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## ATTEMPTED GENERATION AND STRUCTURE OF THE 4-(1,2,4-TRIAZOYL) CATION

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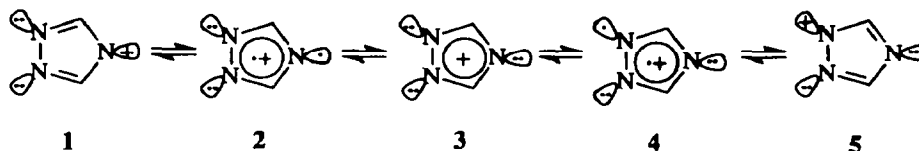
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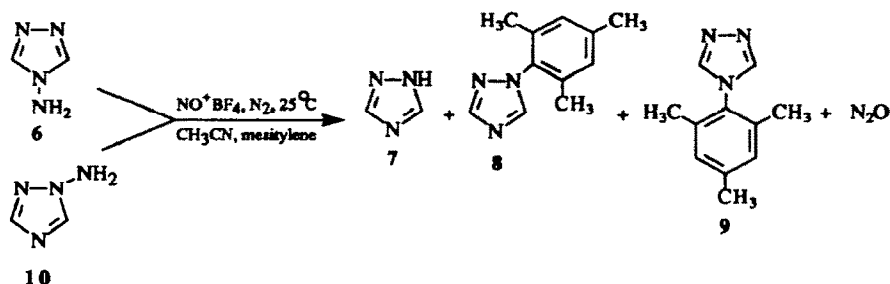
**Abstract:** 4-(and 1-) Amino-1,2,4-triazoles have been treated with nitronium tetrafluoroborate or with *iso*amyl nitrite and acetic acid in the presence of mesitylene. The main product is 1,2,4-triazole, together with a small amount of the 1- and trace amounts of the 4-mesityl derivatives. *Ab initio* calculations of the putative 4-(1,2,4-triazoyl) cation show the electronic ground state to be a closed shell singlet  $^1A_1$  ( $4\pi e$ ) (3), with a low-lying  $^3B_1$  triplet (4) only 1 kcal/mol above it; the  $\sigma$ -cation (1) is not a local minimum on the potential energy surface. Possible explanations of the results are proposed.

Nitrenium ions continue to receive significant attention.<sup>1</sup> There have been relatively few reports concerning the generation of nitrenium ions in which the nitrogen atom is part of a heterocyclic ring<sup>2</sup> and only a possible one<sup>3</sup> when it is part of a heteroaromatic 5-membered ring. We conceived that if the 4-(1,2,4-triazoyl) cation (1) were formed it could undergo electronic reorganization to the  $5\pi$  diradical cation (2), to the  $4\pi$  cation (3) (antiaromatic if fully conjugated), to an isomeric  $5\pi$  diradical cation (4) and to a  $\sigma$ -cation 5 isomeric with 1. Of course, singlet and triplet multiplicities would be possible.<sup>4</sup>

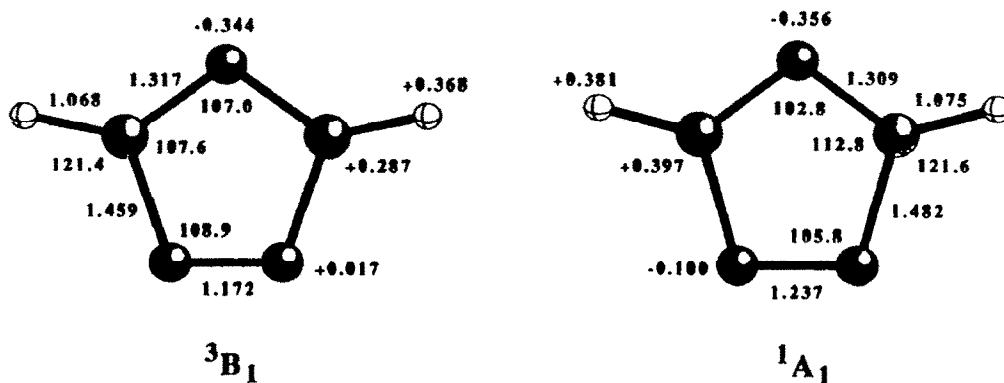


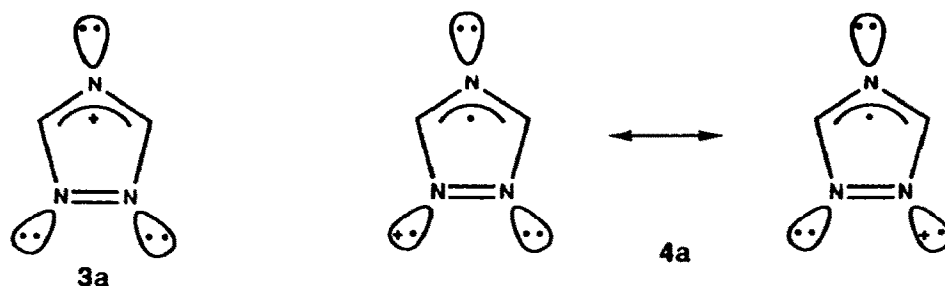
Treatment of 4-amino-1,2,4-triazole (6) with  $\text{NO}^+\text{BF}_4^-$  in acetonitrile gave only 1,2,4-triazole (7), no Ritter reaction-type products being detected. When the same reaction was carried out in the presence of mesitylene at room temperature triazole 7 was again isolated (77%); nitrogen and nitrous oxide (infrared) were evolved. In addition, 1-(2,4,6-trimethylphenyl)-1,2,4-triazole (8) (1%) was isolated,<sup>5</sup> and a trace of 4-(2,4,6-trimethylphenyl)-1,2,4-triazole (9) was detected by GC/MS and identified (authentic sample<sup>3</sup>). The same

products, in approximately the same ratio, were observed when **6** was treated with *isoamyl* nitrite in the presence of acetic acid and excess mesitylene or when 1-amino-1,2,4-triazole (**10**) was treated as above with  $\text{NO}^+\text{BF}_4^-$ .



*Ab initio* M.O. calculations<sup>6</sup> predict the electronic ground state to be a triplet of  $B_1$  symmetry with  $5\pi$  electrons corresponding to diradical cation **4**;  $S_0$  corresponds to a  $4\pi$  cation singlet of  $A_1$  symmetry (**3**). The  $6\pi$  electron singlet state corresponding to the  $\sigma$ -cation **1** lies high in energy above the ground state. The optimum  $C_{2v}$  structure calculated for **1** shows one negative vibrational frequency of  $b_2$  symmetry, indicating that this is not a local minimum on the corresponding potential energy surface. The CASSCF/6-31G(d) optimized geometries are shown below along with calculated total atomic charges. The equilibrium bond lengths  $\text{N}_1\text{-C}_5$  and  $\text{N}_2\text{-C}_3$  in the  $^3B_1$  and  $^1A_1$  states are somewhat long compared with 1,2,4-triazole,<sup>8</sup> while the  $\text{N}_1\text{-N}_2$  bonds are remarkably short. Two separate (non-conjugated) moieties in **4a** and **3a**, account for this. Fully conjugated antiaromatic **3** is thus avoided in **3a**. At the CASSCF/6-31G(d) level, the  $^3B_1\text{-}^1A_1$  energy separation is 4.6 kcal/mol. If configuration interaction of all single and double excitations (CISD) with the 6-31G(d) basis set (CASSCF/6-31G(d)-optimized geometries, GAMESS program) are included, the singlet energy then falls 2 kcal/mol *below* the triplet. When zero-point vibrational energy corrections are added, the final singlet-triplet separation is 1.16 kcal/mol in favor of **3a**, a very small difference indeed.





The experimental results agree with the computations: to the extent that dissociation of an intermediate 1,2,4-triazol-4-diazonium ion occurs, the species eventually formed is the singlet cation **3a** which is easily converted to the diradical cation **4a**. The latter can abstract two hydrogen atoms (from solvent) to give 1,2,4-triazolium tetrafluoroborate (2 steps) which gives **7** on isolation. An alternate (and simpler) explanation envisions the formation of a hydroxyazo intermediate<sup>9</sup> or a labile *N*-nitrosamine<sup>10</sup> (rather than a diazonium ion) followed by loss of  $\text{N}_2\text{O}$  (observed).<sup>9</sup>

That the *same* ratios of small amounts of **8** and **9** from either 1- or 4-amino-1,2,4-triazole are formed suggests a common intermediate -- **3a** or **4a**. Were mesitylene reacting directly with the two diazonium salts from **6** or **10** via  $\text{S}_{\text{N}}2'$  processes, different ratios of **8** to **9** might be expected. The formation of a small amount of a  $\pi$ -type complex between the highly electron-attracting triazolodiazonium salt and the electron-rich mesitylene, followed by dissociation and migration of the arene to nitrogen *within the complex* could be an alternate explanation.

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