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SPECTRAL AND ELECTROCHEMICAL PROPERTIES OF ortho-AMINO-1-METHYLNITROPYRAZOLES

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The influence of the electron density distribution in the pyrazole ring and the efficacy of the action of amino and nitro groups in the ortho position of amino-1-methylnitropyrazoles on their electrochemical characteristics and IR and electron absorption spectra has been studied.

The influence of features of the electron density distribution in the pyrazole ring on the physicochemical properties of 3- and 4-substituted 1-R-pyrazoles has been the subject of a considerable amount of attention in the literature [1]. At the same time, disubstituted 1-R-pyrazoles have scarcely been studied at all from these points of view and there are no experimental results permitting an estimate of the efficacy of the transfer of electron interactions between substituents along the $C_{(3)}$—$C_{(4)}$ and $C_{(4)}$—$C_{(5)}$ bonds, which have different π-orders in the pyrazole ring [2].

We have previously synthesized amino-1-methylnitropyrazoles [3, 4] containing amino and nitro groups in neighboring positions of the heterocycle and forming the pyrazole analogs of o-nitroaniline, characteristic features of which have been studied by various spectral methods.

In the electronic absorption spectrum of o-nitroaniline (I) (Table 1), the long-wave band is caused by an electronic transition having a contribution of the transfer of charge from the electron donor to the electron-acceptor ($CT_{NH_2}^{NO_2}$ band) [5], and the band in the 280 nm region has a contribution of the transfer of charge from the π-system to the nitro group ($CT_{\pi}^{NO_2}$ band). The electronic spectrum of 4-amino-1-methyl-5-nitropyrazole (II) is very close to the spectrum of o-nitroaniline, which permits an analogous refinement of the absorption bands. In the spectra of 4-amino-1-methyl-3-nitropyrazole (III), 3-amino-1-methyl-4-nitropyrazole (IV), and 5-amino-1-methyl-4-nitropyrazole (V), the number of bands is the same as in the spectra of compounds (I) and (II) but the position and intensity of the long-wave band depend greatly on the mutual positions of the amino and nitro groups in the pyrazole ring.

A feature of the $CT_{NH_2}^{NO_2}$ band is the large value of the bathochromic shift with a change from a nonpolar solvent to a polar solvent, but the presence of an intramolecular hydrogen bond in the o-nitroaniline molecule leads to a decrease in this magnitude as compared, for example, with the spectra of p-nitroaniline. The strength of the intramolecular hydrogen bond is characterized by the increase in the distance between the ν_sNH and ν_{as}NH bands in the IR spectra [6], and for o-nitroaniline in chloroform $\Delta\nu$ is 118 cm^{-1} (Table 1), which considerably exceeds $\Delta\nu$ for m-nitroaniline (91 cm^{-1}) [7]. We have obtained the IR spectra of compounds (I-IV) in chloroform (the isomer (V) is practically insoluble in chloroform) which

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TABLE 1. Characteristics of the Electronic Absorption Spectra, the IR Spectra, the PMR Spectra, and Polarographic Reduction of Compounds (I-VII)

Compound	Electronic absorp. spectrum, λ_{max}, nm (ϵ)			IR spectrum, cm^{-1}			PMR spectrum, δ, ppm	$-E_{1/2}$, V
	ethanol		benzene					
	$CT^{NO_2}_{\pi}$	$CT^{NO_2}_{NH_2}$	$CT^{NO_2}_{NH_2}$	$\nu_{as}NH$	$\nu_s NH$	$\Delta\nu$	NH_2	
I	277 (4900)	405 (5300)	397 (5000)	3525	3407	118	7,32	1,19
II	287 (4300)	408 (3940)	392 (5210)	3512	3403	109	6,23	1,29
III	279 (5220)	394 (3300)	370 (3230)	3502	3405	97	5,40	1,10
IV	278 (4820)	350 (3800)	345 (4040)	3511	3408	103	6,08	1,30
V	269 (3600)	339 (5910)	330 (6400)				7,37	1,44
VI	267 (8600)							1,05
VII	273 (9850)							1,23

shows that the intramolecular hydrogen bond in the molecules of the o-aminonitropyrazoles is weaker than in o-nitroaniline. This is apparently due to an increase in the distance between the atoms participating in the formation of the hydrogen bond as a consequence of the difference in the valence angles in the pyrazole and benzene rings and the greater basicity of the amino group in the aminonitropyrazoles (II-IV) than in o-nitroaniline.

The weakest intramolecular hydrogen bond among the compounds considered is possessed by 4-amino-3-nitropyrazole (III), in which the amino group is present in the π-excessive position 4 and in the ground state interacts insufficiently through the $C_{(4)}-C_{(3)}$ bond with the nitro group. In the IR spectrum of compound (III) reflections are observed on the left-hand slopes of the ν_sNH and ν_{as}NH bands which, as in the spectrum of m-nitroaniline [7], are due to the interaction of the amino group, which possesses a fairly high basicity, with chloroform. The weak hydrogen bond in the molecule of the aminonitropyrazole (III) appears in the electronic absorption spectra as an increase in the bathochromic shift of the $CT^{NO_2}_{NH_2}$ band when benzene is replaced by ethanol (Table 1) as compared with the spectra of compounds (I, II, IV, and V).

For a comparative qualitative evaluation of the electron-donating properties (basicity) of the amino group in the aminonitropyrazoles it is possible to use the values of the chemical shifts of its protons, since, according to the results of quantum-chemical calculations of compounds (IV) and (V) [8], these magnitudes are correlated with the electron densities of the nitrogen atom of the amino group. In the PMR spectra, the signals of the protons of the amino group of 4-amino-3-nitropyrazole (III) (Table 1) are present in the strong field, and the increase in δ in the spectra of the aminonitropyrazoles (II-IV) takes place symbatically with the shift in the high-frequency direction of ν_{as}NH in the IR spectra.

In the case of 4-amino-5-nitropyrazole (II), the amino group and the nitro group interact through a bond having a high π-order, which leads to an increase, as compared with 4-amino-3-nitropyrazole (III), in the conjugation of the amino group with the π-system of the pyrazole, to a decrease in the electron density on the nitrogen atom, and to a strengthening of the intramolecular hydrogen bond.

A convenient method for evaluating the electron-accepting capacity of a nitro group and its interaction with other substituents in aromatic compounds is formed by the polarographic half-wave reduction potentials ($E_{1/2}$) of the nitro derivatives in aprotic solvents [9, 10]. In anhydrous aprotic solvents the first reduction wave of nitro compounds has been identified as a one-electron irreversible polarographic wave, and the value of $E_{1/2}$ characterizes the energy of the lowest unoccupied molecular orbital (LUMO) [10]. We performed the polarographic reduction of nitrobenzene, 1-methyl-3-nitropyrazole (VI), 1-methyl-4-nitropyrazole (VII), and compounds (I-V) in acetonitrile (Table 1). The differences in the $E_{1/2}$ values of 3-amino-4-nitropyrazole (IV), 5-amino-4-nitropyrazole (V), and 4-nitropyrazole (VII) ($\Delta E_{1/2}$) can serve as a measure of the efficiency of the transmission of electronic influences between the amino and nitro groups. In the first case, the value of $E_{1/2}$ was 0.07 V, and in the second case 0.21 V, which is due to the difference in the orders of the $C_{(3)}-C_{(4)}$ and $C_{(5)}-C_{(4)}$ bonds in the pyrazole ring. The low efficiency of the interaction of the amino and nitro groups through the $C_{(3)}-C_{(4)}$ bond was also confirmed by the $\Delta E_{1/2}$ value (0.05 V) obtained for 3-nitropyrazole (VI) and 4-amino-3-nitropyrazole (III).

The $E_{1/2}$ values for 3-nitropyrazole (VI) (—1.05 V) and for nitrobenzene (—1.09 V) show that the 1-methyl-3-pyrazolyl radical exhibits some electron-accepting properties in comparison with the phenyl radical, i.e., the electrophilicity of the "pyridine" nitrogen in pyrazole is not completely compensated by the electron-donating influence of the "pyrrole" nitrogen. 4-Nitropyrazole (VII) ($E_{1/2} = -1.23$ V) is reduced with considerably greater difficulty than 3-nitropyrazole (VI) and nitrobenzene, which is connected with the excess π-electron density in position 4 of the pyrazole ring.

The position of the $CT^{NO_2}_{NH_2}$ long-wave band in the electronic spectra of the aminonitropyrazoles (II-IV) must be determined by the electron-donating capacity (ionization potential) of the amino group, the electron-accepting capacity (energy of the LUMO) of the nitro group in a concrete compound, and the capacity of the $C_{(3)}—_{(4)}$ and $C_{(4)}—C_{(5)}$ bonds in the pyrazole ring for transferring charge on the passage of the molecule from the ground state into an excited state. The latter circumstance — namely the greater π-order of the $C_{(4)}—C_{(5)}$ bond as compared with the $C_{(3)}—C_{(4)}$ bond, leading to the formation of the limiting charge-transfer structures — is apparently responsible for the greater intensity of the long-wave bands in the spectra of compounds (II) and (V) as compared with the intensities of the analogous bonds in the spectra of the isomers (III) and (IV). The same circumstance is the reason for the bathochromic shift of the $CT^{NO_2}_{NH_2}$ band in the electronic spectrum of 4-amino-5-nitropyrazole (II) relative to the same band in the spectrum of 3-amino-4-nitropyrazole (IV), in spite of the circumstance that according to the facts given (Table 1), the amino groups in these compounds are characterized by approximately identical electron-donor capacities and the energies of the LUMOs should practically coincide. For the same reason, even in the case of 4-amino-3-nitropyrazole (III), in which the electron-donating capacity of the amino group is greater and the energy of the LUMO smaller than the corresponding characteristics of 4-amino-5-nitropyrazole (II), the long wave band is shifted hyposochromically relative to the $CT^{NO_2}_{NH_2}$ band in the spectrum of compound (II). In the molecule of 5-amino-4-nitropyrazole (V), transfer of charge also takes place through the $C_{(4)}—C_{(5)}$ bond, but the $CT^{NO_2}_{NH_2}$ band in the spectrum of this compound is shifted hypsochromically in comparison with the analogous band in the spectrum of 3-amino-4-nitropyrazole (IV). This is apparently connected with the high efficiency of charge transfer between the amino and nitro groups even in the ground state, which sharply lowers the electron-donating properties of the amino group and the electron-accepting properties of the nitro group and raises the energy of charge transfer on the passage of the 5-amino-4-nitropyrazole molecule in the corresponding excited state.

EXPERIMENTAL

The electronic absorption spectra of compounds (I-VII) were recorded on a Specord UV instrument, and the IR spectra of o-nitroaniline and of the aminonitropyrazoles (II-IV) on a UR-20 instrument in anhydrous chloroform at a concentration of 0.025 M. The PMR spectra of compounds (I-V) were measured on a Tesla BS-467 instrument (60 MHz, HMDS) in DMSO-d_6. The polarographic reduction of the nitro compounds (I-VII) and of nitrobenzene was carried out at room temperature in anhydrous acetonitrile purified as described by Wawzonek and Runner [11]. The concentration of depolarizer in all cases was $5 \cdot 10^{-4}$ M, and tetrabutylammonium iodide (0.1 M) was used as the supporting electrolyte.

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