Full Paper _____ *Thematic Section:* Quantum-Chemical Research.
Reference Object Identifier – ROI: jbc-02/15-44-12-164 *Subsection:* Organic Chemistry.
Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings/ *(English Preprint)*
Contributed: November 21, 2015.

Quantum chemical and experimental study of anionic σ-adducts of 2-methyl-5,7-dinitrobenzo[d]oxazole with methoxide ion

© **Loik Gurgovich Mukhtorov**,[1] **Igor V. Blokhin**,[1+] **Irina V. Shakhkeldyan**,[1]
Yury M. Atroshchenko,[1] **Vyacheslav A. Arlyapov**,[2] **Konstantin I. Kobrakov**,[3]*
and **Aleksey N. Shumsky**[4]

[1] *Department of Chemistry. Tula State Lev Tolstoy Pedagogical University.*
Lenina pr., 126. Tula, 300026. Russia. Phone: +7 (4872) 35-78-08. E-mail: reaktiv@tspu.tula.ru
[2] *Department of Chemistry. Tula State University. Lenina pr., 92. Tula, 300012. Russian Federation.*
Phone: +7 (4872) 35-18-40. E-mail: v.a.arlyapov@gmail.com
[3] *Department of Organic Chemistry. Moscow State University of Design and Technology.*
Sadovnicheskaya St., 33. Moscow, 117997. Russian Federation. Phone: +7 (495) 955-35-58.
E-mail: kobrakovk@mail.ru
[4] *Emanuel Institute of Biochemical Physics of Russian Academy of Sciences.*
Kosygina St., 4. Moscow, 119334. Russia. Phone: +7 (495) 939-73-66. E-mail: shumsky@mail.ru

*Supervising author; [+]Corresponding author

Keywords*:* 2-methyl-5,7-dinitrobenzo[d]oxazol, nucleophilic addition, anionic σ-adduct, semi-empirical PM6 method.

Abstract

The charges on atoms and the contributions of p_z-orbitals of the atoms in LUMO in the molecules 2-methyl-5,7-dinitrobenzo[d]oxazole was calculated by semi-empirical method PM6 in the gas phase and in methanol. The standard heat of formation of the anticipated products of addition of the methoxide ion to the substrate, the standard enthalpy and Gibbs energy of reactions was calculated. It is found that in methanol the decisive role played by the charge factor, the attack of the nucleophile is most likely at the carbon atoms C-2, C-4 and C-6 of the substrate. The σ-adduct, which is a structure with the position of the methoxyl group at the second carbon atom of oxazole cycle, was selected under the action of cesium carbonate on 2-methyl-5,7-dinitrobenzo[d]oxazole in methanol at room temperature. The structure of the obtained compounds was proved by NMR (^{1}H NMR, ^{13}C NMR, HSQC, HMBC), IR spectroscopy, and elemental analysis.