# CHARACTERISTIC FEATURES OF THE REACTION OF 3(5)AMINO-5(3)-METHYLPYRAZOLE WITH 1-NITROANTHRAQUINONE-2-CARBOXYLIC ACID

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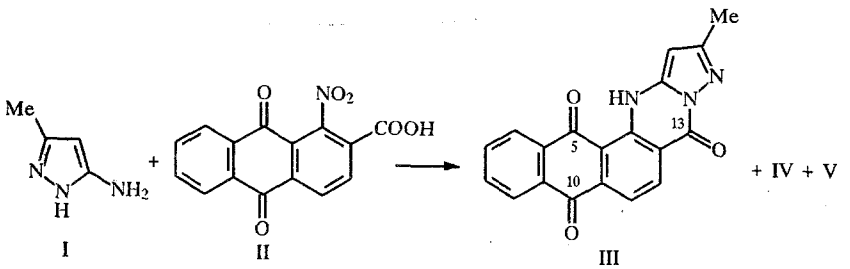
*In the reaction of 3(5)-amino-5(3)-methylpyrazole with 1-nitroanthraquinone-2-carboxylic acid in sulfolane at 150°C, 2-methyl-pyrazolo[5,1-b]naphtho[2,3-h]quinazoline-5,10,13-trione is formed with an admixture of 1-aminoanthraquinone-2-carboxylic acid and 1-aminoanthraquinone. Under similar conditions, from 4-amino-1,5-dimethylpyrazole, only 1-(1,5-dimethyl-4-pyrazolylamino)anthraquinone-1-carboxylic acid is formed.*

As the result of the reaction of 3(5)-amino-5(3)-methylpyrazole (I) with 1-nitroanthraquinone, 2-methyl-8H-pyrazolo[5,1-b]-benzo[e]pyrimidin-8-one is formed with an admixture of 1-amino-anthraquinone [1]. Under similar conditions the reaction of 1-nitroanthraquinone-2-carboxylic acid (II) with aminopyrazole I leads to the formation of three products – 2-methylpyrazolo[5,1-b]-naphtho[2,3-h]quinazoline-5,10,13-trione (III, $M^+$ 329), 1-amino anthraquinone-2-carboxylic acid (IV) and 1-aminoanthraquinone (V) in a ratio of 4:2:1 (after separation by means of TLC).




I II III

The PMR spectrum of compound III was interpreted using the method of homonuclear resonance, and also by comparison with the PMR spectrum of acridone [2]. The position of the signal of the NH group proton at 12.75 ppm confirms the existence of a strong intramolecular hydrogen bond (IHB) [3] between its proton and the carbonyl group of the anthraquinone fragment. The structure of compound III is also indicated by the presence in the IR spectrum of three characteristic stretching vibration bands of the CO groups (1628, 1658 and 1705 $cm^{-1}$).

The formation of products IV and V in the reaction of amino-pyrazole I with 1-nitroanthraquinone [1] and acid II, respectively, may be due to the reducing ability of amine I.

Aminoanthraquinone V is formed, clearly, as the result of decarboxylation of aminocarboxylic acid II under the reaction conditions [4].

This is indicated by the result of the reaction of nitroanthraquinonecarboxylic acid II with 4-amino-1,5-dimethylpyrazole (VI). Thus, only 1-(1,5-dimethyl-4-pyrazolylamino)anthraquinone-2-carboxylic acid is formed (VII, yield 89%) the structure of which was confirmed by the mass- IR and PMR spectral data.

The study of the electronic absorption spectra of compounds III and VII showed a considerable deepening of the light of the ethanolic solution of compound III on alkalinization ($\Delta\lambda_{max}$ 148 nm), which indicates a possible lactam-lactim tautomerism in the solution and serves as additional evidence for the structure of product III.

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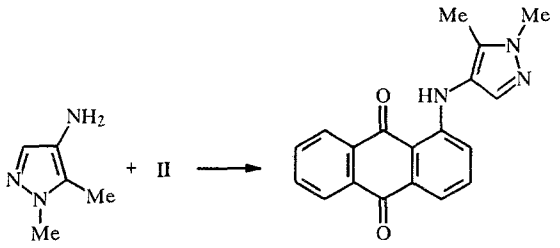

VI VII

## EXPERIMENTAL

The electronic absorption spectra were recorded on a Specord UV spectrophotometer in ethanol ($10^{-4}$ mole/liter), and the IR spectra on a UR-20 spectrophotometer (KBr tablets). The PMR spectra were measured on a Perkin–Elmer spectrometer (250 MHz, internal standard HMDS), for compound III using the method of homonuclear resonance. The mass spectra of the compounds were recorded on a Hewlett-Packard 5985 quadropole chromato-mass spectrometer with direct introduction of the sample into the ionization source at a ionizing voltage of 70 eV and an admission temperature which was lower than the melting point of the sample by 10-15°C. The TLC was carried out on Silufol UV-254 plates using a benzene–acetone 3:2 mixture as eluent.

The data of the elemental analysis of compounds III and VII corresponded to the calculated values.

**2-Methylpyrazolo[5,1-b]naphtho[2,3-h]quinazoline-5,10,13-trione (III, $C_9H_{11}N_2O_3$).** A 0.74 g portion (2.5 mmoles) of nitrocarboxylic acid II was dissolved with heating to 110°C in 10 ml of sulfolane, and a solution of 0.48 g (5 mmoles) of aminopyrazole I in 5 ml of sulfolane and 0.2 g of $Na_2CO_3$ were added. The reaction mixture was held for 4 h at 150°C up to the disappearance of acid II (TLC monitoring). The solvent was distilled off in vacuo, and the residue was neutralized with 5% HCl. The precipitate was filtered off, washed with water and dried. Then, 0.82 g of the mixture of products obtained was separated on plates (silica gel 5/40$\mu$, eluent benzene–acetone, 3:2) to yield 0.05 g of aminoanthraquinone V, $R_f$, 0.74 (corresponds to the reference spot) and 0.45 g (55%) of compound III, $R_f$, 0.59; mp 338-340°C (dec.); $M^+$ 329; $\lambda_{max}$ 485 nm (3.60), $\lambda_{max}$ 633 nm (3.71) (ethanol + NaOH). PMR spectrum (DMSO-$d_6$), 2.35 (3H, s, 2-$CH_3$), 6.35 (1H, s, 3H), 7.90 (2H, m, 7-, 8-H), 7.96 (1H, m, 11-H), 8.22 (2H, m, 6-, 9-H), 8.68 (1H, d, 12H), 12.75 ppm (1H, s, 4-H). In addition, 0.2 g (32%) of aminocarboxylic acid IV was isolated, $R_t$ 0.33; mp 283-285°C (285-287°C [5]). $M^+$ 267.

**1-(1,5-Dimethyl-4-pyrazolylamino)anthraquinone-2-carboxylic acid (VII, $C_{20}H_{15}N_3O_4$).** A 0.74 g portion (2.5 mmoles) of acid II was dissolved with heating to 110°C in 10 ml of sulfolane and 0.55 g (5 mmoles) of 4-amino-1,5-dimethylpyrazole and 0.2 g of $Na_2CO_3$ were added. The mixture was then heated to 150°C, held for 2.5 h at 150°C up to the disappearance of the initial acid II (TLC monitoring), cooled, diluted with 20 ml of water, and neutralized with 5% HCl. The precipitate that separated out was filtered off, washed with water, and dried to yield 0.8 g (89%) or compound VII, mp 245-247°C (dec.); $M^+$ 361; $\lambda_{max}$ 505 nm (3.34), $\lambda_{max}$ 520 nm (3.40) (ethanol + NaOH); IR spectrum: 1635 1670, 1718 $cm^{-1}$ (C = 0). PMR spectrum (DMFA-$D_7$): 2.13 (3H, 5-$CH_3$), 3.73 (3H, s, 1-$CH_3$), 7.29 (1H, s, 3-H), 7.72-8.3 ppm (8H, m, the remaining protons).

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