Full Paper _____ *Thematic Section:* Quantum Chemistry.
Registration Code of Publication: 12-30-6-26 *Subsection:* Organic Chemistry.
Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings/
Contributed: June 27, 2012

Thematic course: Theoretical study of the mechanism of aromatic nitroso oxides isomerization. Part I.

Influence of the substituent orientation on the activation barrier of *orto*-cyclization

© **Evgeny Yu. Pankratiev**,[+] and **Rustam L. Safiullin***
Laboratory Chemical Kinetics. Institute of Organic Chemistry. Ufa Scientific Center.
Russian Academy of Sciences. Prosp.Oktyabrya St., 71. Ufa, 450054. Republic of Bashkortostan. Russia.
Phone: +7 (347) 292-14-19. Факс: +7 (347) 235-60-66. E-mail: evgeniy@pankratyev.com

*Supervising author; [+]Corresponding author

Key words: *nitroso oxide, isomerization, cyclization of ortho-, ab initio and DFT-calculations.*

Abstract

In the quantum-chemical approximations G3MP2B3, UB3LYP/6-311+G(d,p), UPBEPBE/Λ2 and UPBEPBE/3ζ there has been studied the influence of the substituent orientation (on the example of CH_3−O−, CH_3−S−, CH_2=CH−, CH_3−CH_2−) of the aromatic cycle phenyl-*cis*-nitroso oxide on the activation barriers of *ortho*-cyclization reaction. A method was proposed for computing the effective activation parameters to account for the influence of conformational transitions on the activation barriers of *ortho*-cyclization of substituted phenyl-*cis*-nitroso oxides. Activation *ortho*-cyclization barrier for *para*- methoxyphenyl-*cis*-nitroso oxide, in approximation UB3LYP/6-311+G(d,p) making up 70.4 kJ/mol has been ascertained.