(\pi,\pi^*)$	A'	4.210	0.677	8.067	279	4.44	7.74	
	$S_3(n,\pi^*)$	A"	4.303	0.016	7.185				
	$S_4(\pi,\pi^*)$	A'	4.465	0.001	10.255				
	$S_5(\pi,\pi^*)$	A'	4.950	0.000	11.533				
	$S_6(\pi,\pi^*)$	A'	5.125	0.001					
	$S_7(n,\pi^*)$	A"	5.608	0.259					
	$S_8(n,\pi^*)$	A"	6.050	0.524		200	6.20	16.25	
	$S_9(\pi,\pi^*)$	A'	6.101	0.002					
	$S_{10}(\pi,\pi^*)$	A'	7.266	0.000					
2,3,6-Trimethyl-4-nitropyridine N-oxide	S_0				1.238				1.20
	$S_1(n,\pi^*)$	A"	3.347	0.000	11.256				
	$S_2(\pi,\pi^*)$	A'	4.129	0.568	8.549	3.22	3.85		
	$S_3(\pi,\pi^*)$	A'	4.247	0.024	7.658				
	$S_4(\pi,\pi^*)$	A'	4.500	0.001	9.714				
	$S_5(\pi,\pi^*)$	A'	4.963	0.001	11.621				
	$S_6(\pi,\pi^*)$	A'	5.028	0.003					
	$S_7(n,\pi^*)$	A"	5.518	0.369		246	5.04		
	$S_8(n,\pi^*)$	A"	6.073	0.023					
	$S_9(n,\pi^*)$	A"	6.083	0.417		204	6.07		
	$S_{10}(\pi,\pi^*)$	A'	7.101	0.000					

A comparison of the spectra of the studied compounds shows the intensity of the CT band being decreased by *ortho* substituents to NO_2 group in the following order: 2,3,6- > 2,3- > 3,5- > 2,3-. The partial disorder of the conjugation effect of the nitro group is a result of the mutual electrostatic as well as steric interactions between the 3-methyl and 4-nitro group (*ortho* effect) [1]. The twist of the nitro group from the molecular plane Q was evaluated on the basis of the relation: $\varepsilon/\varepsilon_0 = \cos^2 Q$, where ε_0 is the absorption coefficient at 329 nm CT of 4-nitropyridine N-oxide. It is clear that the 329 nm $^1A_1$ (CT) band decreases in intensity with the twist of the NO_2 group, especially at angles lower than ~ 50°, although the transition energy does not vary so markedly. The value of 72°10' obtained for 2,3,6-trimethyl-4-nitropyridine N-oxide is the highest among all the compounds studied. The value of the twist angle of the nitro group decreased in the following order: 2,3,6- (72°10') > 3,5- (67°30') > 3- (59°18') > 2,5- (57°48'). Yamakawa [1] measured the UV spectrum in ethyl ether of 3,5-dimethyl-4-nitropyridine N-oxide and obtained the value Q = 60°.

In this study the nature and importance of intramolecular charge transfer in the excited state was examined. The calculated electric dipole moments of the ground and five excited singlet states provide a measure of the electron transfer.

The change in the dipole moment during electron excitation to the first excited singlet state is calculated as 10.07-10.75 D for the derivatives with one methyl group, 9.76-11.53 D for the ones with two methyl groups, and 10.02 D for one compound with three methyl groups. On transition from the ground state to the first excited state in the compounds studied, the value of the negative charge at the oxygen of the N-oxide group is lowered and increases at position 4. The above observations, as well as the increase in the negative charge at the carbon atom in positions 3 and 5 in the first excited state, show that the intramolecular charge transition occurs from the oxygen atom of N-oxide group to the ring. Among the compounds studied, the degree of the above-mentioned intramolecular charge transfer is the highest in 2,6-dimethyl-4-nitropyridine N-oxide.

The values of LUMO energies (*E*) on electrophilic substitution are as follows: *E*(2,3,6-) > *E* (3,5-) > *E*(2,6-) > *E* (2,5-) > *E* (2-) > *E* (3-). Values of the difference in HOMO-LUMO energies oscillate for the compounds examined from -8.028 or to -8.179 eV and are smaller than those for 2-halopicoline N-oxides (-9.31 - -9.35 eV) and pyridine N-oxide (-8.97 eV) [22]. These facts point to the higher susceptibility of photochemical reactions in comparison with 2-halopicoline N-oxides, pyridine N-oxide, and their carboxyl and thiol derivatives [22, 25-27].

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