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ABSORPTION SPECTRA OF NITRO DERIVATIVES. 2-ALKYLAMINO-4-NITROPICOLINES AND THEIR N-OXIDES

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The UV spectra of 15 2-N-substituted 4-nitropicolines and their N-oxides in ethanol have been determined. The spectra of all investigated compounds with the exception of 2-alkylnitramino-4-nitropicolines contain three main bands: two absorption bands are attributed to $\pi \rightarrow \pi^*$ excitation of the π-electron of the aromatic system. The third ICT in the longest wavelength region is assigned to the 4-nitro group via the pyridine ring. The bands in the spectra of 3-methyl derivatives are characterized by smaller intensity than 5-methyl derivatives due to the disturbance of the mutual electronic interaction of the substituent by the steric ortho *effect.*

Heterocyclic compounds, particularly pyridine N-oxides, have aroused much chemical interest owing to their importance as synthetic reagents, catalysts, ligands, and the biological activity associated with some of the naturally occurring species [1]. They have been investigated in the photochemical field [2], for example, and have been subjects of physicochemical measurements [1]. UV spectroscopy, in particular, has been prominent [3-9].

The importance of the overlapping between the highest occupied molecular orbital (HOMO) of an electron donor and the lowest unoccupied molecular orbital (LUMO) of an electron acceptor in determining the favorable position and spatial direction of a chemical reaction is emphasized by setting up the following auxiliary principles: the principle of positional parallelism between the charge-transfer and the bond-interchange; the principle of narrowing of the interfrontier energy-level separation; and the principle of growing frontier density along the reaction path. These subprinciples work in a cooperative manner to enable us to arrive at this general governing principle: most of the chemical interactions are liable to occur at the positions (at the direction) where the overlapping of the HOMO and LUMO of the respective reactants is at its maximum in an electron-donating reactant, the HOMO predominates in the overlapping interaction with the MO's of the other reactant, whereas the LUMO does in an electron-accepting reactant; in the reactants which possess singly-occupied MO's, these play the part of HOMO or of LUMO, or of both. These particular MO's, HOMO, LUMO, and singly-occupied, are "generalized frontier orbitals" in chemical reactions [10]. Fukui [11] found some parallelism between the LUMO energy level and the fungicidal activity. The properties of 4-nitropyridine N-oxide and its methyl derivatives are especially interesting because of their antifungal activity [12, 13] and optical nonlinearity on the molecular as well as the macroscopic level [14, 15].

An indispensable prequisite 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 electron-acceptor groups communicating through a π-conjugated molecular framework.

In the literature there are no data on the UV spectra of 2-N-substituted 4-nitropyridine N-oxide and their methyl derivatives; there are few data on the spectra of 2-nitraminopyridine [9, 16, 17]. In recent papers the UV spectra of 2-alkylamino-, 2-phenylamino-, 2-morpholyl-3- or -5-nitro-4-, or -6-methylpyridines are reported [8, 9, 18]. The aim of this paper is to determine the mutual communication of NO and NO_2 groups and its modification by the steric effects of the methyl and 2-methylamino group.

EXPERIMENTAL

The title compounds were prepared as described previously [19]. 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 the temperature at 25°C, the quartz cell being of 0.097 cm thickness.

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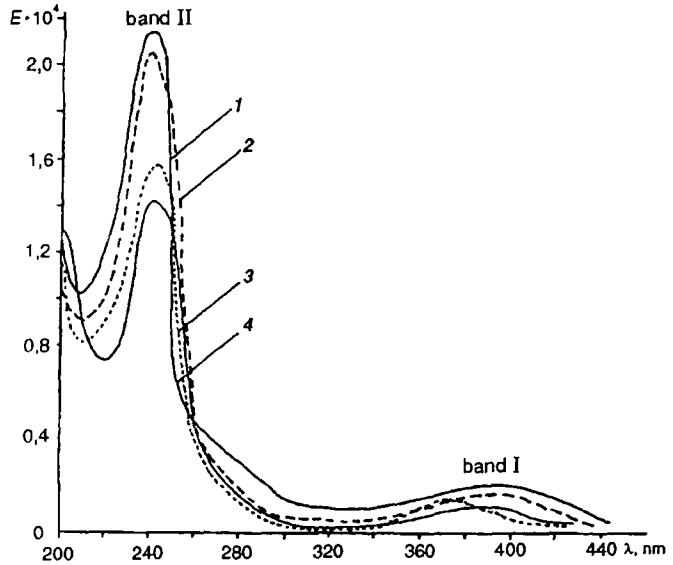

Fig. 1. UV absorption spectra of 2-alkylamino-4-nitropicoline N-oxides in ethanol: 1) 2-methylamino-5-methyl-4-nitropyridine (III); 2) 2-ethylamino-5-methyl-4-nitropyridine (IV); 3) 2-methylamino-3-methyl-4-nitropyridine (I); 4) 2-ethylamino-3-methyl-4-nitropyridine (II).

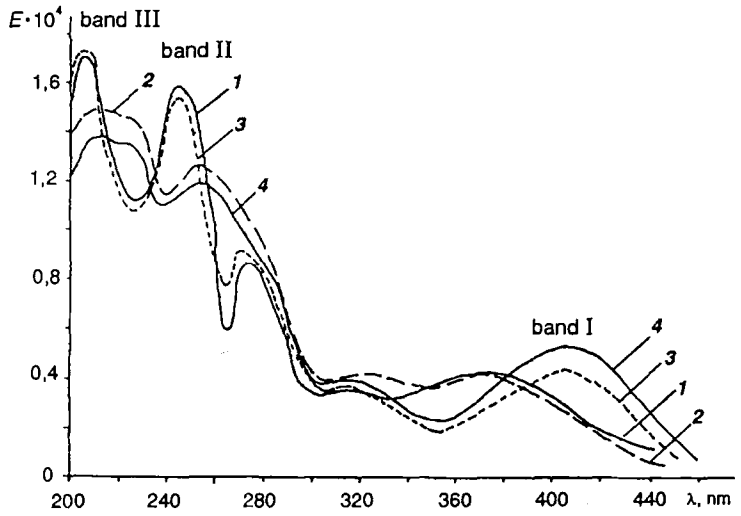

Fig. 2. UV absorption spectra of 2-alkylamino-4-nitropicoline N-oxides in ethanol: 1) 2-ethylamino-5-methyl-4-nitropyridine N-oxide (VIII); 2) 2-ethylamino-3-methyl-4-nitropyridine N-oxide (VI); 3) 2-methylamino-5-methyl-4-nitropyridine N-oxide (VII); 4) 2-methylamino-3-methyl-4-nitropyridine N-oxide (V).

RESULTS AND DISCUSSION

Figure 1 shows typical absorption spectra of 2-alkylamino-3- (I, II) or -5-methyl-4-nitropyridines (III, IV) in ethanol. Introduction of the 2-alkylamino group and the 4-nitro group to 3-methylpyridine results in the absorption shift toward the longer wavelengths (λ_{max} 263 nm, ε_{max} 3110 → λ_{max} 196 nm, 241-244 nm, 364-370 nm, ε_{max} 13,422-13,446, 14,222-15,711, 1132-1158) due to enlargement of the conjugated system. In the case where the methyl group is situated in the *para*-position to the 2-alkylamino group the maximum shifts to red and the intensities are increased (λ_{max} 263 nm, ε_{max} 3110 → λ_{max} 194

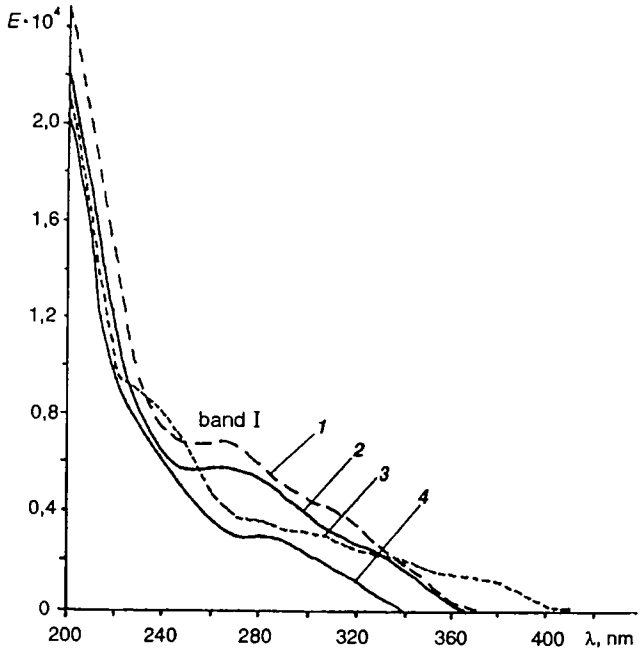

Fig. 3. UV absorption spectra of 2-alkylnitramino-4-nitropicoline in ethanol: 1) 2-ethylnitramino-5-methyl-4-nitropyridine (XII); 2) 2-methylnitramino-5-methyl-4-nitropyridine (XI); 3) 2-ethylnitramino-3-methyl-4-nitopyridine (X); 4) 2-methyl-nitramino-3-methyl-4-nitropyridine (IX).

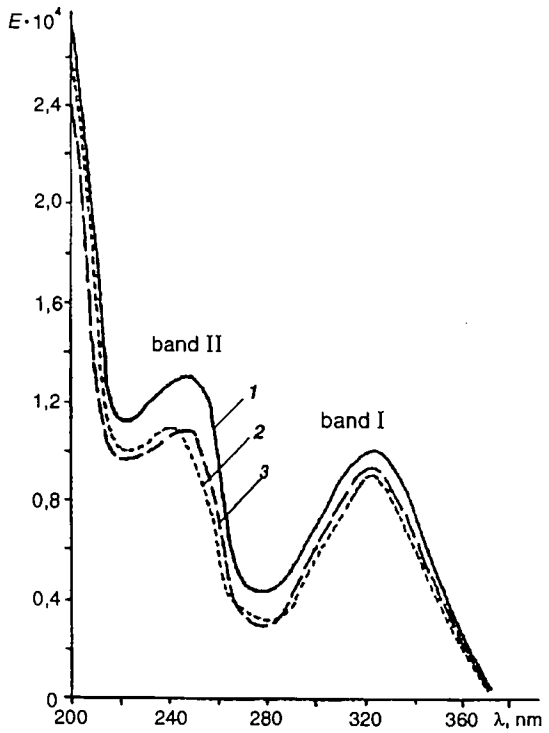

Fig. 4. UV absorption spectra of 2-alkylnitramino-4-nitropicoline N-oxides in ethanol: 1) 2-ethylnitramino-5-methyl-4-nitropyridine N-oxide (XV); 2) 2-ethylnitramino-3-methyl-4-nitropyridine N-oxide (XIV); 3) 2-methylnitramino-3-methyl-4-nitropyridine N-oxide (XIII).

TABLE 1. Wavelengths, Molar Extinction Coefficients of 2-Alkylamino-3- or -5-methyl-4-nitropyridines, 2-Alkylnitramino-3- or -5-methyl-4-nitropyridines, and Their N-Oxides

Compounds	λ_{max}	ε_{max}
2-Methylamino-3-methyl-4-nitropyridine (I)	196, 241, 364	13446, 15711, 1132
2-Ethylamino-3-methyl-4-nitropyridine (II)	196, 244, 370	13422, 14222, 1158
2-Methylamino-5-methyl-4-nitropyridine (III)	194, 241, 397	12193, 21819, 1875
2-Ethylamino-5-methyl-4-nitropyridine (IV)	194, 243, 396	11892, 21279, 1565
2-Methylamino-3-methyl-4-nitropyridine N-oxide (V)	210 (253, 278 sh), 371	13845 (11537, 8623), 4130
2-Ethylamino-3-methyl-4-nitropyridine (VI)	210 (253, 278sh), 371	14963 (12444, 9333), 4148
2-Methylamino-5-methyl-4-nitropyridine N-oxide (VII)	206 (245, 275), (317, 405)	17146 (15450, 8479), (3768, 4334)
2-Ethylamino-5-methyl-4-nitropyridine N-oxide (VIII)	206 (245, 275), (317, 405)	17083 (15837, 8542), (3915, 4270)
2-Methylnitramino-3-methyl-4-nitropyridine (IX)	196, 290	22180, 3195
2-Ethylnitramino-3-methyl-4-nitropyridine (X)	197, 294	23342, 3329
2-Methylnitramino-5-methyl-4 -nitropyridine (XI)	196, 263	23755, 6089
2-Ethylnitramino-5-methyl-4-nitropyridine (XII)	196, 266	25373, 6131
2-Methylnitramino-3-methyl-4-nitropyridine N-oxide (XIII)	197, 238, 322	25578, 10884, 9524
2-Ethylnitramino-3-methyl-4-nitropyridine N-oxide (XIV)	196, 239, 323	26831, 11001, 9391
2-Ethylnitramino-5-methyl-4-nitropyridine N-oxide (XV)	198, 238, 322	28606, 13070, 10851
4-Nitropyridine	199, 226, 282	12218, 11171, 2543
4-Nitropyridine N-oxide	196, 233, 329	13487, 12422, 20231

nm, 241-243 nm, 396-397 nm, ε_{max} 11,892-12,193, 21,279-21,819, 1565-1875) due to enlargement of the conjugated system and the complementary effect of substituents situated between the 2-alkylamino group and the 5-methyl group.

Figure 2 shows the spectra of 2-alkylamino-3- (V, VI) or -5-methyl-4-nitropyridine N-oxides (VII, VIII). On passing from 2-alkylamino-3 or -5-methyl-4-nitropyridine to their N-oxides the absorption is shifted toward longer wavelengths and the intensity is increased due to electron migration to the pyridine ring from the N-oxide group (Table 1). As seen from Table 1 the maximum wavelength lies in the order $5CH_3 > 3CH_3$ and, remarkably, the intensity decreases in the same order. This is partly regarded as being due to the obstruction of the coplanarity of this molecule caused by steric or electrostatic interactions between the 3-methyl and 4-nitro group, particularly in the presence of the 2-alkylamino group.

Figure 3 shows the spectra of 2-alkylnitramino-3- (IX, X) or -5-methyl-4-nitropyridine (XI, XII); the spectral parameters are summarized in Table 1. Introduction of the nitro group instead of the hydrogen atom in the 2-alkylamino group causes the disappearance of band III (originating from excitation of the π electron of the pyridine ring) in the spectra of 3-methyl and 5-methyl derivatives as well as deformation of the responsible band; band II overlaps band III, resulting in its deformation. This deformation is caused by the change of the electron nature of the substituent from electron donor (2-alkylamino group) to electron acceptor (2-nitralkylamino group). The significant increase of intensity and the blue shift of the CT band (I) (λ_{max} 396-397 nm, ε_{max} 1132-1875 → λ_{max} 263-294 nm, ε_{max} 3195-6131) compared to the analogous band in the spectra of 2-alkylamino derivatives results from competition of both electron-acceptor groups, i.e., 4-nitro and 2-nitralkylamino groups.

It should be noted that N-oxidation of the above-mentioned 2-alkylnitramino-4-nitropicolines to form 2-alkylnitramino-4-nitropicoline N-oxides XIII-XV reintroduces the three-band structure (Fig. 4, Table 1). N-oxidation of 2-alkylnitramino-4-nitro-5-methyl derivatives results in an absorption shift towards the longer wavelength (λ_{max} 196 nm, 263-294 nm → 196-198 nm, 238-239 nm, 322-323 nm) with the appearance of a third separate band in the longer wavelength and with the significant increase of intensities (ε_{max} 23,755-25,373, 6089-6131 → 28,606, 13,070, 10,851). The increase of intensity can be explained

by the complementary effect of substituents. The electron-donating N-oxide group is situated in the resonance position to the strong electron-attracting 4-nitro group, and the weaker electron-donating 5-methyl group is situated in the resonance position to the electron-attracting 2-nitralkylamino group. Introduction of the nitro group instead of the hydrogen atom in the 2-alkylamino group of 2-alkylamino-5-methyl-4-nitropyridine N-oxides results in absorption shifts toward the shorter wavelength [λ_{max} 206 nm, (245, 275 nm), (317, 405 nm) → 198 nm, 238 nm, 322 nm] and in increase of their intensity [ε_{max} 17,083-17,146, (15,450-15,837, 8479-8542), (3768-3915, 4270-4334) → 28,606, 13,070, 10,851] due to competition between 4-nitro and 2-nitralkylamino groups. It is worthwhile to note that the acceptor effect of the 4-nitro group is significantly greater than that of the 2-nitralkylamino group. This fact is mainly responsible for the similarity of spectra of nitralkylamino-4-nitropicoline N-oxides to the spectra of 4-nitropyridine N-oxide.

All spectra of 5-methyl derivatives are characterized by higher intensity than the corresponding spectra of 3-methyl derivatives. It has been found that the twist angle (Q) of the 4-nitro group has an important influence on the intramolecular CT effect [20]. The twist angle of the nitro group from the molecular plane was examined on the basis of the relation $\varepsilon/\varepsilon_0 = \cos^2 Q$, where ε_0 is the absorption coefficient at 329 nm of 4-nitropyridine N-oxides and at 282 nm of 4-nitropyridine. The value Q (63°) obtained for 2-ethylamino-3-methyl-4-nitropyridine N-oxides is higher than that for 2-ethylamino-3-methyl-4-nitropyridine (47°).

The spectra of all compounds exhibit their characteristic bands in the regions 200-240 nm, 240-300 nm, and 300-450 nm. These bands are due to the $\pi^* \leftarrow \pi$ transition of the aromatic amine N-oxides in which N−O and C=C groups form a conjugated system. The band I in the region 300-450 nm contributes, as in the spectrum of 4-nitropyridine N-oxide, a large share of the electron transition from the highest occupied MO's and brings about a large charge transfer from the N-oxide group to the nitro group via the pyridine nucleus, i.e., CT band.

Summing up, the spectra of all the studied compounds with the exception of 2-nitralkylamino-3- or -5-methyl-4-nitropyridines are characterized by three-band structures. The spectra of N-oxide derivatives are characterized by greater intensity and an absorption shift toward longer wavelengths in comparison with parent base due to enlargement of the conjugated system. All spectra of 3-methyl derivatives have a smaller intensity than their 5-methyl analogs due to disturbance of the substituent by the steric *ortho* effect.

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