**Short Communication**

Quantum-chemical Modeling of the Cyclic-Pentameric Mechanism for the 1H-3H Proton Transfer in Imidazole Derivatives

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Abstract

About of the cyclic-pentameric model for the 1H-3H proton transfer in the imidazole derivatives is reported. The activation energy (ΔE*) and reaction energy (ΔE) of the proton transfer as well as the bond orders (P_{N...H}) and (P_{N...i}) by means of Density Function Theory (DFT) are calculated. It is shown that proton transfer is energetically more advantageous in nitroimidazole. The values ΔE* and ΔE from the point of view of chemical transformations vary in rather reasonable limits, what indicates on the competence of the proposed cyclic - pentameric model. It is the new nonionic and oligomeric cyclic model, where 1H-3H proton transfer with one stage occurs.

Keywords: Proton transfer, cyclic-pentameric mechanism, imidazole, DFT calculations.

Introduction

1H-3H proton transfer in imidazole is one of the basic stages of chemical and biochemical reactions. Collective mechanisms of this process that contain imidazole trimers were proposed in the Zimmerman’s work. However, the existence of the linear oligomeric structure of imidazole seems to be unlikely because the IR spectra have no absorption bands of the NH group, which must be present in this structure. In works Ten G. et. al., intra- and intermolecular mechanisms of 1H-3H proton transfer in imidazole are discussed. With using of the quantum-chemical and spectrometric methods, it was demonstrated that the intramolecular 1H-3H proton transfer is energetically less advantageous. A two-dimensional nitrogen-15 exchange NMR study of 15N-labeled imidazole demonstrates that the conduction mechanism does not involve the reorientation of the imidazole ring invoked in current models. Self-association in imidazole and methylimidazole was also studied by the spectrometric method and dimerization and polymerization tendencies were noted.

The intramolecular one-stage 1H-3H proton transfer is structurally complicated and therefore a cyclic-trimer model for 4-fluorine-imidazole was built. The opinion about existence of a cyclic-dimer mechanism was also expressed in our work. Mangiatordi et al. observed the 1H-3H proton transfer in protonated imidazole using the quantum-chemical method studied, however, this proposed modeling cannot lead to a stable structure of 3H-imidazole. Iannuzzi and Parrinello (11) studied proton transfer in crystalline polymer chains of imidazole and notes the ionic nature of this process. Kurzepa et al. studied energy characteristics of tautomeric forms of 5-substituted imidazole by spectrometric and quantum-chemical methods. It was shown that COOH and BH groups stabilize the N3H tautomer, whereas stabilization of the N3H tautomer by F and O groups is not so intensive. This latter conclusion is not consistent with the notion that NH2 and NO2 are strong electron donors and electron acceptors, respectively. Quantum-chemical (DFT) calculations were made for different imidazole tautomers and was pointed out that 1H-imidazole is more stable than non-aromatic tautomer. However, this stability changes completely when hydrogen atom is substituted by O or F groups, for example, the stability of 1-F-1H-imidazole< 2-F-2H imidazole.

Results and Discussion

The purpose of the proposed research is to build a nonionic oligomeric model of imidazole where 1H-3H proton transfer can occur without substantial energy losses. In our opinion this model represents the cycle of five molecules imidazole, along which 1H-3H proton transfer may be realized (figure-1).

The activation energy (ΔE*) and reaction energy (ΔE) of the proton transfer in the cyclic-pentamer model of the five imidazole derivatives as well as the bond orders (P_{N...H}) and (P_{N...i}) by means of modern quantum-chemical method-Density Function Theory (DFT) are calculated.

The calculations are executed using the software “Nature” in the reaction coordinate regime using the PBE approximation and its modification mPBE. In addition, for comparison the functional BLYP and local density approximations were used. The results of calculation are given in table-1.
The activation energy (ΔE*) and reaction energy (ΔE) of the proton transfer in the cyclic-pentamer model of the five imidazole derivatives as well as the bond orders (P_{NH}) and (P_{N...H}) by means of modern quantum-chemical method - Density Function Theory (DFT) are calculated. The calculations are executed using the software “Nature” in the reaction coordinate regime using the PBE approximation and its modification mPBE. In addition, for comparison the functional BLYP and local density approximations were used. The results of calculation are given in table-1.

### Table - 1

<table>
<thead>
<tr>
<th>R</th>
<th>ΔE* kJ/mol</th>
<th>ΔE kJ/mol</th>
<th>P_{NH}</th>
<th>P_{N...H}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂</td>
<td>26.2</td>
<td>-8.60</td>
<td>0.96</td>
<td>0.30</td>
</tr>
<tr>
<td>H</td>
<td>30.1</td>
<td>0.05</td>
<td>0.67</td>
<td>0.33</td>
</tr>
<tr>
<td>NO₂</td>
<td>10.1</td>
<td>-36.70</td>
<td>0.64</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Amino- and nitro-groups were chosen as donor and acceptor of electrons of substitutes that have influence on the bond orders (P_{NH}) and (P_{N...H}). The analysis of the table shows that 1H-3H proton transfer in the amino- and nitro-derivatives is an exothermic process and is energetically more advantageous for the nitro-derivatives. Besides, the the nitro-group causes a relaxation the N-H bond and hence promotes a proton transfer over cycle. For the amino-group the opposite effect is observed, as it the electronodonore group increases the NH bond order. On Figure1, a diagram of the 1H-3H proton transfer energy in unsubstituted imidazole is given as an example.

### Conclusion

As a result of calculations it can be concluded that the activation energy (ΔE*) and reaction energy (ΔE), for the proton transfer in the cyclic-pentamer model of imidazol derivatives as well as bond orders (P_{NH}) vary in rather reasonable limits for chemical processes, which indicates favour of the proposed cyclic-
pentamer mechanism.

This is a non-ionic oligomeric cycle of five molecules imidazole in which 1H-3H proton transfer is carried out in one step.

Acknowledgment

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References