



Short Communication

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

Kereselidze J^{1*}, Kvaraia M² and Mikuchadze G¹

^{1*}Department of Chemistry, Ivane Javachishvili Tbilisi State University, 0179, GEORGIA

²Department of Chemistry, Sukhumi State University, 0186, GEORGIA

Available online at: www.isca.in, www.isca.me

Received 3rd March 2015, revised 9th April 2015, accepted 17th April 2015

Abstract

About of the cyclic-pentameric model for the 1H-3H proton transfer in the imidazole derivatives is reported. The activation energy (ΔE^\ddagger) and reaction energy (ΔE) of the proton transfer as well as the bond orders (P_{NH}) and ($P_{N...H}$) by means of Density Function Theory (DFT) are calculated. It is shown that proton transfer is energetically more advantageous in nitroimidazole. The values ΔE^\ddagger , 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 work¹. However, the existence of the linear oligomeric structure of imidazole seems to be unlikely because the IR spectra have no absorption bands of the N⁺H group, which must be present in this structure². In works Ten G. et. al^{2,3}, 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^{4,5}. 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 models⁶. Self-association in imidazole and methylimidazole was also studied by the spectrometric method and dimerization and polymerization tendencies were noted⁷.

The intramolecular one-stage 1H-3H proton transfer is structurally complicated and therefore a cyclic-trimer model for 4-fluorine-imidazole was built⁸. The opinion about existence of a cyclic-dimer mechanism was also expressed in our work⁹. Mangiatordi et al.¹⁰ 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.¹² studied energy characteristics of tautomeric forms of 5-substituted

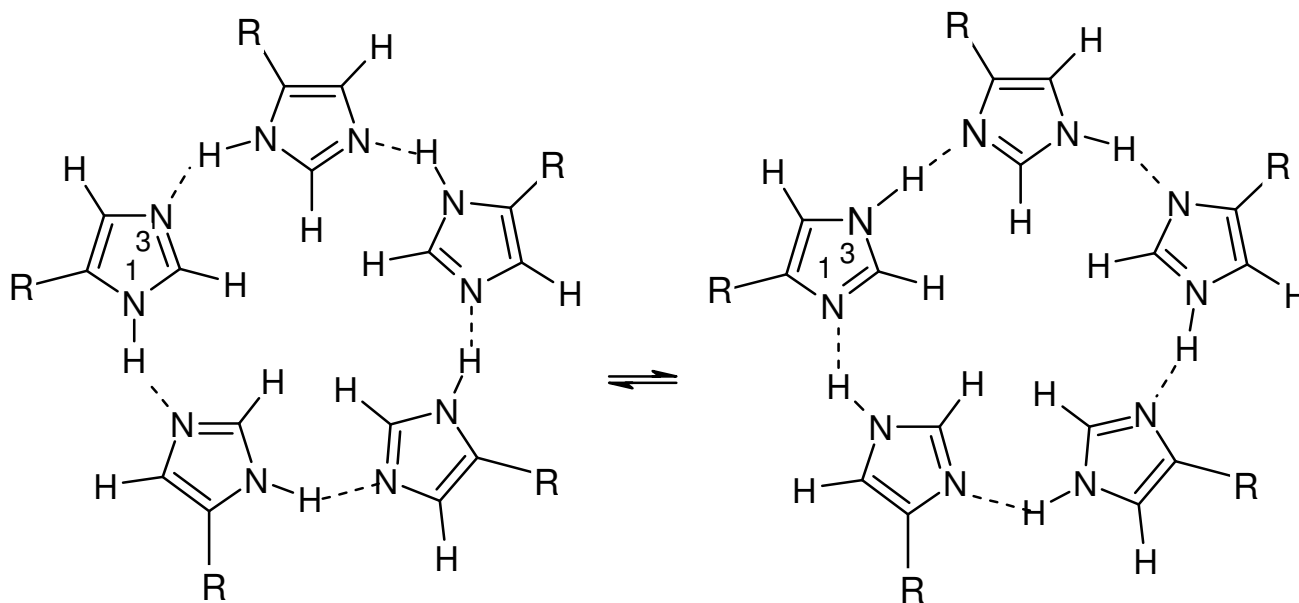
imidazole by spectrometric and quantum-chemical methods. It was shown that COOH and BH₂ groups stabilize the N₁H tautomer, whereas stabilization of the N₃H tautomer by F and O groups is not so intensive. This latter conclusion is not consistent with the notion that NH₂ and NO₂ are strong electron donors 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 tautomer¹³. 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^\ddagger) 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)¹⁴ are calculated.

The calculations are executed using the software "Nature" in the reaction coordinate regime¹⁵ using the PBE approximation and its modification mPBE^{16,17}. In addition, for comparison the functional BLYP and local density approximations were used¹⁸⁻²⁰. The results of calculation are given in table-1.



R = H, NH₂, NO₂.

Figure-2
 Cyclic-pentameric model of the 1H-3H proton transfer in imidazole

The activation energy (ΔE^\ddagger) 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 ($P_{N\dots H}$) by means of modern quantum-chemical method - Density Function Theory (DFT)¹⁴ are calculated. The calculations are executed using the software "Nature" in the reaction coordinate regime¹⁵ using the PBE approximation and its modification mPBE^{16,17}. In addition, for comparison the functional BLYP and local density approximations were used¹⁸⁻²⁰. The results of calculation are given in table-1.

Table - 1
 Energy of activation (ΔE^\ddagger), energy of reaction (ΔE) and bond orders (P_{N-H} , $P_{N\dots H}$)

R	ΔE^\ddagger , kJ/mol	ΔE , kJ/mol	P_{N-H}	$P_{N\dots H}$
NH ₂	26.2	-8.60	0.96	0.30
H	30.1	0.05	0.67	0.33
NO ₂	10.1	-36.70	0.64	0.31

Amino- and nitro-groups were chosen as donor and acceptor of electrons of substitutes that have influence on the bond orders (P_{NH}) and ($P_{N\dots H}$). 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 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 electron-donator group increases the NH bond order. On Figure 1, a diagram of the 1H-3H proton transfer energy in unsubstituted imidazole is given as an example.

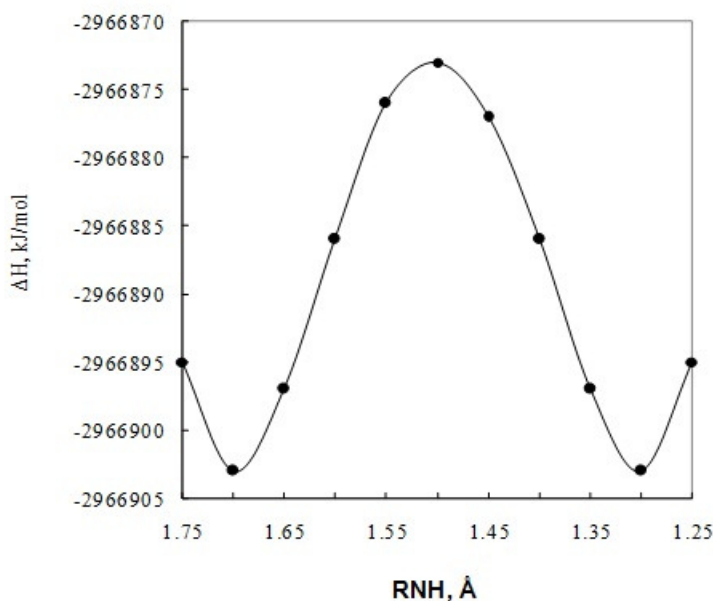


Figure-3
 Dependency of energy of the 1H-3H proton transfer on the reaction coordinate for unsubstituted imidazole

Conclusion

As a result of calculations it can be concluded that the activation energy (ΔE^\ddagger) and reaction energy (ΔE), for the proton transfer in the cyclic-pentamer model of imidazole 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

The project has been supported by European Commission FP7 Project, High-Performance Computing Infrastructure for South East Europe's Research Communities", Grant No: 261 499.

References

1. Zimmermann H., Proton Transfer, Acid-Base Catalysis, *Z. Electrochim.*, **65**, 821-840 (1961)
2. Ten G., Burova T. and Baranov V., On the Mechanism of proton Transfer in Imidazole, *J. Struct. Chem.*, **48**, 623-633 (2007)
3. Nesmeyanov A, Zavelovich E, Babin V., Kochetkova S. and Fedin E, ¹H and ¹³C NMR Study of tautomerism in azoles, *Tetrahedron*, **31**, 1461-1464 (1975)
4. Borisov Yu., Vorob'eva N., Abronin I. and Kolomiets A, On the mechanism of proton transfer imidazole, *Izv. Akad. Nauk, Ser. Chim.*, 2779-2783 (1988)
5. Fedorov L., Saverino A., Viskardi G., Rebrov A. and Barni E., ¹³C NMR Spectroscopy of Tautomeric Conversions in Imidazole Compounds, *Izv. Akad. Nauk, Ser. Khim.*, **2**, 299-308 (1992)
6. Hickman B., Mascal M., Titman J. and Wood I., Protonic Conduction in Imidazole: A Solid - State ¹⁵N NMR Study, *J. Am. Chem. Soc.*, **121**, 11486-11490 (1999)
7. Peral F. and Gallego E., Self-association of imidazole and its methyl derivatives in aqueous solution A study by ultraviolet spectroscopy, *J. Mol. Struct.*, **415**, 187-196 (1997)
8. Kikalishvili T. and Kereselidze J., Trimeric Mechanism of proton transfer in Imidazole, *Chem. Heter. Comp.*, **38**, 1069-1071 (2002)
9. Alkorta I., Goya P., Elguero J. and Singh Sh.A, Simple Approach to the Tautomerism of Aromatic Heterocycles, *Proceed. Natl. Acad. Sci. Lett.*, **30**, 139-159 (2007)
10. Iannuzzi M. and Parrinelo M., Proton Transfer in Heterocycle Crystals, *Phys. Rev. Lett.*, **93**, 025901-025904 (2004)
11. Iannuzzi M., Proton Transfer in imidazole-based molecular Crystals, *J. Chem. Phys.*, **124**, 204710-204717 (2006)
12. Nagata N., Kugimiya Sh. and Kobuke Y., Antenna functions of 5.15-bis (imidazol-4-yl)-10.20-bis (4-dodecyloxyphenyl)-porphyrin supramolecular assembly through imidazole-imidazole hydrogen bonding, *Chem. Commun.*, **15**, 1389-1390 (2000)
13. Zundel G. and Muehlinghaus J, Symmetry of hydrogen Bonds, Infrared Continuous Absorption and proton transfer, *Z. Naturforsch., Chem. Sc.*, **26b**, 546 (1971)
14. Kohn W., Becke A. and Parr R., Density Functional Theory of Electronic structure, *J. Phys. Chem.*, **100**, 12974 - 12980 (1996)
15. Laikov D., Ustynyuk Yu. and Priroda O4, A quantumchemical program suite, New possibilities in the study of molecular systems with the application of parallel computing, *Russ. Chem. Bull., Int. Edn.*, **54**, 820-826 (2005)
16. Perdew J., Burke K. and Ernzerhof M., Generalized Gradient Approximation Made simple, *Phys. Rev. Lett.*, **77**, 3865-3868 (1996)
17. Adamo C. and Barone V., Physically motivated density functional with improved performances, *J. Chem. Phys.*, **116**, 5933-5940 (2002)
18. Becke A, Density functional exchange: Energy approximation with correct asymptotic behavior, *Phys. Rev. A*, **38**, 3098-3100 (1988)
19. Lee C., Yang W. and Parr R., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, **37**, 785-789 (1988)
20. Perdew J. and Wang Y., Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B*, **45**, 13244-13249 (1992)