Full Paper _____ *Thematic section:* Quantum Chemistry.
Registration Code of Publication: 8-13-2-36 *Subsection:* Organic Chemistry.
Publication is available for discussion in the framework of on-line conference "*Butlerov readings*".
http://butlerov.com/readings/
Contributed to the editorial board: December 14 2008.

Quantum-chemical computation of molecular structure of benzolsulfoacid and kindred substances in free hydrated state

© **Evgeniy N. Krylov**
Department of Organic and Biological Chemistry. Ivanovo State University.
Ermak St., 39. Ivanovo, 153025. Russia. Phone: +7 (4932) 37-37-03. E-mail enk2005@rambler.ru

Keywords: *benzosulfoacid, trifluoromethanesulfoacid, quantum chemical computation, hydrates of sulfoacids.*

Abstract

In quantum chemical computation of the molecular structure of benzolsulfoacid (BSA) by semiempirical methods (AM1, PM3) and RHF (3-21G, 3-21G*, 3-21G**, 6-31G*, 6-311G**) it has been found out that the base enlargement results in reduction of reference charge on the atom S(VI) from 2.396 (PM3) to 1.444 (RHF/6-311G**). The changes on the carbon atom of the ring in sulfoacid relative to benzol are consistent by sign and location with the acceptor effect of sulfogroup. Estimation order of the bond C-S is increased from 0.612 (AM1) to 1.322 (6-311G**). Semi-empirical methods underestimate the order of this bond, which is not in agreement with the concept of conjunction of sulfogroup with aromatic ring, and RHF/3-21G overestimates the conjunction degree of atom S(VI). For semi-empirical methods the length of this bond (1.653, 1.770 Å) is not consistent with the order (0.612, 0.724). Comparison of data shows the inferior quality of parametrization on atom S(VI) for semi-empirical methods. Computation in the enlarged basis (RHF/6-311G**) is consistent with the orders of bonds and conjunction effects of sulfogroup. Correlation has been detected between the barriers of rotation of sulfogroup in BSA and nitrogroup in $PhNO_2$, significative of observance of linearity principle of free energies for rotation barriers. In equation of sulfoacid (RSO_2OH, R = CF_3, Ph) clusters are formed with water molecules of different composition ($RSO_2OH*(H_2O)n$, where n = 1,2,3…4. Computation on the level DFT B3LYP/6-311G** has shown that proton of hydroxyl group ($-SO_2O-H$) does not break away from oxygen atom at n=1 or 2, but only at n=3 and more it is transferred to the water molecule with the formation of hydroxonium cation. Energy contributions at sequential introduction of water molecules into cluster have alternation values**.**