Full Paper _____ *Thematic Section:* Quantum-Chemical Research.
Reference Object Identifier – ROI: jbc-01/17-49-3-84 *Subsection:* Physical Organic Chemistry.
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/17-49-3-84
Submitted on Marth 25, 2017.

Theoretical modeling of the interaction of 2-*R*-5,7-dinitrobenzo[d]-oxazoles with methoxideion by DFT method

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Keywords: 5,7-dinitrobenzo[d]oxazole, 2-methyl-5,7-dinitrobenzo[d]oxazole, 2-phenyl-5,7-dinitrobenzo[d]oxazole, nucleophilic addition, anionic σ-adduct, density functional theory, DFT/B3LYP.

Abstract

The interaction of 5,7-dinitrobenzo[d]oxazole, 2-methyl-5,7-dinitrobenzo[d]oxazole and 2-phenyl-5,7-dinitrobenzo[d]oxazole with a methoxide ion has been studied. It has been established that the nucleophile is attached to the carbon atom at position 2 of the heteroaromatic ring, and not to positions 4 and 6 with the formation of classical Mesenheimer complexes. The structure of the obtained σ-adducts was established by IR and NMR spectroscopy methods, as well as by elemental analysis data.Quantum-chemical calculations by the DFT method show that the largest positive charges are concentrated on C2, C3a and C7a atoms in the gas phase and methanol, whereas the presence of a relatively high electron density is observed on carbon atoms C4 and C6. Charges in methanol are slightly higher than in the gas phase. These data do not agree with the results of the calculation by the semiempirical method PM6, obtained earlier. Thus, it is established that the studied reaction proceeds under charge control conditions. The calculation of the total energies of the putative products showed that among the products of addition of the methoxide ion in the gaseous phase to the unsubstituted substrate, the most stable adducts are formed upon attack of the nucleophile at position 2, whereas in the case of 2-phenyl-5,7-dinitrobenzo[d]oxazole, the lowest values of the energy are the anions formed upon the addition of the methoxide ion to position 4. For a substrate with a methyl group at position 2, the difference in the energies of the adducts when the nucleophile is added to positions 2 and 4 is insignificant and is of the order of 0.5 kJ/mol. The attack of the methoxide ion on the carbon atom C-4, leading to the formation of classical adducts of Mesenheimer, is most energetically favorable in methanol for all substrates. Analysis of the contribution of the C-4 carbon atom to the LUMO substrate indicates the possibility of an attack of the methoxide ion over the benzannelated ring.

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