mixture of glacial acetic acid and concentrated sulfuric acid (5.0:0.5) was then added and the product stirred for 30 min at 70°C. After cooling, the reaction mixture was poured into water, the solid filtered off and washed with water and dried to give a yield of 1.5 g (96%). Column chromatography using ether eluent gave VIII as colorless crystals with mp 258°C (decomp.) and R_f 0.6 (benzene-acetone 3:2). IR Spectrum: 3350 cm^{-1} (NH). UV Spectrum, λ_{max} (log ε): 205 (5.21), 207 sh (5.15), 235 (4.39), 242 (4.35), 248 (4.32), 253 (4.27), 260 (4.19), 290 nm (4.18). Found: M^+ 314. Calculated M 314.

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QUANTUM-CHEMICAL INVESTIGATION OF THE FACTORS WHICH DETERMINE STABILITY OF THE 3,5-DIMETHYL-1H-PYRAZOLE-4-DIAZONIUM ION

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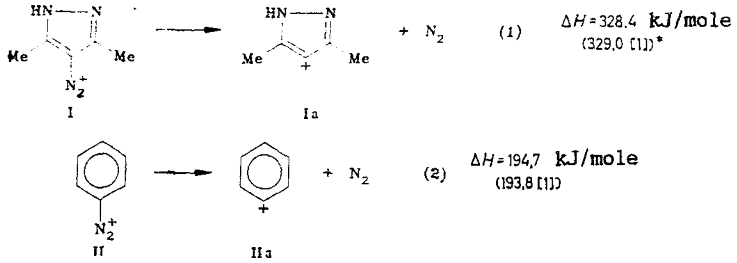
It was shown by MNDO calculations that the stability of the 3,5-dimethyl-1H-pyrazole-4-diazonium ion to decomposition with the elimination of nitrogen is due to the destabilization of the formed carbocation, which has a triplet ground electronic state.

Compared with benzenediazonium chloride, 3,5-dimethyl-1H-pyrazole-4-diazonium chloride has unusual stability [1]. The relative stability of the diazonium cations (I) and (II) can be compared by means of the data from calculation of the enthalpy of the dissociation reactions (1) and (2) (by the MNDO method [2]), which represent the main path in the decomposition of the diazonium ions:



In connection with the fact that the energy profile of the decomposition reactions (1) and (2) is characterized by a monotonic increase of the energy with increase in the length of the $C-N_2$ bond [1], the enthalpies of reactions (1) and (2) can provide a measure not only of the thermodynamic stability but also of the kinetic stability of the

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*Our calculated heats of formation [$\Delta H_f(I) = 1028.5$; $\Delta H_f(II) = 1024.2$; $\Delta H_f(Ia) = 1323.5$ kJ/mole] differ somewhat from the data given in [1].

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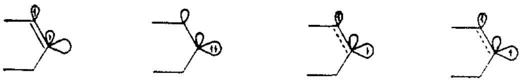
TABLE 1. The Heats of Formation and the Relative Energies of the Various Electronic States of 3,5-Dimethyl-1H-pyrazol-4-inium Ion (Ia), Calculated by the MNDO Method

Electronic state	ΔH_f, kJ/mole	E_{rel}
${}^1(\pi^2)$, ${}^1A'$*	1323,5	77,1
${}^1(\pi\sigma)$, ${}^1A''$	1276,5**	30,1
${}^3(\pi\sigma)$, ${}^3A''$	1246,4	0

*With allowance for the symmetry of only the heterocycle.
**With allowance for configuration interaction (CI 3 × 3).

corresponding diazonium ions. The reason for the enhanced stability of the diazonium ion (I) with respect to thermal decomposition (1) lies, according to [1], in its stabilization as a result of the transfer of π-electron density from the π-MO of the heterocycle (with a significant contribution from the p-AO of the ipso-carbon atom) to the π* orbital of the diazonium group. This effect is substantially less clearly defined in the benzenediazonium ion [1, 3].

In the present work we showed that the interpretation of the stability of the cation (I) proposed in [1], which is increased in comparison with the stability of the cation (II), requires fundamental changes. Since the stability of the diazonium ion to decomposition with the elimination of nitrogen is determined by its thermodynamic stability compared with the stability of the corresponding carbocation, it is necessary also to have data on the destabilization of the latter. Brint and coworkers [1] did not take account of the fact that four lowest electronic states are possible for the cations (Ia) and (IIa), i.e., singlet states ${}^1(\pi^2)$ and ${}^1(\sigma^2)$ with a closed electron shell* and singlet and triplet states $[{}^1(\pi\sigma), {}^3(\pi\sigma)]$ of the diradical type:



The analysis of the stability of the diazonium ion (I) [1] was based on examination of the ${}^1(\pi^2)$ state of the carbocation (Ia) as electronic ground state. However, our calculations (Table 1) showed that the electronic ground state of the carbocation (Ia) is the triplet ${}^3(\pi\sigma)$ and not the singlet ${}^1(\pi^2)$ state considered in [1]. Moreover, a singlet state of diradical type ${}^1(\pi\sigma)$ has a lower energy than the ${}^1(\pi^2)$ state (Table 1). Calculation of the eigenvalues of the Hessian (e.g., see [4]) indicates that the structure (I) and the ${}^1(\pi^2)$, ${}^3(\pi\sigma)$, and ${}^1(\pi\sigma)$ states of structure (Ia) correspond to minima on the corresponding potential energy surfaces.

The stability of the diazonium ions (I) and (II) can be compared by calculating the enthalpy of the isodesmic [5] reaction (III), which formally represents the difference of the reaction schemes (1) and (2):

$$\mathrm{I} + \mathrm{IIa} \rightarrow \mathrm{Ia},\ {}^1(\pi^2) + \mathrm{II} \quad (\Delta H = 133.7\ \text{kJ/mole}). \tag{3}$$

The positive value of ΔH in Eq. (3) indicates greater stability for (I) than for (II). The possibility of comparing the above-mentioned factors (the relative stabilization of

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*Or more accurately, $[{}^1(\pi^2) - \lambda {}^1(\sigma^2)]$ and $[{}^1(\sigma^2) + \mu {}^1(\pi^2)]$, where $0 < \lambda, \mu < 1$.

the diazonium ion and the destabilization of the carbocation) separately is provided by reactions (4)* and (5), where ΔH(3) = ΔH(4) − ΔH(5):

$$\mathrm{I} + \text{benzene} \rightarrow \text{3,5-dimethyl-1H-pyrazole} + \mathrm{II} \quad (\Delta H = 50.5\ \text{kJ/mole}); \tag{4}$$

$$\mathrm{Ia},\ {}^{1}(\pi^{2}) + \text{benzene} \rightarrow \text{3,5-dimethyl-1H-pyrazole} + \mathrm{IIa} \quad (\Delta H = -83.2\ \text{kJ/mole}). \tag{5}$$

The positive value of ΔH in Eq. (4) shows that the benzenediazonium ion (II) is destabilized more in relation to the corresponding neutral molecule (benzene) than the cation (I) is destabilized in relation to 3,5-dimethyl-1H-pyrazole. The negative value of ΔH in Eq. (5) shows that the stability of the phenyl cation is greater than the stability of the 3,5-dimethyl-1H-pyrazole-4-yl cation (Ia), $^{1}(\pi^{2})$. [In this case "stability" is taken to mean the ease of abstraction of H- for benzene compared with 3,5-dimethyl-1H-pyrazole with the formation of the carbocation (Ia).]

Thus, together with the stabilization of the diazonium ion (I) observed in [1] as a result of the transfer of electron density from the heterocycle to the diazonium group, an important reason which determines the higher decomposition energy of the cation (I) than of the cation (II) is the greater destabilization of the carbocation (Ia) compared with the stabilization of the phenyl cation (IIa). Here the ground state of the carbocation (Ia), in contrast to the phenyl cation [6], is not the singlet state $^{1}(\pi^{2})$, as supposed by the authors in [1], but the triplet state $^{3}(\pi\sigma)$.

EXPERIMENTAL

Calculation Procedure. The calculations were conducted by the MNDO method by means of the programs in [7, 8]. The excited states were calculated in the "half-electron" approximation [9].

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*Our calculated heat of formation of 3,5-dimethyl-1H-pyrazole is ΔH_f = 143.5 kJ/mole (by the MNDO method).