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ULTRAVIOLET ABSORPTION SPECTRA OF 2-ALKYLAMINO-, 2-PHENYLAMINO-, 2-MORPHOLINO-3-(OR 5)-NITRO-4-METHYLPYRIDINES AND SOME 2-ALKYLAMINO-3,5-DINITRO-4-METHYLPYRIDINES

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Electronic spectra of thirteen title compounds were measured and the substituent effect on λ_{max} and ε_{max} were discussed. It was found that there is a disturbance of mutual electronic interaction of substituent by a steric ortho-effect. *The obtained results provide evidence that the investigated 2-alkylamino compounds exist in amino form.*

In the literature there are poor data about the UV spectra of 2-aminopyridine [1-3]. In a recent paper the UV spectra of 2-akylamino-, 2-phenylamino-, 2-morpholino-3-(or 5)-nitro-6-methylpyridines are reported [3].

The purpose of this paper is to show the influence of the 4-methyl group and its interaction with other substituents on spectral parameters (λ_{max}, ε_{max}), taking into account that the substituents interact through steric, inductive, and conjugation effects.

In addition, it should be mentioned that these compounds have found applications as new transacylation catalysts [4], nucleophilic substitution catalysts [5], as intermediates for fungicides [6], and herbicides [7].

EXPERIMENTAL

2-Alkyl(CH_3, C_2H_5, $(CH_3)_2$, C_3H_7, C_4H_9)amino-, 2-phenylamino-, 2-morpholyl-, and 2-alkyl(CH_3, C_2H_5) amino-3,5-dinitro-4-methylpyridines were prepared as described previously [8, 9].

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

RESULTS AND DISCUSSION

Figures 1 and 2 show typical absorption spectra of title compounds in ethanol. The observed values of wavelengths and molar extinction coefficients are listed in Table 1.

Introduction of the 2-alkylamino group to 4-methyl-5-nitropyridine moiety [10] results in the absorption shift towards shorter wavelengths (λ_{max} 242 nm → 192-198 nm, 230-237 nm) and in the appearance of the intense third separate band in the longer wavelength (364-370 nm) with significant increase of intensity (ε_{max} 5170 → 11200-18530, 8400-19200, 10600-16170). The great increase of intensity of bands in the spectra of the above mentioned compounds can be explained by the complementary effect of substituents. The electron-donating 2-alkylamino group is situated in the resonance position to the strong electron-attracting 5-nitro group. The spectra of 2-substituted 5-nitro-4-methyl derivatives show the similarity to their

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TABLE 1. Wavelengths and Molar Extinction Coefficients of 2-Alkylamino-, 2-Phenylamino-, 2-Morpholyl-(3 or 5)-nitro-4-methylpyridines, and Some 2-Alkylamino-3,5-dinitro-4-methylpyridines

N	Compounds	λ_{max} (nm)	ε_{max}
1	2-Methylamino-5-nitro-4-methylpyridine	197, 230, 364	11200, 8400, 10600
2	2-Ethylamino-5-nitro-4-methylpyridine	196, 230, 364	16400, 10800, 14800
3	2-Propylamino-5-nitro-4-methylpyridine	197, 230, 364	15600, 11180, 15340
4	2-Butylamino-5-nitro-4-methylpyridine	197, 230, 364	15850, 10840, 15570
5	2-Dimethylamino-5-nitro-4-methylpyridine	197, 231, 368	16340, 10450, 15640
6	2-Phenylamino-5-nitro-4-methylpyridine	198, 253, 371	35240, 16850, 18860
7	2-Morpholino-5-nitro-4-methylpyridine	192, 234, 364	18530, 11460, 16170
8	2-Methylamino-3-nitro-4-methylpyridine	196, 230, 408	9800, 18400, 4700
9	2-Ethylamino-3-nitro-4-methylpyridine	196, 231, 408	14170, 15620, 3630
10	2-Phenylamino-3-nitro-4-methylpyridine	197, 254, 294, 417	39650, 10560, 5130, 2400
11	2-Morpholino-3-nitro-4-methylpyridine	192, 247, 290	16720, 13230, 3250
12	2-Methylamino-3,5-dinitro-4-methylpyridine	198, 220, 339	17200, 16000, 16200
13	2-Ethylamino-3,5-dinitro-4-methylpyridine	198, 220, 339	17000, 16400, 13600

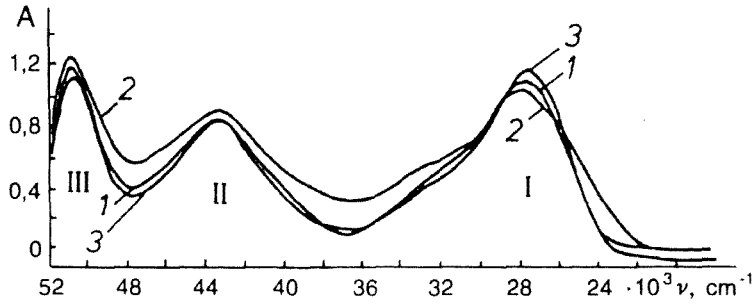

Fig. 1. UV absorption spectra of 2-alkylamino-5-nitro-4-methylpyridines in ethanol: 1) 2-methylamino-, 2) 2-ethylamino-, 3) 2-propylamino-.

6-methyl isomers [3]. The band III in the shortest wavelength region (192-198 nm) involves a lower level from all atoms and a higher level with dominant contributions from the skeletal carbons. The maximum wavelengths of this band lie in the order: $N(Me)_2$ = NHBu = NHPr = NHMe > NHEt > NC_4H_8O, and the intensity decreases in the order: NHPh > NC_4H_8O > $N(Me)_2$ > NHEt > NHBu > NHPr > NHMe.

The band II in the region 230-237 nm is ascribed to excitation of π-electrons of the aromatic system, since the position of this band is little influenced by changing the polarity of the medium. The position of these bands do not show considerable differences, but the intensity decreases in the order: NC_6H_5 > NC_4H_8O > NHPr > NHBu > $N(Me)_2$ > NHEt > NHMe due to the conjugation effect of 2-substituent.

The band I contains a charge contribution of electron transition from the highest occupied MO to the lowest vacant MO and brings about a quite large transfer from substituent in 2-position to the 5-nitro group via pyridine nucleus, i.e., a CT band.

The band I in the spectra of the above discussed compounds (λ_{max} 364-371 nm, ε_{max} 10600-18860) is blue-shifted in comparison to an analogous band in the spectra of their 6-methyl isomers [3], due to the steric *ortho*-effect of the 4-methyl group.

The intensities of band I of 2-substituted 5-nitro-4-methylpyridines show the clear dependence with the nature of alkylamino substituent and are changed in the order NC_6H_5 > NC_4H_8O > $N(Me)_2$ > NHBu > NHPr > NHEt > NHMe.

The spectra of 2-morpholyl-substituted derivatives show a great similarity to alkylamino derivatives and a great difference with spectra of 2-phenyl derivative. This fact can be explained by conjugation effect of π-electrons of benzene ring with pyridine ring.

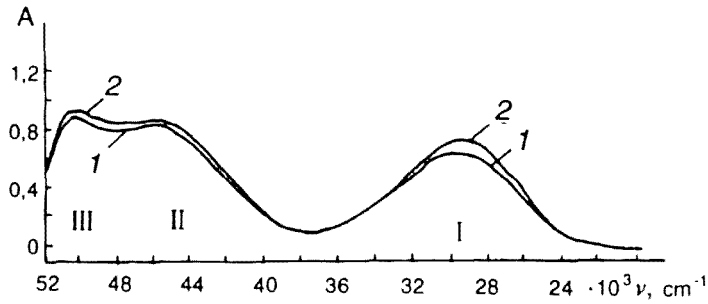

Fig. 2. Absorption spectra of 2-alkylamino-3,5-dinitro-4-methylpyridines in ethanol: 1) 2-methylamino-, 2) 2-ethylamino-.

The similarity of the spectra of 2-dimethylamino-4-methyl-5-nitropyridines to the latter of 2-alkylamino-4-methyl-5-nitropyridines testifies that all these compounds exist in amino form.

2-Substituted 3-nitro-4-methylpyridines absorb in the longer wavelength region (196-417 nm) than 5-nitro derivatives (192-371 nm) and with the significantly smaller intensity of bands I and II. These facts are partly regarded to be due to the non-coplanarity of the nitro group in this molecule caused by the steric or electrostatic interaction between substituents.

The introduction of the methylamino group to 3-nitro-4-methylpyridine [10] results in the slight decrease of the longest wavelength band intensity (ε_{max} 5170 → 4700) and in a significant red shift, due to electron-donor ability of methyl group. Bigger steric effect and smaller electron-releasing effect of ethyl group results also in the decrease of intensity of band I (ε_{max} 5170 → 3630) [10].

It has been found that the twist angle (θ) of the nitro group has an important influence on the intramolecular CT effect [11]. The twist angle of the nitro group as a measure of its deviation from the molecular plane was estimated on the basis of the relation $\varepsilon/\varepsilon_0 = \cos^2\theta$, where ε_0 is the absorption coefficient at 242 nm of 3-nitro-4-methylpyridine. The value of twist angle (θ) of nitro group in 2-methylamino- (17°) and 2-ethylamino- (33°) is slightly smaller than that in 2-phenylamino derivative (47°), due to the steric effect of the phenylamino group.

Additionally, the spectrum of 2-phenylamino-3-nitro-4-methylpyridine in the region 190-300 nm is irregular, which probably results from the disturbance conjugation between the 2-phenylamino substituent and the 3-nitro group.

Introduction of the second nitro group to the ring of 2-methylamino- and 2-ethylamino-5-nitro-4-methylpyridines results in the blue shift of I and II bands (196-197 nm, 230 nm, 364 nm → 189 nm, 220 nm, 339 nm), due to increase of transition energy due to steric hindrances.

The intensities of all three bands of 3,5-dinitro derivatives increase as compared with mononitro compounds due to enlargement of the conjugation system.

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