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Poster Presentation

An Ab Initio Study of Nitrosonium Complexes of N-Heterocyclic Compounds

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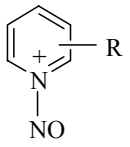
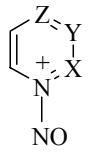
A knowledge of properties of nitrosonium complexes of heterocyclic compounds is important for understanding of some chemical and biochemical reactions[1,2]. The subject of this work is quantum chemical studies on complexes of N-heterocyclic compounds with the nitrosonium cation.

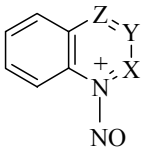


1a-e

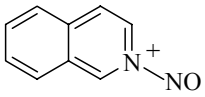
R=H(**a**), 3-Me(**b**), 2-Cl(**c**), 4-Cl(**d**), 3-F(**e**)



X=N Y=Z=CH (**2**)
Y=N X=Z=CH (**3**)
Z=N X=Y=CH (**4**)



X=Y=Z=CH (**5**)
X=N Y=Z=CH (**6**)
Z=N X=Y=CH (**7**)



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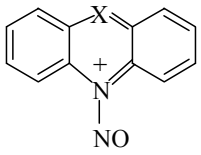
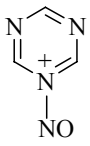


X=CH (**9**)
X=N (**10**)



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The following nitrosonium complexes have been studied using *ab initio* HF/6-31G, HF/6-31G(d), HF/6-31G(d,p), HF/6-31G+(d), HF/6-31G(2d), HF/6-31G(2d,p), and MP2/6-31G methods:

Substitution of N for C atom of a cycle results in decrease of the affinity of N-heterocyclic compounds to the nitrosonium cation (A_{NO}^+). As opposed to the effect of N substitution, annelation or introduction of an electron-donor substituent into the cycle increases A_{NO}^+. The best agreement between the calculated A_{NO}^+ values for precursors of complexes **1a,b,d,e** and the corresponding experimental data[2] has been obtained by HF/6-31G(2d,p) method.

The A_{NO}^+ values for the N-heterocyclic compounds under study are lower than the respective proton affinity (PA) values (*cf.* ref.[3]), A_{NO}^+ vs. PA[3] correlation displaying a linearity.

1. G.I. Borodkin and V.G. Shubin, *Usp. Khimii.* **2001**, *70*, 241.
2. F. Cacace, G. De Petris, and F. Pepi, *Proc. Natl. Acad. Sci. USA*. **1997**, *94*, 3507.
3. M. Mautner, *J. Amer. Chem. Soc.* **1979**, *101*, 2396.

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