QUANTUM-CHEMICAL STUDIES OF INTERNAL AND INTERMOLECULAR PROCESSES IN 2,6-DI-TERTBUTYL-4-HYDROXYPHENOXYL

Sadykova A.T., Chagandai I.M., Nikolskiy S.N.

Academician Ye.A. Buketov Karaganda State University,
Karaganda, Kazakhstan
sergeynikolsky@mail.ru

Semiquinone radicals are acid spin probes that have inter and intramolecular dynamics of the hydrogen atom [1-3]. Intramolecular processes of 2,6-di-tert-butyl-4-hydroxyphenoxyl in EPR spectra can be described by using a two jump model [4]. Tautomeric forms of 2,6-di-tertbutyl-4-hydroxyphenoxyl differentiate by the position of hydroxyl group hydrogen atom within the plane of the radical benzene ring. Calculations of the radical structure were carried out by rotation the hydroxyl group dihedral angle within the plane of benzene ring on 360° by semiempirical and ab-initio methods.

It was found that the structure with a dihedral angle ∠(COH)=180 ° has the lowest energy, and the structure with a dihedral angle ∠(COH)=90 ° has the largest one. It was noted that the difference in energies of these states is approximately 9.0 kJ/mol. It is well correlates with early obtained experimental ESR spectroscopic data.

It was shown on the basis of data analysis that constants of benzene ring protons hyperfine structure practically do not change when the dihedral angle is varied in the range from 0 to 90 °. However, the HFS constant of the hydroxyl group hydrogen atom varies within wide range and even the sign of the HFS constant changes.

The intermolecular proton transfer was calculated in hydrogen bond complexes of ionic and molecular types. Calculations were carried out by using the ab-initio approximation with basis UHF 3-21G. It was obtained that the length of hydrogen OH ... N bond in the molecular complex is 2.7 Å and in the ionic complex is 3.1 Å. The molecular complex is thermodynamically more stable (ΔE=196.0 kJ/mol) than the complex of ionic type on. Calculations of the p-semiquinone radical were carried out by using the Gaussian 09W program.

References:

1. MASALIMOV, A.S., TUR, A.A., NIKOLSKIY, S.N. 2016. *J.Theor. and Exp.Chem*., **52** (1), pp.57-65.
2. NIKOLSKIY, S.N. 2008. *Bulletin of the University of Karaganda-Chemistry*, 2 (50), pp.11-15.
3. NIKOLSKIY, S.N. 2009. *Bulletin of the University of Karaganda-Chemistry*, 1 (53), pp.39-44.
4. NIKOLSKIY, S.N. 2006. *Bulletin of the University of Karaganda-Chemistry*, **1** (41), pp.17-20.