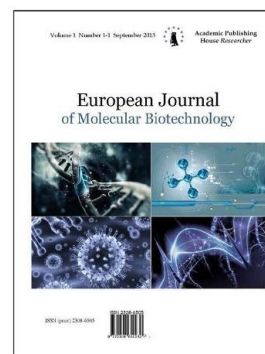


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Published in the Slovak Republic
 European Journal of Molecular Biotechnology
 Has been issued since 2013.
 E-ISSN: 2409-1332
 2018, 6(1): 16-24

DOI: 10.13187/ejmb.2018.1.16
www.ejournal8.com



The Contribution to Bonding by Lone Pairs in the Hydrogen Transfer of Adenine Tautomerization ($3H \rightarrow 9H$) in the First Excited Electronic State: ELF Analysis

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Abstract

The hydrogen transfer of adenine tautomerization ($3H \rightarrow 9H$) is performed by using ELF topological analysis, this study has been carried out at TD-DFT method with B3LYP and 6-311G++(d,p) basis set. Our investigation leads us to conclude that lone pairs electrons of nucleophilic nitrogen atom are not a non bonding electrons, although the lone pairs may contribute to the covalently bond with an electrophile (H atom) behind TS (second phase), whereas excited electrons are highly contributed to the first phase before TS location, the contribution to bonding by lone pairs is depending generally on the evolution of chemical structure along IRC. Therefore, lone pairs electron are considerably helped for hydrogen transfer of adenine tautomerization in the first electronic state. Subsequently, lone pairs and non bonding electrons are not strictly equivalent to each other.

Keywords: Adenine tautomers; H-transfer; Electronic state; ELF; Lone pairs; TD-DFT.

1. Introduction

The tautomerization reaction constitutes a very successful example of photochemistry reaction (Nir et al., 2001), this process received considerable attention, since thermal energy may easily transform one conformer to another, a number of lower energy conformer may coexist in same time. In addition, hydrogen transfer reaction is considered to be a first step in the mutation of DNA (Salter, Chaban, 2002). Interestingly, the contribution of lone pairs or non-bonding electrons in the reactivity between the reagents through participating in the covalent bond and others chemical bonding is a very significant subject, lone pairs entre the description of Lewis structure for simple and complex molecules to give explanation of the bonding interaction, bonding evolution is one of the most attractive topics of experimental and theoretical chemist (Berski et al., 2006; Benallou et al., 2018); where bonds are placed, how bonded type interaction and where lone pairs are located. For this instance, lone pairs are an essential element of the valence shell electron repulsion theory (Gillespie, 1972; Gillespie et al., 1991). The role of the lone pair in the molecular interaction between charged, radicals and ionic molecules are in very important interest. The contribution of lone pairs to the chemical bonding is fundamental to our work. In this sense, hydrogen bonded complexes exist as single species because of the stabilizing interaction between a donor lone pair (O, N...) and acceptor hydrogen on the other.

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In our classical example to evaluating the role of lone pairs in the chemical bonding, we have reported the tautomerization reaction of adenine, H-proton transfer of the most stable and favorable monomer (3H-adenine) to the unstable monomer (9H-adenine), in gas phase situation, of the lowest excited state is evaluated.

Adenine an important product that represents a base in DNA and RNA, thus the role of hydrogen cyanide (HCN) in the prebiotic formation of adenine is taken a significant interest of by the experimental and theoretical chemists (Alfredsson et al., 1996; Heikkil, Lundell, 2000; Moser et al., 1976; Benallou, 2017; Wentrup et al., 1987; Evans et al., 1991; Jobst et al., 2008), Adenine is a molecule that in a quite abundant under primitive conditions in the universe and the early Earth, 5 HCN molecules in the primitive conditions, we can reproduce adenine as below, however this process is highly energetic (Benallou, 2016; Benallou, 2017).

$\text{HCN} + \text{HCN} \rightarrow \text{H}_2\text{C}_2\text{N}_2(\text{dimer}) + \text{HCN} \rightarrow \text{H}_3\text{C}_3\text{N}_3(\text{trimer}) + \text{HCN} \rightarrow \text{H}_4\text{C}_4\text{H}_4(\text{tetramer}) + \text{HCN} \rightarrow \text{H}_5\text{C}_5\text{N}_5(\text{adenine}).$

For that reason, quantum chemical studies of chemical reactions usually are restricted for determination of structures of reactants and transition state, very little attention is paid to the analysis of chemical bonds which are important during the chemical reaction. Lone pair in general do not enter directly into the atoms in molecules (AIM) theory (Bader, 1994), while, electron localization function (ELF) (Fuster, Silvi, 2000) theory takes into account the basin where electron pairs tend to exist, considering the bonding situation, to elaboration of the bonding evolution theory (BET) which merges the ELF.

In order to evaluate the contribution to bonding by lone pairs, the mechanism of H-transfer in the adenine tautomers is completely analysed from a point of view of the bonding evolution theory, we focus on a comparison of results achieved using the ELF analysis, then a characterization of the electron density redistribution following the hydrogen transfer along IRC is realized, finally a determination of lone pair or non-bonding electron contribution in the formation of N9-H and N3-H bonds. Note that this work will be performed in the first excited electronic state in which 3H adenine monomer is more stable to that of 9H adenine.

2. Computational methods

The geometry optimizations of such critical points were performed using the density functional formalism with the TD-DFT method and B3LYP exchange-correlation energy functional (Becke, 1993; Lee et al., 1988). All the calculations were realized with GAUSSIAN G09 program package (Frisch et al., 2009) and visualization of the output files is performed using the Gauss-View 5.0.8 software. The surface mapping was determined using a 6-311G** basis set level and the critical points (minima and transition states) were optimized and checked by calculating the intrinsic reaction coordinates (IRCs) with this basis set. All energies have been corrected for zero-point energy (ZPE) contributions calculated at the same level. For the BET analysis a reaction path was taken from an IRC calculation in mass-weighted Cartesian coordinates, the electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method (Reed et al., 1988) and by ELF topological analysis. The ELF study was carried out with the Multiwfn program (Tian, Feiwu, 2012) using the corresponding mono determinant wave functions of the selected structures.

3. Results and discussion

The relative stability and abundance of adenine monomers are mostly studied in latter decade. 9H-adenine is well known more stable and has the lowest energy in the gas phase to compare with the other conformers such as 3H-, 7H-, and 1H-adenine of ground state situation. However, in the first excited electron 3H-adenine is relatively more stable and not much high in energy (Nowak et al., 1996). It is worthy to note that all adenine conformers have been found to coexist (Laxer et al., 2001; Chenon et al., 1975). So, hydrogen atom-transfer in the 3H, and 9H conformer, where the lone pairs are probably will contribute to covalent and other chemical bonds of hydrogen atom transfer in the first electronic state will be detailed step by step in this section.

3.1. Chemical structure of adenine tautomerization in the lowest electronic state

In the literature (Chenon et al., 1975), 3H-adenine is most stable to compare with 9H-adenine in the lowest excited electronic state. So, in order to investigate the transition state and reactants, we report all stationary points integrated into the tautomerization of adenine, lowest

electronic state is taken into consideration in this study, furthermore, TD-DFT method with 6-311++G(d,p) basis set are performed, and thus, the schematic pictures of adenine tautomerization (3H→9H) in the lowest electronic state is depicted in Figure 1.

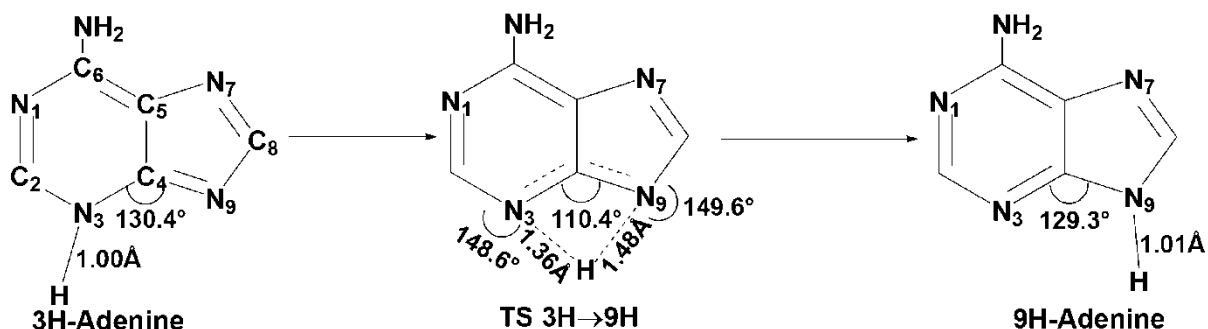


Fig.1. H-transfer of adenine tautomerization (3H→9H), in the lowest electronic state

The chemical structure of hydrogen atom transfer (3→9 tautomerization) for the first electronic state is analyzed, the results show that TS-structure is bent with two rings forming an angle of about 148.6° and 149.6° for C2N3Ha and C8N9Ha sequences respectively. Another observation is taken of this tautomerization reaction such as Ha atom transfer is somewhat closer to N3 instead of N9, 1.36Å. Whereas H-proton is almost positioned identically to both tautomers, 1.00Å for the N3-Ha bond and 1.01Å for the N9-Ha bond of 3H and 9H conformers of adenine respectively. However, this mechanism process is moderately energetic (Kim et al., 2007).

3.2. ELF bonding analysis of the IRC path of hydrogen atom transfer (3H→9H)

In this section, we will estimate the contribution of lone pairs electron to bonding in the hydrogen transfer, to this end, a characterization of the distribution of electronic density along the progress of the reaction is in very significant importance. For this purpose, an ELF analysis along IRC of the H-transfer will be performed. The electronic populations of the most relevant ELF valence basins of selected structures (points) along IRC are listed in Table 1, while the attractor positions for the most relevant points associated with the formation and breaking of the N3-Ha and N9-Ha bonds, are shown in Figure 2.

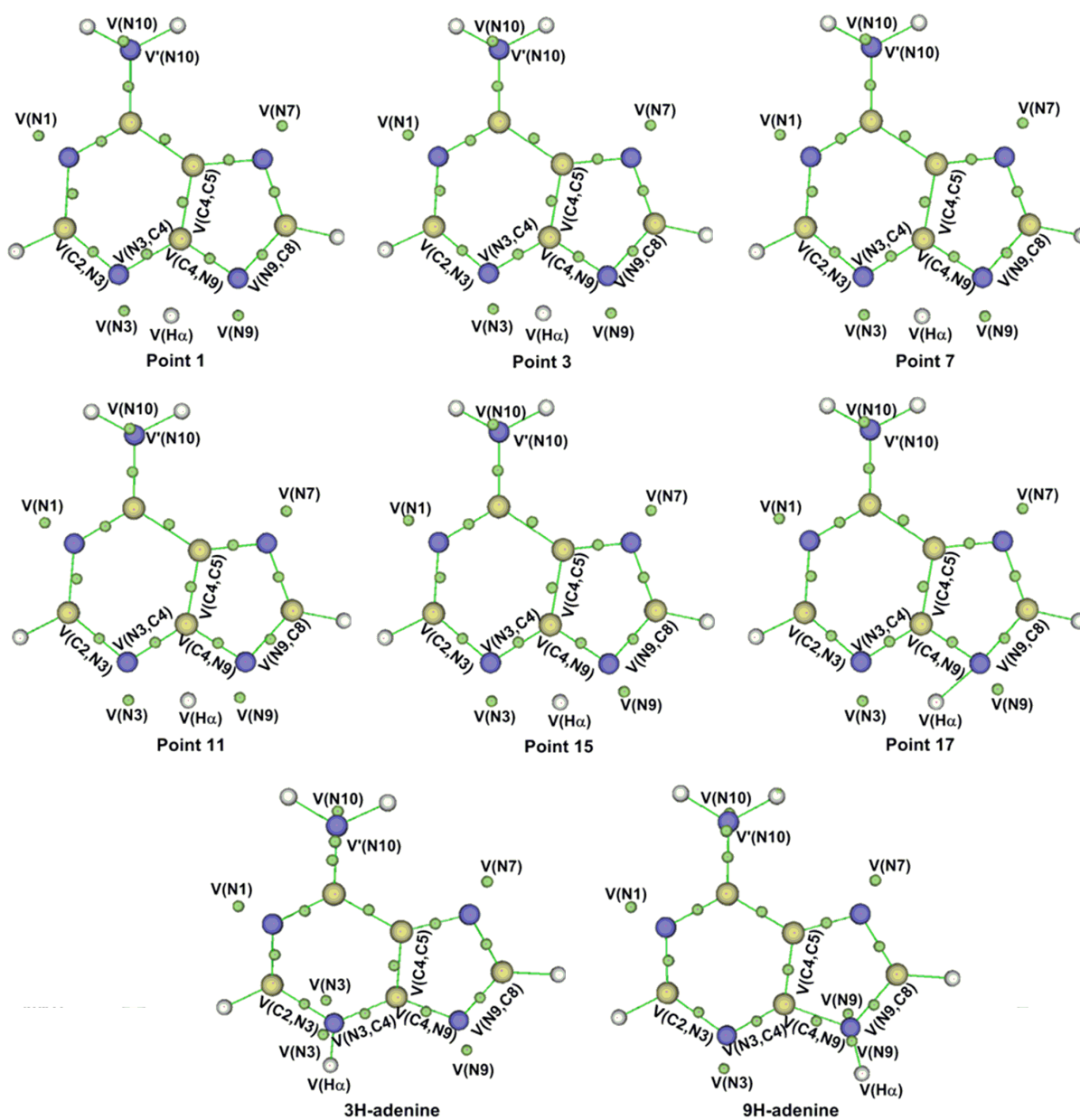


Fig.2. ELF attractors of some selected points of the IRC associated with the hydrogen transfer of adenine tautomerization ($3\text{H} \rightarrow 9\text{H}$)

Table 1. Valence basin populations of the hydrogen transfer calculated from the ELF of adenine tautomerization, associated with the $\text{N}_3\text{-H}_\alpha$ and $\text{N}_9\text{-H}_\alpha$ bonds formation/breaking step. Electron density in e (NBO) and bond distances in angstrom (\AA)

| Points | 3H | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 | P11 (TS) |
|---------------------------------|---------------|------|------|------|------|------|------|------|------|------|------|----------|
| $d(\text{N}_3\text{-H}_\alpha)$ | 1.00 | 1.34 | 1.36 | 1.37 | 1.39 | 1.40 | 1.41 | 1.42 | 1.43 | 1.44 | 1.44 | 1.45 |
| $d(\text{N}_9\text{-H}_\alpha)$ | 2.75 | 1.49 | 1.48 | 1.46 | 1.45 | 1.43 | 1.42 | 1.40 | 1.39 | 1.37 | 1.37 | 1.36 |
| V(N1) | 2.77 | 2.88 | 2.87 | 2.86 | 2.85 | 2.83 | 2.80 | 2.79 | 2.76 | 2.75 | 2.75 | 2.75 |
| V(N3) | 0.56/ 0.56 | 2.87 | 2.90 | 2.93 | 2.86 | 2.98 | 3.02 | 3.04 | 3.06 | 3.08 | 3.09 | 3.09 |
| V(N7) | 3.00 | 2.95 | 2.94 | 2.94 | 2.95 | 2.95 | 2.95 | 2.94 | 2.95 | 2.95 | 2.95 | 2.95 |
| V(N9) | 2.96 | 3.10 | 3.10 | 3.09 | 3.08 | 3.07 | 3.06 | 3.05 | 3.04 | 3.02 | 3.02 | 3.02 |
| V(N10) | 0.89 | 1.46 | 1.47 | 1.48 | 1.49 | 1.50 | 1.50 | 1.50 | 1.50 | 1.52 | 1.52 | 1.52 |
| V'(N10) | 2.12 | 2.11 | 2.12 | 2.11 | 2.12 | 2.11 | 2.12 | 2.12 | 2.11 | 2.11 | 2.12 | 2.12 |
| V(C2,N3) | 2.16 | 2.32 | 2.28 | 2.26 | 2.24 | 2.20 | 2.17 | 2.13 | 2.11 | 2.06 | 2.06 | 2.06 |

| | | | | | | | | | | | | |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|
| V(N3,C4) | 2.21 | 2.14 | 2.16 | 2.17 | 2.18 | 2.20 | 2.24 | 2.25 | 2.25 | 2.27 | 2.27 | 2.28 |
| V(C4,N9) | 2.42 | 2.20 | 2.18 | 2.18 | 2.17 | 2.16 | 2.15 | 2.13 | 2.11 | 2.10 | 2.10 | 2.09 |
| V(N9,C8) | 2.34 | 2.09 | 2.09 | 2.10 | 2.10 | 2.11 | 2.13 | 2.13 | 2.15 | 2.17 | 2.18 | 2.18 |
| V(C4,C5) | 2.73 | 2.95 | 2.95 | 2.95 | 2.95 | 2.95 | 2.94 | 2.94 | 2.94 | 2.94 | 2.94 | 2.94 |
| V(H α) | 2.09 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 |

Table 1 (next).

| Points | P12 | P13 | P14 | P15 | P16 | P17 | P18 | P19 | P20 | P21 | 9H |
|-------------------|-----------|-----------|------|------|------|------|------|------|------|------|-----------|
| d(N3-H α) | 1.48 | 1.51 | 1.55 | 1.59 | 1.63 | 1.67 | 1.72 | 1.77 | 1.81 | 1.86 | 2.78 |
| d(N9-H α) | 1.33 | 1.30 | 1.27 | 1.23 | 1.20 | 1.16 | 1.13 | 1.10 | 1.08 | 1.06 | 1.01 |
| V(N1) | 2.77 | 2.77 | 2.78 | 2.79 | 2.80 | 2.82 | 2.82 | 2.83 | 2.83 | 2.84 | 2.79 |
| V(N3) | 3.07 | 3.07 | 3.06 | 3.05 | 3.04 | 3.02 | 3.01 | 3.00 | 2.99 | 2.98 | 2.95 |
| V(N7) | 2.94 | 2.93 | 2.92 | 2.95 | 2.92 | 2.90 | 2.90 | 2.89 | 2.88 | 2.87 | 2.94 |
| V(N9) | 1.48/1.50 | 1.32/1.57 | 1.58 | 1.59 | 1.59 | 1.59 | 1.58 | 1.57 | 1.57 | 1.56 | 0.63/0.63 |
| V(N10) | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 | 1.52 | 1.52 | 1.52 | 1.52 | 0.93 |
| V'(N10) | 2.13 | 2.12 | 2.13 | 2.13 | 2.11 | 2.12 | 2.12 | 2.12 | 2.12 | 2.12 | 2.12 |
| V(C2,N3) | 2.09 | 2.16 | 2.20 | 2.24 | 2.28 | 2.32 | 2.94 | 2.36 | 2.38 | 2.40 | 2.21 |
| V(N3,C4) | 2.28 | 2.28 | 2.28 | 2.28 | 2.28 | 2.28 | 2.27 | 2.27 | 2.26 | 2.26 | 2.50 |
| V(C4,N9) | 2.10 | 2.10 | 2.09 | 2.07 | 2.08 | 2.05 | 2.05 | 2.05 | 2.05 | 2.05 | 2.16 |
| V(N9,C8) | 2.14 | 2.13 | 2.12 | 2.11 | 2.10 | 2.09 | 2.08 | 2.07 | 2.06 | 2.05 | 2.12 |
| V(C4,C5) | 2.94 | 2.94 | 2.95 | 2.97 | 2.97 | 2.97 | 2.97 | 2.97 | 2.98 | 2.98 | 2.84 |
| V(H α) | 0.54 | 0.58 | 1.94 | 1.94 | 1.95 | 1.95 | 1.96 | 1.97 | 1.98 | 1.99 | 2.07 |

The results noted in [Table 1](#) reveal that the most important changes of electron density are contributed exclusively to the lone pairs of the N3, N9 and H α atom, these atoms are directly integrated into the hydrogen atom transfer of adenine tautomerization in the lowest excited state. However, the remaining attractors are not having more changes along IRC. So, in this case, we will focus especially on the basins relative to the V(N3), V(N9) and V(H α) attractors. To this end, the electronic population associated with the basins of lone pairs and hydrogen atom transfer will be summarized, the results are given in [Figure 3](#).

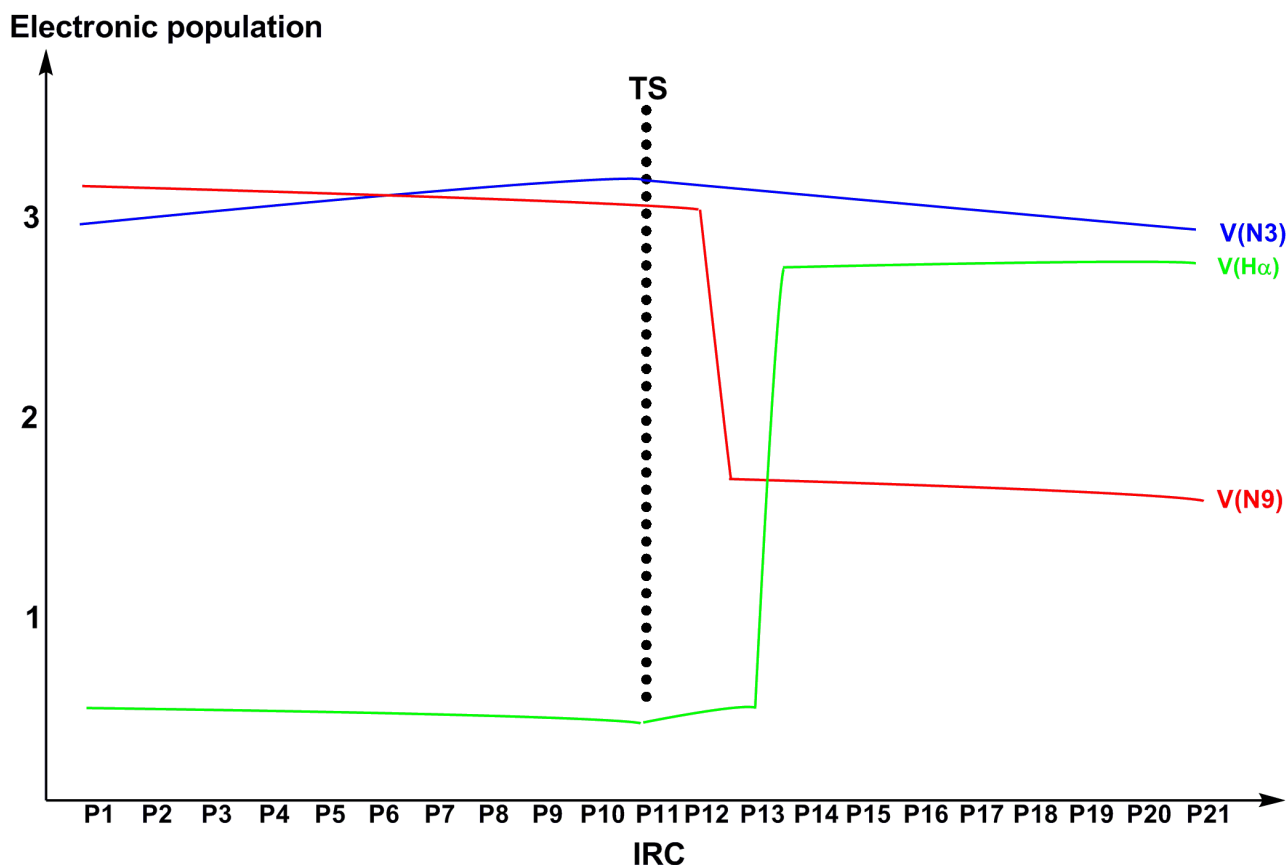


Fig.3. Electronic population in (e) along IRC of hydrogen transfer of the most significant atoms involved in the adenine tautomerization in the lowest electronic state

Showing the results given in Fig.3, we can separate the change of electron density of such attractor's ($V(N_3)$, $V(N_9)$ and $V(H_\alpha)$) along IRC into two important phases:

First phase: is located between point 1 and TS. In this phase the electronic population of lone pairs N_3 and N_9 does not have more changes, the variation of electron density of both monosynaptic basin $V(N_3)$ and $V(N_9)$ relative to the lone pairs is generally stable along IRC. So, no contribution of lone pairs electron towards hydrogen atom can be stated. For this instance, the electronic population of the monosynaptic basin $V(H_\alpha)$ related to the hydrogen atom has not increased or decreased along IRC, this result is quite consistent with that found for $V(N_3)$ and $V(N_9)$ basins. Therefore, the contribution to bonding by lone pairs electron in the hydrogen transfer in the first phase is practically negligible; we suppose that lone pair of N_3 atom is contributed to bonding in the hydrogen atom transfer, the electron density of such atom should increase along IRC, as long as N_3 and H_α bond is broken at TS. So the electronic population of lone pairs of N_3 must take a maximum value and that is never likely going to take place. Subsequently, taking into account the main role of valence shell electrons in the chemical bonding to compare with core electrons, furthermore H_α atom is very distant to N_3 atom along this first phase (N_3 - H_α bond distances). Therefore, the excited electrons are evidently assisted by participating in the bonding of hydrogen atom transfer of adenine tautomerization.

Second phase; In this phase (TS to Points 21) the situation is completely different to that of the first phase, while H_α atom becomes very distant to N_3 and closer to N_9 , N_3 - H_α bond is broken, at this point a new N_9 - H_α bond is begun to form, the electronic population of the monosynaptic basin of each attractor of lone pairs and hydrogen atom has been modified, principally to the N_9 and H_α atom, whereas $V(N_3)$ basin is not varied. We have remarked the presence of a pseudo-horizontal symmetry axis between $V(N_9)$ and $V(H_\alpha)$ basins, as far as the electronic population related to the monosynaptic basin $V(H_\alpha)$ increases we have stated a decreases of $V(N_9)$ basin along the second phase of IRC (P11→P21). Therefore, the contribution to bonding by lone pairs of hydrogen atom transfer in the lowest excited electronic state is principal behind TS, in which N_9 - H_α covalently bond is formed.

Consequently, in the hydrogen atom transfer of adenine tautomerization in the lowest electronic state, two phases characterize the contribution to bonding by lone pairs; first phase (in the beginning of the reaction until TS; N3-H α covalently bond), the contribution to bonding by lone pairs is negligible, and then the excited electrons play a significant role of hydrogen transfer by assisting to afford the necessary energy to breaking N3-H α bond. However, in the second phase (TS until the formation of the N9-H α bond), herein the contribution to bonding by lone pairs is more considerable, such as a very important part of electron density related to the N9 lone pair shifts regularly to the H α atom to form the covalent bond of N9-H α .

Subsequently, the lone pairs are not a non-bonding electron, but they are very useful for some system reactions. Lone pairs play a key in the hydrogen transfer by contributing to the covalently bond especially in the second phase behind TS between a good nucleophile (N9) and a hydrogen atom H α (electrophile), while in the first phase the excited electrons are probably integrated into the transfer of hydrogen atom. A schematic picture of the lone pair contribution to the bonding is given in figure 4, while a representation of some significant point is depicted in figure 5.

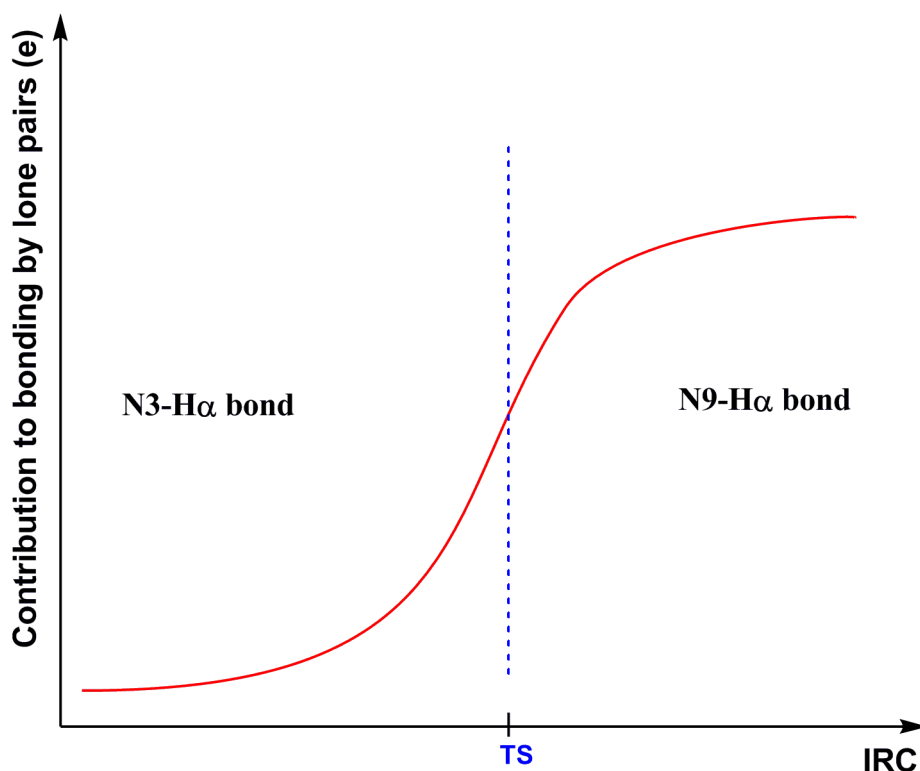


Fig. 4. Contribution to bonding by lone pairs of H-transfer (adenine tautomerization) along IRC

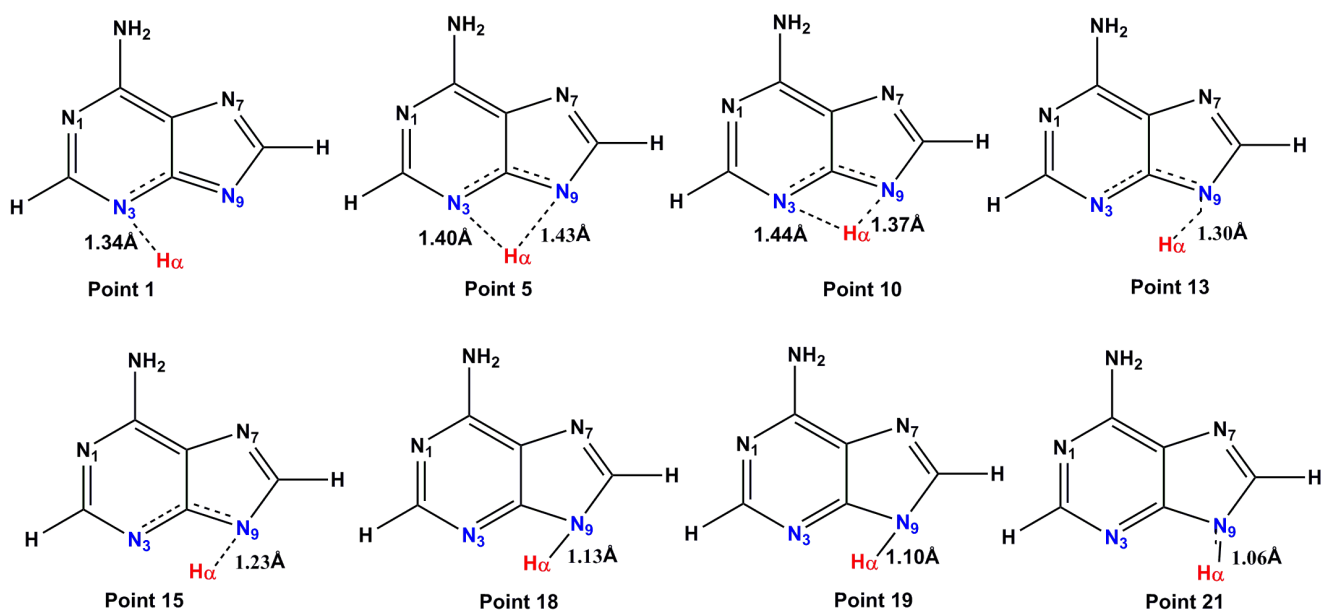


Fig. 5. Some significant points involved in the hydrogen transfer of adenine tautomerization. In brief, the contribution to bonding by lone pairs is depending generally on the evolution of chemical structure along IRC and the relative stability of each tautomers of adenine

4. Conclusion

ELF analysis of adenine tautomerization (H-transfer, $3\text{H} \rightarrow 9\text{H}$) is performed in lowest electronic state at B3LYP and 6-311++G(d,p) basis set level. Two phases describe the contribution to bonding by lone pairs in the hydrogen transfer; the first phase (the beginning of reaction until TS along IRC), which H atom is closer to the N3 atom (N3-H α covalently bond), the contribution of lone pairs is trivial, for this instance, 3H adenine conformer is very stable at the first electronic state, and then the excited electrons have been probably helped for the hydrogen atom transfer. However, in the second phase, the N3-H α is broken while a new bond of N9-H α is formed (behind TS), the contribution of lone pairs is very important. Subsequently, the contribution to bonding by lone pairs is depending generally on the evolution of chemical structure along IRC and the relative stability of each adenine tautomers. So, lone pairs are not non-bonding electrons but are playing a very considerable role in the formation of chemical bonding.

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