



Polarizability, hardness and electrophilicity as global descriptors for intramolecular proton transfer reaction path



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ABSTRACT

Potential energy (PE) curves for intramolecular proton transfer in the ground (GS IPT) and excited (ESIPT) states of 1-hydroxy-2-acetonaphthone (1H2AN) is studied using DFT-B3LYP/6-31+G(d,p) and TD-DFT/6-31+G(d,p) level of theory respectively. Our calculations suggest the non-viability of ground state intramolecular proton transfer in 1H2AN. Excited states PE calculations support the viability of ESIPT process in 1H2AN. Here, for the first time, polarizability, chemical hardness and electrophilicity are being used as global reactivity descriptors to locate the transition state for intermolecular proton transfer process. Both the minimum polarizability principle (MPP) and maximum hardness principle (MHP) are being obeyed along the intrinsic reaction co-ordinate (IRC) for intramolecular proton transfer process. We have also raised the decade old issue i.e. the use of O–H distance of enol tautomer as proton transfer co-ordinate instead of IRC. Our computation of these global reactivity descriptors along the proton transfer co-ordinate support intrinsic reaction coordinate (IRC) as the effective proton transfer co-ordinate, instead of variation of O–H distance of enol tautomer.

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1. Introduction

Excited state intramolecular proton transfer (ESIPT) reactions are of great scientific and technological interest. Since its introduction [1], the photoinduced excited state intramolecular proton (or hydrogen) transfer reaction, which generally incorporate transfer of a hydroxyl (or amino) proton to the carbonyl oxygen (imine nitrogen) through a pre-existing intramolecular hydrogen bonding (IMHB) configuration, has received considerable attention, because it has led to a wide range of application, such as laser dyes [2,3], polymer stabilizer [4], Raman filters [5], environmental probes in bio-molecules [6], and proteins [7–11]. Main requirement of ESIPT reaction is that the molecule must have acid and basic groups and the strong intramolecular hydrogen bond (IMHB) between the two groups at the same time. Electronic excitation of the normal enol form (N) leads to the excited (N^{*}) form, which in the course of photochemical reaction is transformed into a proton transferred keto tautomer (T^{*}). T^{*} relaxes radiatively or non-radiatively to the metastable ground state keto tautomer 'T', which converts to 'N' state via reverse proton transfer.

The field of the photoinduced proton-transfer process, despite the great efforts devoted since Weller [1], still poses challenges both theoretically and experimentally. The understanding of ESIPT

requires detailed knowledge of excited-state energy surfaces as a first prerequisite for the treatment of its photodynamics. The calculation of energy surfaces in electronically excited states is still a formidable task considering especially the large size of the molecules, which are of practical interest. Because of the possibility of surface crossings and conical intersections, the appropriate methodological approach would be to use multi-reference methods. Such investigations have been performed at the complete active space self-consistent field (CASSCF) and complete active space perturbation theory to second order (CASPT2) [12] as well as at the multireference configuration interaction with singles and doubles (MR-CISD) [13] and multireference averaged quadratic coupled cluster (MR-AQCC) [13] levels. However, required computational times for such calculations are very large and limit these kinds of investigations to benchmark examples. Hybrid HF/DFT methods have been proposed as a reliable tools for computing static and dynamic properties of hydrogen-bonded systems [14–16]. One such method, B3LYP [17], nicely predicts the available experimental data, as well as the results obtained with the highest post-HF method [18]. The time-dependent (TD) DFT version has been applied successfully on a series of molecular systems showing ESIPT e.g. *o*-hydroxybenzaldehyde (OHBA), salicylic acid (SA), and 7-hydroxy-1-indanone (7HIN) [12]. In view of its wide spread success for the calculation of large molecules [19–27] we have decided to choose density functional approach for the present study on the excited state intramolecular proton transfer process in 1H2AN.

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1-Hydroxy-2-acetonaphthone usually exhibit two strongly separated bands in their fluorescence spectrum due to ESIPT reaction, leading to two excited forms, the normal N^* and the tautomer T^* ones. Experimental work of Catalan and del Valle [28] showed that ESIPT is not involved in 1H2AN. On the other hand, Douhal et al. [29] have reported that the emission from the vibrationless level of the S_1 state of isolated 1H2AN in a supersonic expansion exhibited a dual fluorescence in two close but different spectral regions, one is from normal N^* isomer ($\lambda_{em} = 426$ nm) and the other from T^* tautomer ($\lambda_{em} = 452$ nm).

Again there is a school of thought where the variation of O–H distance of enol tautomer is being used as intramolecular proton transfer co-ordinate and this is known as distinguished co-ordinate approach is literature [15]. There is another choice for proton transfer process i.e. internal reaction co-ordinate (IRC). In this present communication, we have used global reactivity descriptor i.e. average polarizability (α_{av}), chemical hardness (η), chemical potential (μ) electrophilicity index (ω) and their optimum principle along the proton transfer reaction path to explain which one is better choice. Our study shows that the computation of global reactivity parameter obey their optimum principle along the IRC path but it show a large deviation of O–H distance as proton transfer coordinate. There are some reports in literature [30–33] where polarizability and chemical hardness were used to verify MPP and MHP along IRC for some benchmark problems. This is for the first time that the above global reactivity descriptors are being used to understand the nature of potential surface for intramolecular proton transfer processes.

2. Theoretical calculations

All ab initio calculations reported in this paper were carried out in gas phase using Gaussian 09 package program [34]. We found that the DFT based calculations using hybrid functional (B3LYP) with 6-31+G(d,p) basis set is the optimal one in terms of price-performance ratio for carrying out present electronic structure calculations. Analytic vibrational frequency computations at the optimized structure were done to confirm the optimized structure to be an energy minimum or a transition state structure. We have performed the IRC job to get potential energy profile along IRC co-ordinate connecting the enol and keto tautomer. Polarizabilities and chemical hardness are computed for each IRC point at a frequency of static field 0.00 eV and 1.67 eV corresponding to the Nd:YAG frequency.

2.1. Computation of average polarizability (α), chemical hardness (η), chemical potential (μ) and electrophilicity index (ω)

From detailed theoretical studies it was found that molecules arrange themselves so as to be as hard as possible and this is known as maximum hardness principle, MHP [35,36]. It was also stated that the natural direction of evolution of any system is toward a state of minimum polarizability (minimum polarizability principle, MPP) [37,38]. Chemical potential (μ), and chemical hardness (η) can be used as complementary tools in the description of thermodynamic aspects of chemical reactivity. The first order partial derivatives of total energy (E) with respect to the number of electrons (N) at constant external potential, $v(r)$, define the chemical potential (μ) and the second partial derivatives of total energy (E) with respect to the number of electrons (N) at constant external potential, $v(r)$, define the global hardness (η) of the system [35,39].

$$\mu = (\partial E / \partial N) v(r) \quad (1)$$

$$\eta = 1/2(\delta^2 E / \delta N^2) v(r) \quad (2)$$

Operational schemes for the calculation of chemical hardness are based on a finite difference method and thus,

$$\mu \approx -1/2(I.P + E.A) \quad (3)$$

$$\eta = 1/2(I.P - E.A) \quad (4)$$

where I.P = Ionization Potential and E.A = Electron Affinity. Using the Koopmans' theorem in terms of the energies of highest occupied molecular orbital (E_H) and lowest unoccupied molecular orbital (E_L), Eqs. (3) and (4) can be expressed as

$$\mu \approx 1/2(E_{HOMO} + E_{LUMO}) \quad (5)$$

$$\eta = 1/2(E_{LUMO} - E_{HOMO}) \quad (6)$$

Electrophilicity index proportionally related to the chemical potential and inversely related to the chemical hardness. The value of electrophilicity index can be calculated using the following expression [40].

$$\omega = \mu^2 / 2\eta \quad (7)$$

These global quantities, as well as the mean polarizability values (α), have been found very useful and complementary tools for the description of chemical reactivity in connection with minimum polarizability [38] and maximum hardness principles [41,42].

Polarizability is an even-order derivative of energy with respect to the applied electric field. Even for centrosymmetric molecules the polarizability never becomes zero. Also, from an experimental viewpoint, anisotropic polarizability ensures that all the states from GS \rightarrow TS can be traced by Raman spectroscopy. Polarizability is the property of a molecule which has and it becomes minimum value for most stable conformer and maximum for least stable species like transition state. Average polarizability is calculated using the following equation.

$$\alpha_{av} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

Change of average polarizability, chemical hardness, chemical potential and electrophilicity index of the titled compound have been computed along the intrinsic reaction co-ordinate (see SI Table 1) and as well as distinguished co-ordinate approach (see SI Table 2) using DFT-B3LYP/6-31+G(d,p) level of theory.

3. Results and discussion

Ground state optimized structure of 1H2AN shows that enol form (N') is the most stable form due to the presence of strong intramolecular hydrogen bonds (Scheme 1). Ground state bond angle and dihedral angle data (see SI Table 3) suggest that the six membered ring formed due to intramolecular hydrogen bond of 1H2AN is planar and it is in the same plane that of the aromatic naphthalene ring.

Free energy calculations for the ground state enol \rightleftharpoons keto equilibria of 1H2AN gives positive value of free energy change ($\Delta G = 5.65$ kcal/mol) and the calculated equilibrium constant is $\sim 7.49 \times 10^{-5}$. On the basis of the equilibrium constant, the population ratio in the gas phase for enol vs. keto form in the ground state is 1.33×10^4 : 1. This clearly explains that intra molecular proton transfer in the ground state is not thermodynamically favorable in 1H2AN.

3.1. Ground and excited state potential energy of 1H2AN along the IRC

Fig. 1 shows the variation of potential energy (PE) along the intrinsic reaction co-ordinate for both the ground and the first excited singlet state of 1H2AN. Ground state PE curve shows a minimum at an IRC value 0.5 and this is due to the N' form of 1H2AN.

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