



# Computation of polarizability, hyper-polarizability and hardness as descriptor for enol–keto tautomerizations of 2-hydroxy pyridines



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## ABSTRACTS

Density functional theory (DFT) based calculations on a series of intra-molecular proton-transfer reactions e.g. 2-hydroxy pyridine (2HP), 5-methyl-2-hydroxy pyridine (5Me2HP) and 5-fluoro-2-hydroxy pyridine (5F2HP) are performed to understand the variation of the quantum chemical reactivity parameters e.g. polarizability, hardness, ionization potential along the proton transfer co-ordinate. Variations in optical gap and first hyper-polarizability which are measures of non-linear optical parameters are also computed along the proton transfer co-ordinate of the species. The average polarizability ( $\alpha_{av}$ ), first hyper-polarizability ( $\beta$ ), chemical hardness ( $\eta$ ), ionization potential (I.P) and optical gap ( $\Delta E$ ) show their optimum value at the same IRC point which corresponds to the transition state (TS) for all the three titled intra-molecular proton transfer systems. The maximum polarizability and minimum chemical hardness at the transition state (TS) are due to greater extents of charge transfer which arise from smaller optical gap.

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## 1. Introduction

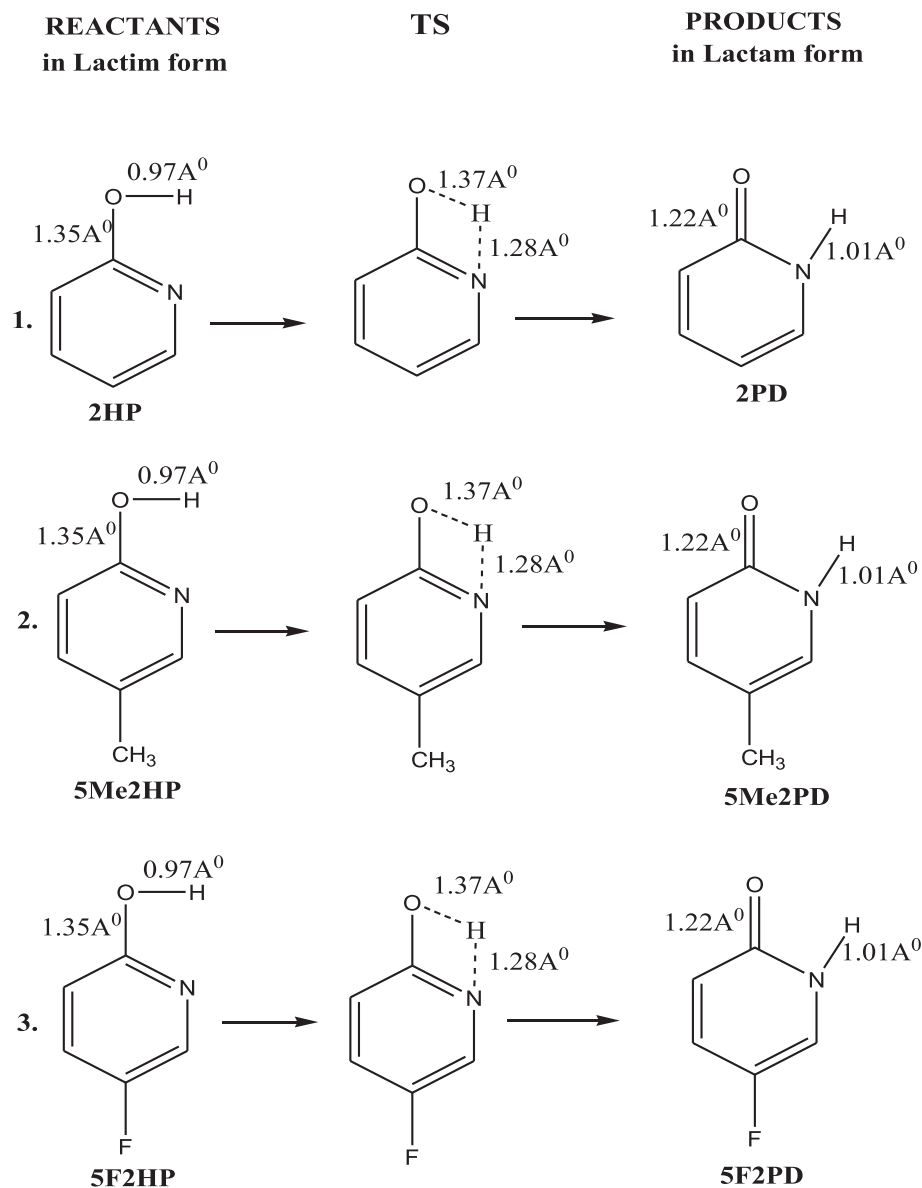
The keto–enol tautomeric equilibrium is one of the most important processes in chemical and biological system where proton transfers occurs [1]. It is indeed shown by the nucleic acid bases e.g., cytosine [2,3], thymine [4,5], uracil [6,7] and it has been related to the appearance of DNA and RNA mutations induced by proton transfer reactions [8]. One of the model systems of this type of equilibrium in heterocyclic compounds is the pair 2-hydroxypyridine/2-pyridone (2HP/2PD) where a hydrogen atom is transferred between the N and O sites of the molecule.

A great amount of both experimental and theoretical works have been devoted to understand the proton transfer process of 2-pyridone, a medium sized organic molecule, because of its ability to form non-covalent dimers or complexes with other molecules which are model systems for DNA base pairing. The ionized species of DNA, RNA base and analogues have a lots of interest because of their relevance to the radiation damage of nucleic acids (DNA and RNA) after their interactions with ionizing radiation, atomic ion beams, slow or energetic electrons. The major consequences of these damages on living tissues are DNA and RNA lesions, such as single strand breaks or the production of mutagenic and carcinogenic by-products through a wide variety of ionization, excitation, and energy transfer processes, involving RNA or DNA base ions [9–14]. The complex mechanisms liable for these processes are still

under investigation. 2-pyridone is also widely studied as a model to understand the binding of DNA bases to other possible hydrogen-bonding molecules. For instance, Pratt and Roscioli [15] demonstrated the clear evidence of the formation of non-covalent complexes between 2-pyridone and 2-aminopyridine in the gas phase. From their rotationally-resolved electronic spectra, they showed that these two molecules exhibit a Watson–Crick interaction which induces a 6° dihedral angle between the two planes. The complex formed by 2-pyridone and 9-methyladenine can mimic Hoogsteen or Watson–Crick base pairing. Leutwyler and co-workers have carried out several spectroscopic studies on these isolated complexes and showed that Hoogsteen and Watson–Crick interactions survive in the gas phase and have similar strengths [16]. 2-Pyridone possesses two tautomers. One is lactam form i.e. 2-pyridone and the other is lactim form i.e., 2-hydroxypyridine (see Scheme 1). The tautomerism of neutral 2-pyridone has been widely studied. Interestingly, the internal energy difference between the two tautomers is small and does not strongly depend on the surrounding environment. It has been measured as 0.025 eV in the gas phase, 0.092 eV in solution and 0.034 eV in the solid state [17] in favor of the lactim (enol). The lactim form is mostly present in the solid phase and in polar solvents, whereas lactim and lactam forms coexist in apolar solvents and three-quarters of isolated 2-pyridone is found in lactim form [15,16]. Experimental works by means of NMR, microwave, IR, Raman, laser induced fluorescence (LIF) and standard UV spectroscopies have already been performed on this molecular system and lead to accurate determination of the geometric and electronic structures of

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**Scheme 1.** Optimized structure of reactants, transition states (TS) and products for enol → keto tautomerizations using DFT-B3LYP/6-31G(d) level of theory.

the neutral ground and excited states in the gas phase, along with its vibrational wave numbers and rotational constants, and those are in conformity with the quantum chemically calculated data using density functional theory (DFT) or the Møller–Plesset perturbation theory [18–23].

Although the existence of both tautomeric forms (2HP and 2PD) in the ground electronic state has been verified earlier suggesting that bare 2HP is more stable than 2PD, and the barrier for tautomeric conversion in the gas phase is quite high (~40 kcal/mol) depending on employed methods and basis sets [24–28]. But to the best of our knowledge theoretical investigation about the variation of the quantum chemical reactivity parameters e.g. polarizability, hardness, ionization potential etc. along the proton transfer co-ordinate for the above tautomeric equilibrium has not been done so far.

During the last few years widespread studies were carried out on the hardness ( $\eta$ ), softness ( $S$ ), and polarizability ( $\alpha$ ) on time-dependent systems [29]. These studies include chemical reactions

as well as intramolecular vibrations and rotations [29,30]. From detailed theoretical studies it has been found that “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible” (maximum hardness principle, MHP) [29]. It was also stated that “the natural direction of evolution of any system is toward a state of minimum polarizability” (minimum polarizability principle, MPP) [31,32]. The latter principle can be thought of as a consequence of the inverse relationship between  $\alpha$  and  $\eta$  and the validity of the maximum hardness principle. In this communication we have verified a similar principle for ionization potential which can be stated as, “a stable configuration/conformation of a molecule is associated with a maximum value of its ionization potential.”

In this study, detailed theoretical investigations of the homogeneous gas-phase proton transfer of 2-hydroxy pyridine (2HP), 5-methyl 2-hydroxy pyridine (5Me2HP) and 5-fluoro 2-hydroxy pyridine (5F2HP) are carried out. Our primary aim is to account qualitatively the role of average polarizability ( $\alpha_{av}$ ), hyper-

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