Electronic Spectra of 2-*N*-Substituted Derivatives of 2-Amino-4-nitropicolines I. 2-Alkylamino-3- (or -5)-methyl-4-nitropyridine *N*-Oxides

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The UV spectra of 2-methyl- and 2-ethylamino-3- (or -5)-methyl-4-nitropyridine *N*-oxides in ethanol have been examined and compared with results (transition energies, intensities) of modified INDO calculations in order to make the assignment of allowed bands. The influence of substituents in the molecule on λ_{max} and ε_{max} of spectral bands is discussed. The electronic spectra of 2-alkylamino-3- (or -5)-methyl-4-nitropyridine *N*-oxides and the effect of steric hindrance on the spectra are interpreted. The preparation procedure of four new 2-alkylamino-4-nitropicoline *N*-oxides is described.

The nitro derivatives of pyridine and their *N*-oxides are important in the field of organic and biological chemistry [1—3]. The properties of 4-nitropyridine *N*-oxide and its methyl derivatives are especially interesting because of their antifungal activity [2, 3] and optical nonlinearity on the molecular as well as the macroscopic level [4, 5].

In physicochemical research scheme carried out in our laboratory on the reactivity of 2-substituted 4-nitropyridine *N*-oxides it was necessary to measure their UV spectra and compare them with those of 2-halo-4-nitropyridine *N*-oxide [6—8]. An indispensable prerequisite for achieving large second-order nonlinear optical response in an organic molecule is the existence of intramolecular charge transfer (ICT) resulting from the electron donor and acceptor groups communicating through a π-conjugated molecular framework.

It may be expected that the introduction of a methyl group in position 3 or 5 and an alkylamino group in position 2 modifies the charge transfer mainly by means of steric interactions.

In this research we have concentrated upon the influence of substituents in the molecule on λ_{max} and ε_{max} of spectral bands in four 2-alkylamino-3- (or -5)-methyl-4-nitropyridine *N*-oxides (*I—IV*) (Scheme 1).

EXPERIMENTAL

2-Alkylamino-3- (or -5)-methyl-4-nitropyridine *N*-oxides were obtained in the reaction of 2-chloro-3- (or -5)-methyl-4-nitropyridine *N*-oxides and alkylamine [13].

	CH$_3$ position	R
I	3	CH$_3$
II	3	C$_2$H$_5$
III	5	CH$_3$
IV	5	C$_2$H$_5$
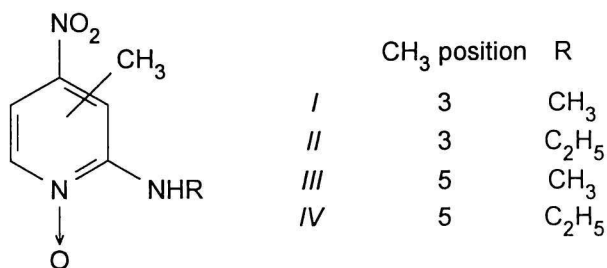
Scheme 1

A sample of 5 g of 2-chloro-3-methyl-4-nitropyridine *N*-oxide and 20 cm^3 of 30 % methylamine in methanol was refluxed for 5 h. Then the reaction mixture was evaporated to dryness. After distilling off methanol and adding water the precipitate was filtered and recrystallized from water.

The ethylamino derivatives were obtained analogously.

The UV absorption spectra were recorded using a UV VIS (Zeiss, Jena) spectrometer (alcohol solutions and heptane solutions, concentration $\approx 10^{-4}$ mol dm^{-3}, cell thickness 0.097 cm). Calculations of electronic spectra of 2-alkylaminopicoline *N*-oxides were performed within the framework of the modified allvalence electrons. INDO method [9] utilizes some of its modifications [10—12] and includes 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 base 3-21G HF.
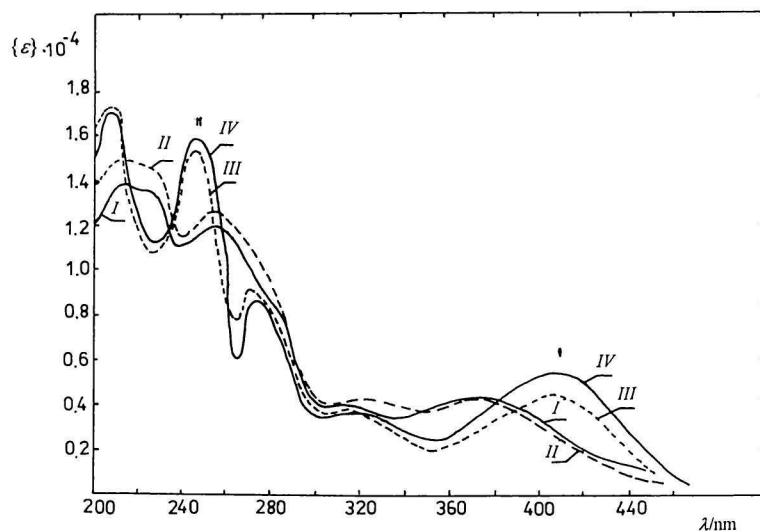
Fig. 1. The UV absorption spectra of 2-alkylamino-4-nitropicoline N-oxides in ethanol. 2-Methylamino-3-methyl-4-nitropyridine N-oxide (*I*), 2-ethylamino-3-methyl-4-nitropyridine N-oxide (*II*), 2-methylamino-5-methyl-4-nitropyridine N-oxide (*III*), 2-ethylamino-5-methyl-4-nitropyridine N-oxide (*IV*).

RESULTS AND DISCUSSION

Spectra and Excited State Properties

Figs. 1 and 2 show the absorption spectra of 2-methyl- and 2-ethylamino-3- (or -5)-methyl-4-nitropyridine N-oxides in ethanol and in heptane. The calculated and experimental electronic spectra in ethanol and in heptane are summarized in Table 1.

Introduction of methyl group into position 3 and of 2-alkylamino group into position 2 in 4-nitropyridine N-oxide results in the absorption shift towards the longer wavelength (λ_{max}: 196 nm, 233 nm, 329 nm $\rightarrow$ 210 nm; 253 nm, 278 nm (sh); 333 nm) with the increase of intensity ($\{\varepsilon_{max}\}$ = 13487, 12422, 20251 $\rightarrow$ 13845—14963; 11537—12444, 8623—9333, 4130—4148). On passing from 4-nitropyridine N-oxide to 2-methylamino-5-methyl-4-nitropyridine N-oxide the spectra exhibit a red shift (λ_{max}: 196 nm, 233 nm, 329 nm $\rightarrow$ 206 nm; 245 nm, 275 nm; 317 nm, 405 nm) because the electron migration from alkylamino group is facilitated by its electron-donor properties and by the 4-nitro group acting as an electron-acceptor group. The increase of the intensity can be explained by two complementary effects of substituents. The strong electron-donating 2-alkylamino group is situated in the resonance position to the 5-methyl group, but the N-oxide group is situated in the resonance position to the strong electron-attracting 4-nitro group. The competition of these two effects results in occurring of two maxima of bands I and II. The spectra of 2-alkylamino-3-methyl-4-nitropyridine N-oxides are blue-shifted in relation to their 5-methyl analogues (λ_{max}: 210 nm; 253 nm, 278 nm (sh); 371 nm $\rightarrow$ 206 nm; 245 nm, 275 nm; 317 nm, 405 nm). A partial dis-
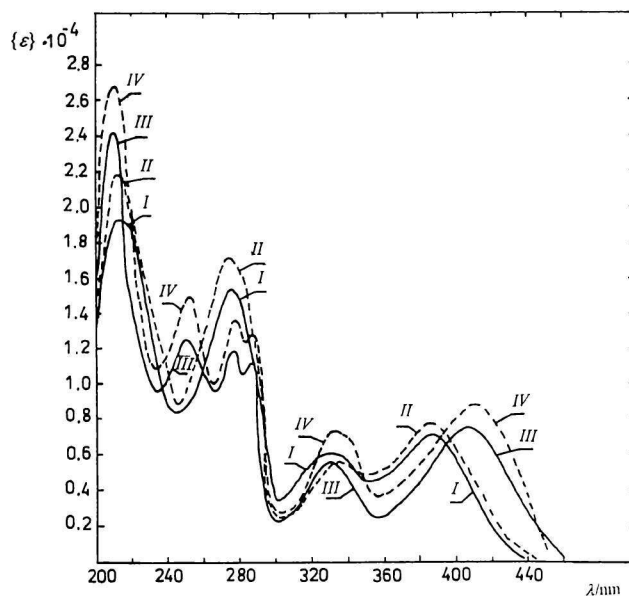

Fig. 2. The UV absorption spectra of 2-alkylamino-4-nitropicoline N-oxides in heptane. 2-Methylamino-3-methyl-4-nitropyridine N-oxide (*I*), 2-ethylamino-3-methyl-4-nitropyridine N-oxide (*II*), 2-methylamino-5-methyl-4-nitropyridine N-oxide (*III*), 2-ethylamino-5-methyl-4-nitropyridine N-oxide (*IV*).

order of conjugation effect of nitro group is a result of the mutual electrostatics as well as steric interaction between 3-methyl and 4-nitro groups, 2-alkylamino and 3-methyl groups, and 2-alkylamino and N-oxide groups. The irregular shape of this spectrum can be explained by accumulation of four substituents in the nearest neighbourhood.

The band III (Fig. 1) involves a lower level with

Table 1. Comparison of the Computed and Experimental Spectra of 2-Alkylamino-3- (or -5)-methyl-4-nitropyridine N-Oxides

Compound	State	Sym	Calculated		Experimental in ethanol			Experimental in heptane		
			Energy	Oscillator strength	Energy		$\{\varepsilon\}$ 10^{-3}	Energy		$\{\varepsilon\}$ 10^{-3}
			eV	kN m^{-1}	eV	nm		eV	nm	
2-Methylamino-	S_0									
3-methyl-4-nitro-	$S_1(\pi,\pi^*)$	A′	3.64	0.018						
pyridine N-oxide	$S_2(\pi,\pi^*)$	A′	3.69	0.203	3.34	371	4.13	3.21	386	7.14
(*syn* form)	$S_3(\pi,\pi^*)$	A′	4.15	0.017	4.46	278	8.62	3.72	333	6.09
	$S_4(\pi,\pi^*)$	A′	4.20	0.002						
	$S_5(\pi,\pi^*)$	A′	4.90	0.001						
	$S_6(\pi,\pi^*)$	A′	4.92	0.334	4.89	253	11.53	4.49	276	15.53
	$S_7(\pi,\pi^*)$	A′	5.78	0.681	5.90	210	13.84	5.76	215	19.31
	$S_8(\pi,\pi^*)$	A′	5.90	0.022						
	$S_9(\pi,\pi^*)$	A′	5.98	0.463						
	$S_{10}(\pi,\pi^*)$	A′	6.97	0.000						
(*anti* form)	S_0									
	$S_1(\pi,\pi^*)$	A′	3.53	0.000						
	$S_2(\pi,\pi^*)$	A′	3.71	0.224	3.34	371	4.13	3.21	386	7.14
	$S_3(\pi,\pi^*)$	A′	4.12	0.034	4.46	278	8.62	3.72	333	6.09
	$S_4(\pi,\pi^*)$	A′	4.20	0.002						
	$S_5(\pi,\pi^*)$	A′	4.71	0.005						
	$S_6(\pi\pi^*)$	A′	4.96	0.289	4.89	253	11.53	4.49	276	15.53
	$S_7(n,\pi^*)$	A″	5.76	0.644	5.90	210	13.84	5.76	215	19.31
	$S_8(n,\pi^*)$	A″	5.88	0.012						
	$S_9(\pi,\pi^*)$	A′	5.99	0.469						
	$S_{10}(\pi,\pi^*)$	A′	6.72	0.001						
Ethylamino-	S_0									
3-methyl-4-nitro-	$S_1(n,\pi^*)$	A″	3.58	0.007						
pyridine N-oxide	$S_2(n,\pi^*)$	A″	3.69	0.218	3.34	371	4.15	3.21	386	7.65
(*syn* form)					3.46	278	9.33	3.76	333	5.59
	$S_3(\pi,\pi^*)$	A′	4.15	0.015						
	$S_4(\pi,\pi^*)$	A′	4.20	0.003						
	$S_5(n,\pi^*)$	A″	4.90	0.002						
	$S_6(\pi,\pi^*)$	A′	4.93	0.318	4.89	253	12.44	4.49	276	17.21
	$S_7(\pi,\pi^*)$	A′	5.75	0.734	5.90	210	14.96	5.73	216	21.89
	$S_8(\pi,\pi^*)$	A′	5.92	0.063						
	$S_9(n,\pi^*)$	A″	5.97	0.405						
	$S_{10}(n,\pi^*)$	A″	6.97	0.000						
(*anti* form)	S_0									
	$S_1(n,\pi^*)$	A″	3.55	0.000						
	$S_2(\pi,\pi^*)$	A′	3.63	0.226	3.34	371	4.15	3.21	386	7.65
					3.46	278	9.33	3.76	333	5.59
	$S_3(\pi,\pi^*)$	A′	4.08	0.029						
	$S_4(n,\pi^*)$	A″	4.14	0.000						
	$S_5(n,\pi^*)$	A″	4.78	0.001						
	$S_6(\pi,\pi^*)$	A′	4.92	0.272	4.89	253	12.44	4.49	276	17.21
	$S_7(\pi,\pi^*)$	A′	5.80	0.615	5.90	210	14.96	5.73	216	21.89
	$S_8(\pi,\pi^*)$	A′	5.88	0.044						
	$S_9(\pi,\pi^*)$	A′	5.96	0.541						
	$S_{10}(n,\pi^*)$	A″	6.85	0.000						
2-Methylamino-	S_0									
5-methyl-4-nitro-	$S_1(\pi,\pi^*)$	A′	3.58	0.000						
pyridine N-oxide	$S_2(n,\pi^*)$	A″	3.64	0.253	3.06	405	4.33	3.03	408	7.40
(*syn* form)					3.91	317	3.77	3.78	328	5.59
	$S_3(\pi,\pi^*)$	A′	4.13	0.000						
	$S_4(\pi,\pi^*)$	A′	4.22	0.018				4.31	287	10.53
	$S_5(n,\pi^*)$	A″	4.88	0.297	4.51	275	8.48	4.46	278	11.18
	$S_6(\pi,\pi^*)$	A′	5.03	0.000						
	$S_7(\pi,\pi^*)$	A′	5.82	0.138						
	$S_8(\pi,\pi^*)$	A′	5.88	0.441	5.06	245	15.45	4.93	251	16.81
	$S_9(\pi,\pi^*)$	A′	5.99	0.654	6.01	206	17.14	5.89	210	22.70
	$S_{10}(n,\pi^*)$	A″	7.05	0.000						

Table 1 (Continued)

Compound	State	Sym	Calculated		Experimental in ethanol			Experimental in heptane		
			Energy	Oscillator strength	Energy		$\{\varepsilon\}$ 10^{-3}	Energy		$\{\varepsilon\}$ 10^{-3}
			eV	kN m^{-1}	eV	nm		eV	nm	
(anti form)	S_0									
	$S_1(n,\pi^*)$	A''	3.47	0.000						
	$S_2(\pi,\pi^*)$	A'	3.60	0.250	3.06	405	4.33	3.03	408	7.40
					3.91	317	3.77	3.78	328	5.59
	$S_3(n,\pi^*)$	A''	4.12	0.000						
	$S_4(\pi,\pi^*)$	A'	4.15	0.034				4.31	287	10.53
	$S_5(\pi,\pi^*)$	A'	4.86	0.250	4.51	275	8.48	4.46	278	11.18
	$S_6(n,\pi^*)$	A''	4.87	0.000						
	$S_7(\pi,\pi^*)$	A'	5.80	0.057						
	$S_8(\pi,\pi^*)$	A'	5.84	0.566	5.06	247	15.45	4.93	251	16.81
	$S_9(\pi,\pi^*)$	A'	5.97	0.628	6.01	206	17.14	5.89	210	22.70
	$S_{10}(n,\pi^*)$	A''	6.88	0.000						
2-Ethylamino-5-methyl-4-nitro-pyridine N-oxide (syn form)	S_0									
	$S_1(\pi,\pi^*)$	A'	3.56	0.000						
	$S_2(n,\pi^*)$	A''	3.63	0.255	3.06	405	4.27	3.00	412	8.97
					3.91	417	3.91	3.74	331	7.28
	$S_3(\pi,\pi^*)$	A'	4.12	0.000						
	$S_4(\pi,\pi^*)$	A'	4.22	0.019						
	$S_5(\pi,\pi^*)$	A'	4.87	0.295	4.51	275	8.54	4.43	280	13.73
	$S_6(\pi,\pi^*)$	A'	5.00	0.000						
	$S_7(n,\pi^*)$	A''	5.81	0.118						
	$S_8(n,\pi^*)$	A''	5.88	0.438	5.06	245	15.84	4.89	253	15.13
	$S_9(\pi,\pi^*)$	A'	5.99	0.672	6.01	206	17.08	5.86	211	26.89
	$S_{10}(n,\pi^*)$	A''	7.02	0.000						
(anti form)	S_0									
	$S_1(\pi,\pi^*)$	A'	3.48	0.000						
	$S_2(n,\pi^*)$	A''	3.60	0.248	3.06	405	4.27	3.00	412	8.97
					3.91	417	3.91	3.74	331	7.28
	$S_3(\pi,\pi^*)$	A'	4.11	0.000						
	$S_4(\pi,\pi^*)$	A'	4.17	0.034						
	$S_5(\pi,\pi^*)$	A'	4.86	0.254	4.51	275	8.54	4.43	280	13.73
	$S_6(\pi,\pi^*)$	A'	4.87	0.001						
	$S_7(n,\pi^*)$	A''	5.80	0.035						
	$S_8(n,\pi^*)$	A''	5.85	0.577	5.06	245	15.84	4.89	253	15.13
	$S_9(\pi,\pi^*)$	A'	5.97	0.631	6.01	206	17.08	5.86	211	26.89
	$S_{10}(\pi,\pi^*)$	A'	6.88	0.000						

more or less uniform contributions from all atoms and higher level with dominant contributions from the skeletal carbons. The maximum wavelength of this band lies in the same position for methylamino and ethylamino derivatives and the intensity decreases in the order: $-NHC_2H_5$ $-NHCH_3$ $(J(-NHC_2H_5) > J(-NHCH_3))$.

The band II is assigned to the excitation of aromatic system since the position of this band is little influenced by changing the polarity of the medium.

The band I contains a large contribution of an electron transmission from the HOMO to the LUMO and brings about a quite large transfer of electrons from N-oxide group to the nitro one and from 2-alkylamino group to 5-methyl one via the pyridine ring, i.e. a CT band. Majority of the first transitions are of $\pi \rightarrow \pi^*$ CT character although the CT absorption band

of a molecule with donor and acceptor groups may be strongly solvent-dependent. A comparison between the calculated excitation energies and the maxima of absorption in the solution (Table 1) shows that the bands I in the studied series undergo a bathochromic shift on passing from ethanol to heptane solution. It may be caused by a better stabilization of the excited state in polar environment. Although the solvent molecules cannot reorientate during the electronic transition, the solvation shell of a polar solvent formed in the polar ground state should stabilize the excited state more effectively than the corresponding shell of nonpolar solvent.

The observed and calculated energy of electronic transition and its intensity are shown in Table 1. The spectra of 2-alkylamino-5-methyl-4-nitropyridine exhibit a clearer relationship between the position of

the methyl group and the intensity, particularly in the region of band II, polarized along the longer axis of the molecule. This effect disappears in the case of 3-methyl derivatives, which may be accounted for the inhibition of conjugation between the 4-nitro and N-oxide groups. The intensities of 2-iodo-4-nitropicoline N-oxides are higher than those of studied compounds owing to the expansion of the valence shell of iodine (d orbital resonance) [7].

It has been found that the twist angle of the nitro group has an important influence on the intramolecular charge-transfer effect [14]. The twist of the nitro group from the molecular plane Q was evaluated on the basis of the relation: $\varepsilon/\varepsilon_0 = \cos^2 Q$ [14], where ε_0 is the absorption coefficient at 329 nm CT of 4-nitropyridine N-oxide. The obtained Q values are $11°12'$ and $55°30'$ for 3-methyl-4-nitropyridine N-oxide and 3,5-dimethyl-4-nitropyridine N-oxide, respectively. Note that these values are closer to those derived from 4-aminonitrobenzene ($23°$ and $56°$ for 2-methyl- and 2,6-dimethyl substitution, respectively) than to those of 1-nitrobenzene ($34°$ and $66°$ for 2-methyl- and 2,6-dimethyl substitution, recpectively), where the angles of twist were also estimated from the UV intensity using the technique mentioned above [14].

From this fact it may be said that the intramolecular CT effect has an important influence on the angle of twist; the stronger the CT effect is, the smaller the twist. It is clear that the 246 nm $^1A_1$ (CT) band decreases in intensity with the twist of the NO_2 group, especially at angles larger than $\approx 50°$, although the transition energy does not vary so markedly. A $Q = 90°$ above the CT band becomes accidentally forbidden, since the MO's pertinent to the electronic transitions belonging to the $^1A_1$ band are separated into NO_2 and pyridine N-oxide parts [14].

The value of the twist angle of 4-nitro group for 3-methyl derivatives ($Q = 47°$ for 2-methylamino- and $48°$ for 2-ethylamino-3-methyl-4-nitropyridine) is higher than for 5-methyl ones ($Q = 22°10'$ for 2-methylamino- and $38°41'$ for 2-ethylamino-5-methyl-4-nitropyridine) [15]. This trend has not kept in N-oxide series. The value of the twist angle for 2-alkylamino-3-methyl-4-nitropyridine N-oxide ($Q = 47°$ for 2-methylamino- and $63°$ for 2-ethylamino derivatives) is of the same order as for 2-alkylamino-5-methyl-4-nitropyridine N-oxide ($63°$ for both isomers). These data are obtained only on the basis of spectra measured in ethanol solutions, because the studied compounds are characterized by poor solubility in heptane and 4-nitropyridine N-oxide is unsolvable in this solvent. It is clear that in the case of strong interaction in the molecule the relation $\varepsilon/\varepsilon_0 = \cos^2 Q$ accounting only steric effect of substituents is not quite correct. On passing from 4-nitropyridine N-oxide to 2-alkylamino-3-methyl-4-nitropyridine N-oxide the nature of bonds is changed. The smaller dis-

crepancy between the twist angle calculated on the basis of the mentioned relation and that using theoretical methods can be obtained when the spectra of 2-alkylamino-3-methyl-4-nitropyridine and 3-methyl-4-nitropyridine N-oxide are taken into consideration. Calculations by an *ab initio* method point out that Q is greater in 2-alkylamino-3-methyl- than in 2-alkylamino-5-methyl-4-nitropyridine N-oxides ($26°75'$ for 2-methylamino, $24°43'$ for 2-ethylamino-3-methyl, and $0°$ for 2-methylamino and 2-ethylamino-5-methyl derivative). Moreover, taking over twist angle $0°$ as well as $70°$ leads to planar structure of 5-methyl derivatives. This fact is stated by *ab initio* and DFT methods.

Satisfactory agreement between the calculated and experimental electronic spectra for both *syn* and *anti* forms confirmed that the tested compounds occur in these forms in comparative quantities, although molecular mechanics calculations (*ab initio* in the base 6-31G HF) predict that *syn* forms for all studied compounds are energetically more stable than their *anti* forms, the difference being *ca.* for *I* 14.85 kJ mol^{-1} for *II* 34.43 kJ mol^{-1}, for *III* 15.52 kJ mol^{-1}, and for *IV* 32.76 kJ mol^{-1}).

Summing up, the spectra of all investigated compounds contain three main bands: two absorption bands derived from $\pi \to \pi^*$ excitation of π electron of the aromatic system. The third ICT in the longest wavelength region is assigned to the transition from N-oxide to the 4-nitro group and from 2-alkylamino to the 5-methyl group *via* the pyridine ring.

The spectra of 3-methyl derivatives are characterized by smaller intensity than that of 5-methyl ones due to the disturbance of the mutual electronic interaction by a steric "*ortho*" effect. The effect of the steric hindrance on the spectra is interpreted. The calculated electronic spectra of the studied compounds agree satisfactorily with the experimental values.

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