

Theoretical study of the isomerization of 1-amino-4-phenylamino-9,10-anthraquinone

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Abstract

This paper presents the results of computer simulation of tautomeric transformations of the molecule 1-amino-4-phenylamino-9,10-anthraquinone. It is known from the literature that the presence of substituents in the 1,4-position of anthraquinone-9,10 leads to various tautomeric transformations, with a shift in the absorption maximum and the appearance of absorption bands in the red wave region in electronic spectra. Both the 1-amino-4-hydroxyanthraquinone described in the literature and the 1-amino-4-phenylamino-9,10-anthraquinone are characterized by two types of prototropic tautomerism – keto-enol and amino-imine. Quantum-chemical modeling contributes to the calculation of the relative energies of tautomers and isomers, the barriers of their interconversions, as well as finding their structural parameters.

The aim of this study was to study the mechanism of the formation of tautomers during hydrogen transfer in the molecule of 1-amino-4-phenylamino-9,10-anthraquinone, as well as the formation of isomers during migration of the OH group. The calculations were performed using the Gaussian09 program. To study of various tautomers of 1-amino-4-phenylamino-9,10-anthraquinone, the B3LYP method with the def2TZV basis was used. A search was conducted for transition states during hydrogen transfer and OH group migration. The descent along the reaction path was calculated to confirm that the transition state is in the path of the desired reaction. The minima corresponding to the starting material and product were localized. The activation enthalpies of the studied reactions were calculated. Migration of the OH group in the 1-amino-4-phenylamino-9,10-anthraquinone molecule leads to the formation of 4-phenylamino-9-amino-1,10-anthraquinone.

As the calculation shows, the keto-form of 1-amino-4-phenylamino-9,10-anthraquinone is energetically more profitable than all the isomers studied in this work, including the enol form. The smallest difference in total potential energies is 23.7 kJ/mol between the initial ketone form of 1-amino-4-phenylamino-9,10-anthraquinone and the last transformation structure – the 4-phenylamino-9-amino-1,10-anthraquinone molecule.

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