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### On the structure of newly synthesized S-methylated 2-thiospirohydantoin and 2,4-dithiospirohydantoin in solution and solid state

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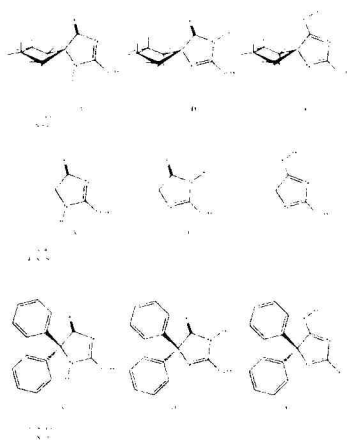
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The synthesis and structure of compounds obtained by methylation of the sulfur atom in cyclopentanespiro-5-(2-thiohydantoin) and cyclopentanespiro-5-(2,4-dithiohydantoin) and a theoretical investigation of the substituent effect in position 5 in the imidazoline ring on the structure and relative stability of the tautomers of compounds **1-6** is presented.



The geometry optimizations of the tautomer structures for compounds **1-6** were carried out at MP2 and B3LYP level using aug-cc-pVDZ and 6-311++G(d,p) basis sets. To estimate the effect of the medium (CCl<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH) on the relative stabilities of the tautomers, we applied the polarizable continuum model (PCM) at the B3LYP/6-311++G(d,p) level for the geometries optimized at the same level of theory. The NMR chemical shieldings were calculated at BPW91/6-311++G(2d,p) level using the GIAO approach and B3LYP/6-311++G(d,p) optimized geometries.

Based on different experimental methods (IR and solid state NMR spectroscopy, and X-Ray) we observed one tautomer in crystal state and another tautomeric form in saturated solution of CCl<sub>4</sub> of compounds **1** and **2**.

Quantum chemical calculations help to clarify the experimental results

### Tautomerism of 3,6-disubstituted cathechols. Synthesis and structure of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol

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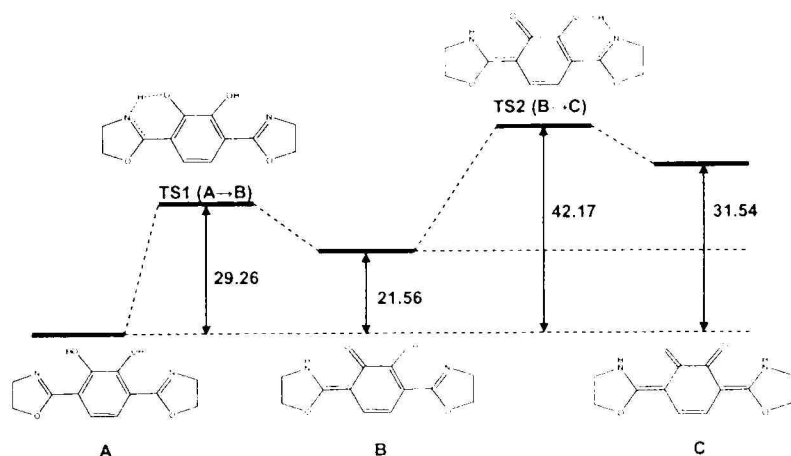
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Proton transfer reactions are among the most fundamental processes in chemistry and are involved in many biochemical transformations. Among many systems undergoing an intramolecular proton-transfer reaction in ground and excited state, particularly interesting and challenging are those where the tautomerization process is relatively slow and the tautomers are in equilibrium.

We consider the tautomerism of a newly synthesized compound 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol, an internally hydrogen-bonded derivative of catechol. The compound can exist in three tautomeric forms.



IR, UV and NMR spectra in solution and solid state were recorded in order to clarify which of the three possible tautomeric forms predominantly exist in these two phases. CASSCF + XMCQDPT2 quantum chemical calculations with the 6-31G(d,p) basis set were carried out, using Firefly 7.1.H and Gaussian 09 A.02.

The theoretical and experimental results indicate that form A is most stable both in solution and solid state. In ethanol solution of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol we observed a strongly shifted fluorescence which suggests that tautomeric conversion could be observed in excited state.

## Theoretical evaluation of the external EF-dependence of the molecular geometry and electronic structure of a model tautomeric system

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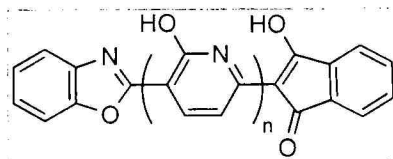
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The idea of using single organic molecules as functional elements of an electronic device has led to the development of a variety of applications such as molecular wires, molecular diodes, molecular storage devices and molecular switches.

It is well known that the structure and electronic properties of a molecule are affected by the external electric field (EF), therefore understanding of the electric field dependent molecular characteristics and their manipulation are important for using molecules as elements in electronics.

The purpose of this study is to focus on a theoretical approach to the design of molecular electronic devices based on tautomeric conversion, and reveal the EF-dependence of the molecular geometry, electronic structure and dipole moment of the studied tautomers. The general structure of the model system is presented below.



For  $n=1$ , all possible tautomers were optimized at second-order Møller-Plesset (MP2) and CASSCF + XMCQDPT2 level of theory. The basis set used was 6-31G(d,p).

Electric field effects were studied by including a field term in the Hamiltonian of the molecule during geometry optimizations. The numerical range of the EF intensities applied was 0.001 to 0.012 a.u. and -0.001 to -0.012 a.u. For  $n=2,3$ , all possible tautomers were optimized at HF/6-31G(d,p) level. The calculations were carried out using Firefly 7.1.H and Gaussian 09 A.02.

The inclusion of dynamical (MP2) and non-dynamical (CASSCF + XMCQDPT2) correlation lead to different relative stabilities of the tautomers. These stabilities are also influenced by the strength and direction of the external electric fields. Because the HOMO-LUMO gaps and spatial distributions of the frontier orbitals of the studied systems strongly depend on the applied electric fields, they could serve as molecular switches, rectifiers or wires.