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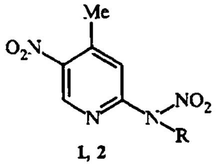
ABSORPTION SPECTRA OF 2-ALKYLNITRAMINO-SUBSTITUTED 4(or 6)-METHYL-5-NITROPYRIDINES AND 2-(N-ALKYL-N-NITROSOAMINO)-SUBSTITUTED 4(or 6)-METHYL-3(or 5)-NITROPYRIDINES

H. Ban-Oganowska, A. Puszko, B. Palasek,
and M. Wandas

Electronic spectra of nine title compounds were measured and the substituent effect on λ_{max} *and* ε_{max} *has been discussed. Competitive electron withdrawing by both the nitro groups in a molecule and a disturbance of mutual electronic interaction of substituent by a steric* ortho *effect were found. The preparation of five new 2-(N-alkyl-N-nitrosoamino)-4-and6-methyl-5-nitro-and2-(N-methyl-N-nitrosoamino)-6-methyl-3-nitropyridines is described.*

In previous papers we described the UV spectra of 2-alkylamino-3(or 5)-nitro-4(or 6)-methylpyridines [1, 2]. In continuation of the investigations on this class of compounds we have determined and interpreted the UV spectra of 2-alkylnitramino- and 2-N-nitrosoalkylaminoderivatives in order to examine the substituent conjugation effects.

It is known that the nitro group in the pyridine ring gives antifungal properties to the compounds [3]. The compounds studied (1—9) are of interest for the study of the interaction of the nitro group with other substituents in a molecule.



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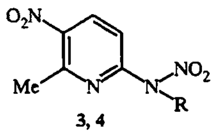

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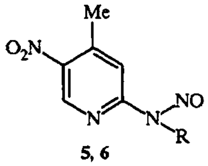

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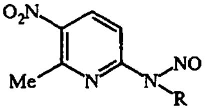

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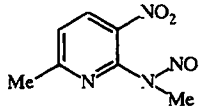

9

1, 3, 5, 7 R = Me; 2, 4, 6, 8 R = Et

EXPERIMENTAL

The 2-(N-alkylnitramino)-4-methyl-5-nitropyridines (**1, 2**) and 2-(N-alkylnitramino)-6-methyl-5-nitropyridines (**3, 4**) were prepared as described previously [4, 5].

2-(N-alkyl-N-nitrosoamino)-4-methyl-5-nitropyridines (5, 6), 2-(N-alkyl-N-nitrosoamino)-6-methyl-5-nitropyridines (7, 8), and 2-(N-methyl-N-nitrosoamino)-6-methyl-3-nitropyridine (9). To 20 ml of 14% HCl 2 g of compound **5—9** were added. After cooling the mixture below −10°C, 10 ml of saturated $NaNO_2$ aqueous solution was added. The reaction

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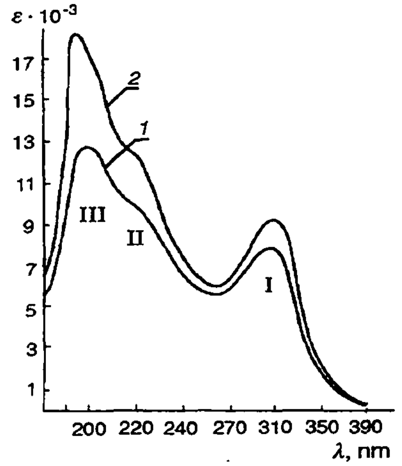

Fig. 1

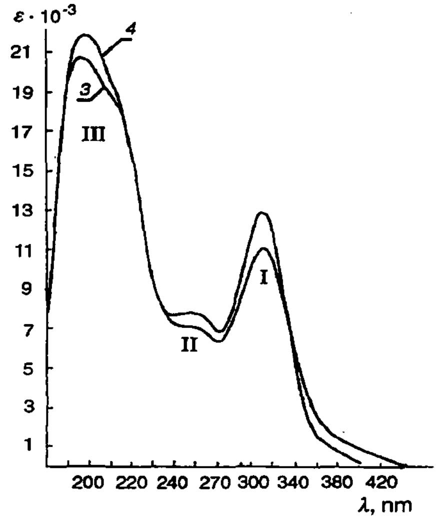

Fig. 2

Fig. 1. Absorption spectra of 2-methylnitramino- (**1**) and 2-ethylnitramino-4-methyl-5-nitropyridine (**2**).

Fig. 2. Absorption spectra of 2-methylnitramino- (**3**) and 2-ethylnitramino--6-methyl-5-nitropyridine (**4**).

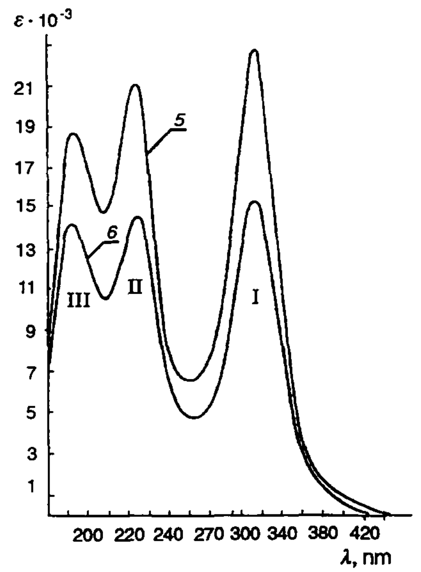

Fig. 3

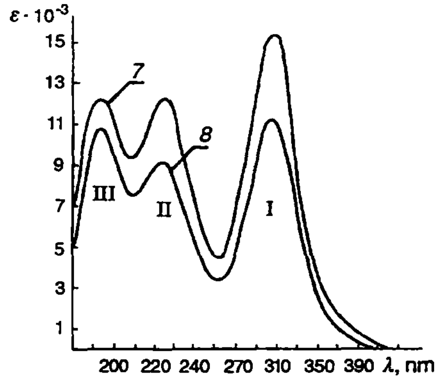

Fig. 4

Fig. 3. Absorption spectra of 2-(N-methyl- (**5**) and 2-(N-ethyl-N-nitrosoamino)-5-nitro-4-methylpyridine (**6**).

Fig. 4. Absorption spectra of 2-(N-methyl- (**7**) and 2- (N-ethyl-N-nitrosoamino)-5-nitro-6-methylpyridine (**8**).

TABLE 1. Some Characteristics of 2-Alkylnitramino-4(or 6)-methyl-5-nitro- and 2-(N-alkyl-N-nitrosoamino)-4(or 6)-methyl-3(or 5)-nitropyridines

Compound	Molecular formula	Found, % Calculated, %			M. p., °C (from ethanol)	IR spectrum (in KBr)	^{1}H NMR spectrum (in $CDCl_3$)	Yield, %
		C	H	N				
5	$C_7H_8N_4O_3$	42,52 42,86	3,92 4,11	27,96 28,56	106	1520 (NO_2) 1340 (NO_2) 1460 (NO)	8,03 (H-3), 9,17 (H-6) 2,70 (4-CH_3) 3,50 (CH_3)	82,0
6	$C_8H_{10}N_4O_3$	45,19 45,71	4,67 4,79	25,63 26,65	63	1520 (NO_2) 1340 (NO_2) 1450 (NO)	8,03 (H-6), 9,17 (H-6) 2,70 (4-CH_3) 4,27 q (CH_2) (J = 6,5) 1,07 t (CH_3) (J = 6,5)	80,0
7	$C_7H_8N_4O_3$	42,45 42,86	3,87 4,11	27,94 28,56	87	1530 (NO_2) 1340 (NO_2) 1450 (NO)	8,50 (H-4) 8,05 (H-3) (J = 9) 3,53 (CH_3) 2,90 (6-CH_3)	75,5
8	$C_8H_{10}N_4O_3$	45,24 45,71	4,69 4,79	25,48 26,65	41	1530 (NO_2) 1340 (NO_2) 1450 (NO)	8,65* (H-4) 8,10 (H-3) (J = 9) 4,25 (CH_2) 2,90 (6-CH_3) 1,05 (CH_3)	70,5
9	$C_7H_8N_4O_3$	42,43 42,86	3,92 4,11	27,53 28,56	68	1540 (NO_2) 1350 (NO_2) 1450 (NO)	8,17 (H-4) 7,25 (H-5) (J = 8) 3,55 (CH_3) 2,63 (6-CH_3)	70,0

*The spectrum has been determined in DMSO-D_6.

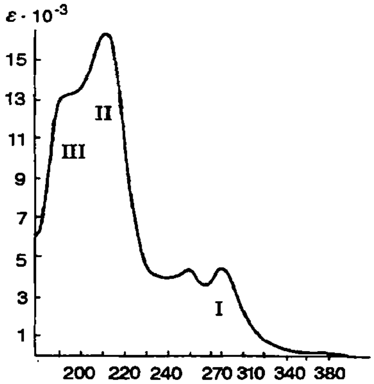

Fig. 5. Absorption spectrum of 2-(N-methyl-N-nitrosoamino)-3-nitro-6-methylpyridine.

mixture was kept at 0°C for 30 min. Then the reaction mixture was poured onto ice. Thus formed 2-(N-alkyl-N-nitrosoamino)derivative was filtered off.

The crude product was recrystallized from ethanol or methanol. The properties and yields of the compounds obtained are summarized in Table 1.

The UV spectra of 0.1 mM solutions in ethanol were recorded by means of a Specord UV-vis spectrophotometer equipped with a thermostated cell compartment, keeping temperature at 25°C, the quartz cell being of 0.097 cm thickness.

TABLE 2. Wavelengths and Molar Extinction Coefficients of 2-N-Alkylnitramino- and 2-(N-Alkyl-N-nitrosoamino)-4(or 6)-methyl-5(or 3)-nitropyridines

Compound	λ_{max}	ε_{max}	Compound	λ_{max}	ε_{max}
1	198	12800	6	196	10250
	303	7800		225	9090
				308	11420
2	196	18200	7	196	18600
	303	9200		222	21000
				312	22800
3	197	20600	8	196	14100
	308	12900		225	14600
				312	15300
4	196	18200	9	196 sh	13300
	303	9200		210	16300
				250	4300
				282	4500
5	196	12210			
	225	12210			
	305	15540			

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption curves of nitramines 1-4; the spectral parameters are summarized in Table 1.

All spectra of 2-alkylamino-5-nitro derivatives [1, 2] are characterized by a three-band structure [for 6-methyl derivatives: λ_{max} 194-198 nm, ε_{max} 7500-20,500 (band III), λ_{max} 228-270 nm, ε_{max} 8800-16,900 (band II), λ_{max} 364-370 nm, ε_{max} 14,500-28,500 (band I) for 4-methyl derivatives: λ_{max} 192-198 nm, ε_{max} 11,200-16,400 (band III), λ_{max} 230-237 nm, ε_{max} 8400-11,800 (band II), λ_{max} 364-370 nm, ε_{max} 10,600-15,640 (band I)]. The intensity of bands in the spectra of 4-methyl derivatives is lower than in those of 6-methyl ones due to the steric effect.

Introduction of the nitro group instead of hydrogen atom in 2-alkylamino group causes the almost complete disappearance of band II (originating from excitation of π electrons of the pyridine ring) in the spectra of 6-methyl derivatives as well as deformation of the responsible band in the case of the spectra of 4-methyl derivatives: band II nearly merges with band III, resulting in its deformation (Fig. 1 and 2). This deformation is caused by the change of the electron nature from electron-donor (2-alkylamino group) to electron-acceptor (2-alkylnitramino group).

The significant decrease in intensity of the CT band (I) as compared to the analogous band in the spectra of 2-alkylamino derivatives [1, 2] (for 6-methyl derivatives: ε_{max} 18,500-22,400 → 11,100-12,900, for 4-methyl derivatives: ε_{max} 10,600-14,800 → 7800-9200) results from competition of both the nitro substituents. For the same reason the position of this band is shifted towards the shorter wavelength.

The spectra of 2-(N-alkyl-N-nitrosoamino)-5-nitro derivatives, as also of the 2-alkylamino ones, show three-band structure. However, the intensity of their CT bands is higher in comparison to the analogous bands in spectra of the mentioned 2-alkylnitramino derivative (Figs. 1-4). This fact can be explained by the smaller acceptor effect of the nitroso group compared to the nitro group.

However, the N-nitroso group, situated in the neighborhood of the nitro group as in 2-(N-methyl-N-nitrosoamino-6-methyl-3-nitropyridine, is responsible for the CT (I) band losing its high intensity, specific of 5-nitroderivatives, and contains two maxima (Fig. 5) probably originating from π-electron excitation of both the nitro and N-nitroso group.

It has been found that the twist angle (θ) of the nitro group has an important influence on the intramolecular effect [6]. The twist angle of the nitro group in 2(N-methyl-N-nitrosoamino)-6-methyl-3-nitropyridine in relation to the molecular plane was determined on the basis of the relation $\varepsilon/\varepsilon_0 = \cos^2\theta$, where ε_0 is the absorption coefficient at 408 nm of 2-methylamino-6- methyl-3-nitropyridine. The value of this angle (76°20′) is significantly greater than that in 2-methylamino-6- methyl-3-nitropyridine (36°) [1].

The spectrum of 2-(N-methyl-N-nitrosoamino)-6-methyl-3-nitropyridine contains only one well-defined band at 210 nm and shoulder at 196 nm, which could be assigned to the interaction between the 3-nitro and 2-N-methyl-N-nitrosoamino group (steric *ortho* effect). This fact results from the lack of complementarity between the 3-nitro and 2-N-alkyl-N-nitrosoamino group contrary to 5-nitro derivatives.

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