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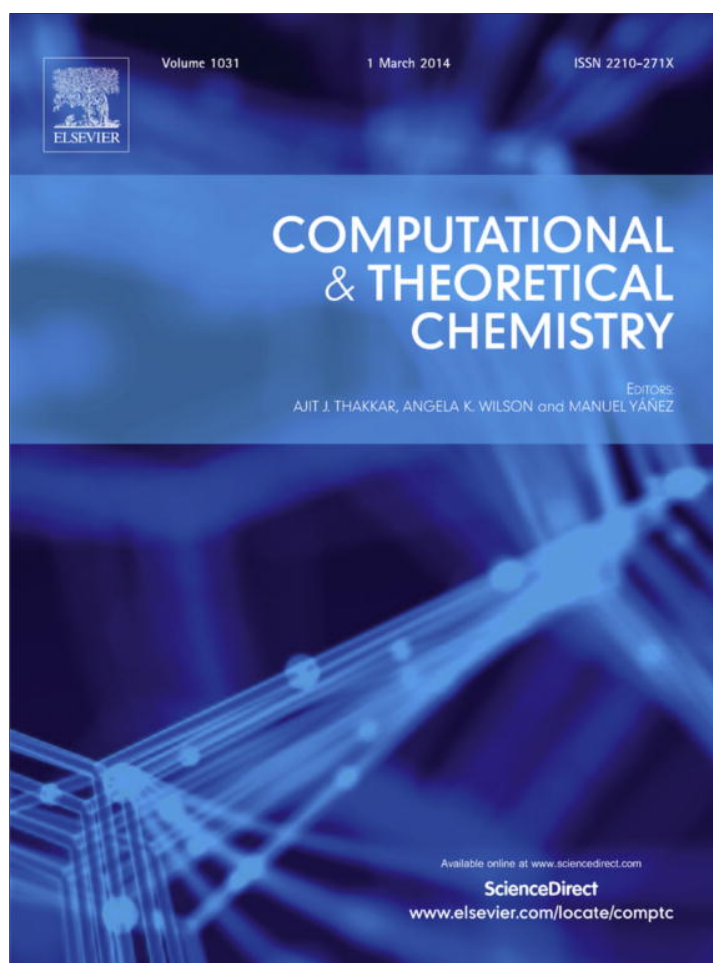


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Polarizability, hardness and electrophilicity as global descriptors for intramolecular proton transfer reaction path

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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].

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

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

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.

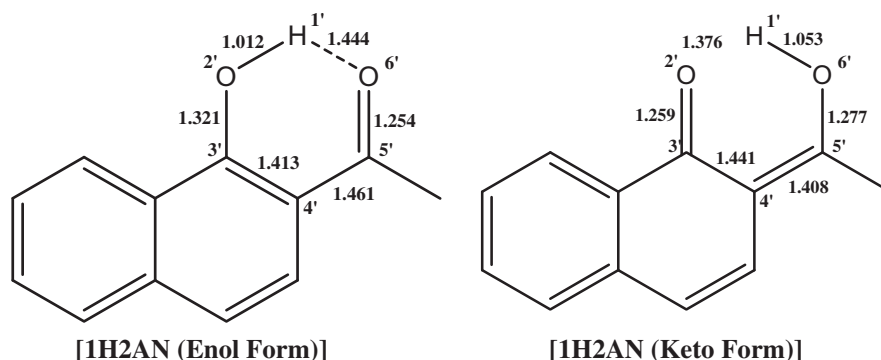
3. Results and discussion

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.



Scheme 1. Optimized structure of enol and keto form of 1H2AN using the intrinsic reaction co-ordinate (IRC).

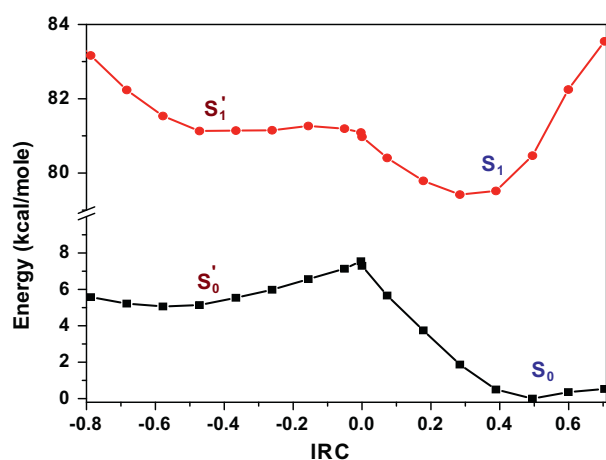


Fig. 1. GS IPT and ES IPT curves of 1H2AN as obtained from DFT-B3LYP/6-31+G(d,p), TD-DFT-B3LYP/6-31+G(d,p) level of theory along the intrinsic reaction co-ordinate (IRC).

Ground state potential energy curve increases steadily as the IRC decreases from 0.5 to 0 and at -0.4 to -0.8 curve (S'_0) shows a wide minimum corresponds to keto tautomer, 'T'. Franck–Condon (FC) potential energy curve for the first excited singlet state shows two minima, one at 0.5 and other which is slightly higher (2 kcal/mol) in energy and having IRC value -0.5 . The former is due to the locally excited enol form (N^*) and the latter minima is due to excited keto tautomer (T^*). Wide minima with small depth around the keto tautomer position of GS IPT curve (S'_0) and small energy gap between S'_0 and S'_1 state suggest that the keto tautomer emission will be broad, structureless and red shifted. Small proton transfer barrier (2 kcal/mol) and exothermal nature of the excited potential energy surface (PES) will help to populate the S'_1 state. Again the low barrier and downhill potential while going from S'_0 to S_0 state will depopulate the S'_0 state through back proton transfer. Catalan and de Paz [43] observed a large Stokes shifted, emission band of 1H2AN in 2-methylbutane solution maximized at ~ 473 nm. The red shifted emission is due to excited keto tautomer (T^*) resulted from ES IPT along the proton transfer co-ordinate. Experimental investigations of Tobita et al. [44] showed that λ_{\max} of 1H2AN in cyclohexane is ~ 355 nm. On the other hand, our calculated λ_{\max} in the gas phase is ~ 348 nm and this is in good agreement with their experimental findings.

3.2. Variation of global reactivity parameters along the IRC: Average Polarizability (α_{av})

Variation of average polarizability (α_{av} , in a.u.), along the intrinsic reaction co-ordinate (IRC) of 1H2AN is shown in Fig. 2. At each

scan step, α_{av} is computed at static field zero frequency, ($\omega = 0.00$ eV) and at Nd: YAG frequency, ($\omega = 1.67$ eV), a wavelength used for many Hyper Rayleigh Scattering (HRS) experiments [45]. Polarizability at higher field strength will be more since more and more excited states will be available and greater will be the charge separation. Fig. 2 shows that the average polarizability increases as ground state enol form of 1H2AN moves toward TS structure. The average polarizability (α_{av}) reaches its maximum at the TS and then decreases as the TS structure changes to keto tautomer form. This variation of average polarizability along the IRC with its minimum value at enol tautomer position supports the minimum polarizability principle.

3.2.1. Chemical hardness (η)

Chemical hardness (η) can be used as complementary tool to describe the thermodynamic aspects of chemical reactivity. Our computational study shows that enol tautomer possess highest chemical hardness (η). Variation of chemical hardness (η) along the IRC co-ordinate (Fig. 3) shows that hardness value gradually decreases from enol to TS form and then increases to reach a higher value at relatively stable keto tautomer. This variation of chemical hardness along the IRC supports the maximum hardness principle.

3.2.2. Electrophilicity index (ω) and chemical potential (μ)

Variation of electrophilicity index (ω) and chemical potential (μ) along the intrinsic reaction co-ordinate of the compound is shown in Fig. 4. The electrophilicity index (ω) increases as the GS structure moves from enol to TS but chemical potential (μ)

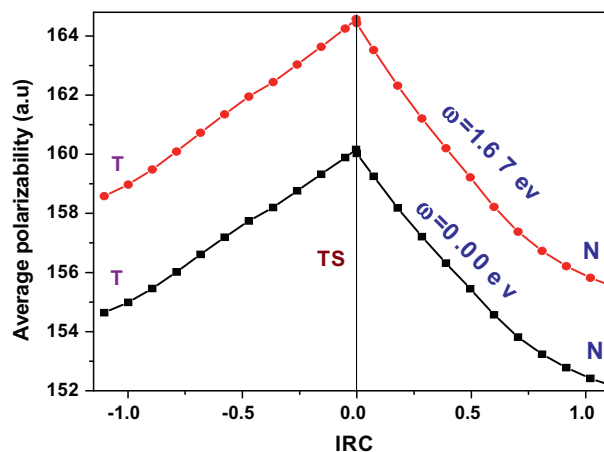


Fig. 2. Variation of average polarizability (α_{av}) (at $\omega = 0.00$ eV and $\omega = 1.67$ eV) along the intrinsic reaction co-ordinate (IRC) of 1H2AN, obtained using DFT B3LYP/6-31+G(d,p) level of theory.

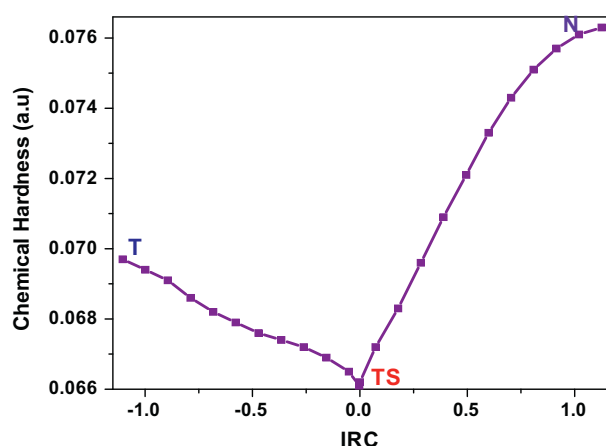


Fig. 3. Variation of chemical hardness (η) along the intrinsic reaction co-ordinate (IRC) of 1H2AN as obtained from DFT-B3LYP/6-31+G(d,p) level of theory.

having highest value for enol tautomer decreases as the GS structure moves from enol to TS. After reaching its highest value at TS electrophilicity index (ω) decreases and reaches to minimum value at keto tautomer position. On the other hand chemical potential (μ) shows a reverse trend i.e. increases till it reaches a relatively higher value at keto tautomer position.

Therefore one can use average polarizability (α_{av}), chemical hardness (η), electrophilicity index (ω) and chemical potential (μ) as descriptor for reactant, product and TS along the intrinsic reaction co-ordinate (IRC).

3.3. Variation of PE and global reactivity parameters along the distinguished co-ordinate

There is a school of thought where O–H distance of the enol tautomers is being used as proton transfer co-ordinate. Earlier study by Catalan et al. [15], Maheshwari et al. [46] illustrated that the use of O–H distance of enol tautomer of some naphthalene derivatives and salicylic acid as proton transfer co-ordinate and they termed it as distinguished co-ordinate approach in the literature. We also have used their idea i.e., the variation of O–H distance of enol tautomer as proton transfer co-ordinate to compute the potential energy curves of the titled compound (Fig. 5). Our computed ground state potential energy curve using DFT-B3LYP/6-31+G(d,p) level of theory for 1H2AN show one global minimum

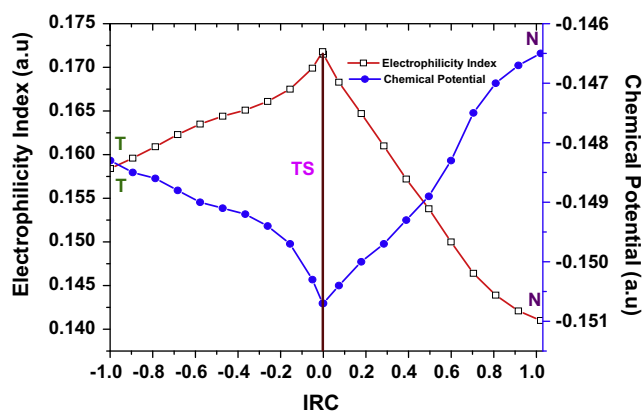


Fig. 4. Variation of electrophilicity index (ω) and chemical potential (μ) along the intrinsic reaction co-ordinate (IRC) of 1H2AN as obtained from DFT-B3LYP/6-31+G(d,p) level of theory.

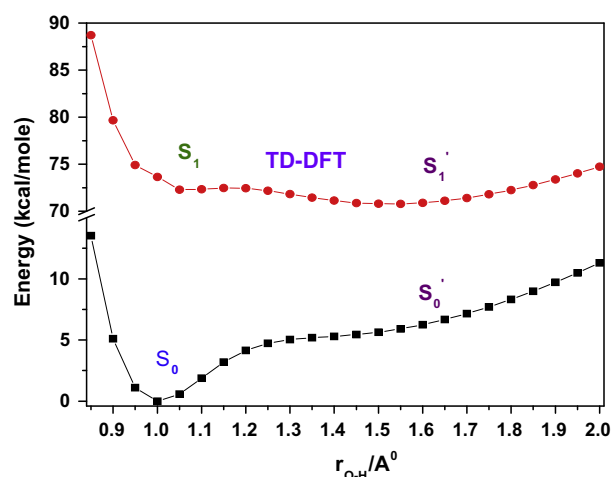


Fig. 5. GS IPT and ES IPT curve of 1H2AN as obtained from DFT-B3LYP/6-31+G(d,p), TD-DFT-B3LYP/6-31+G(d,p) level of theory along distinguished co-ordinate as proton transfer co-ordinate.

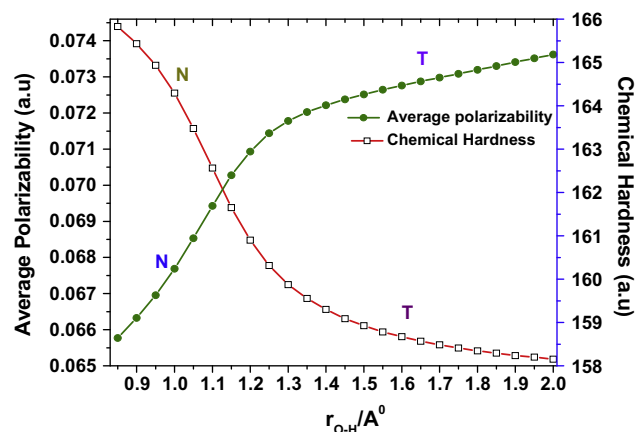


Fig. 6. Variation of average polarizability (α_{av}) and chemical hardness (η) with r_{O-H} bond distance of 1H2AN, obtained using DFT B3LYP/6-31+G(d,p) level of theory.

at $r_{O-H} = 1.00$ Å for enol tautomer and a wide minimum at r_{O-H} ranging from 1.5 to 1.6 Å for the keto tautomer. Again the excited state potential energy curve computed using TD-DFT-B3LYP/6-31+G(d,p) level of theory shows very little barrier between the excited enol and keto tautomer. Therefore the nature of PE curve suggests the feasibility of ES IPT in 1H2AN.

In order to understand the feasibility to use the O–H distance as proton transfer co-ordinate, we have computed the global reactivity descriptors i.e. average polarizability (α_{av}), chemical hardness (η), chemical potential (μ) and electrophilicity index (ω) along this proton transfer co-ordinate (Figs. 6 and 7). Surprisingly we observe that the average polarizability (Fig. 6) increases as we passes from enol to keto tautomer through the transition state (TS) without showing any maximum at TS. But according to minimum polarizability principle (MPP), the TS structure which is the least stable one along the proton transfer co-ordinate must have highest value of average polarizability. Therefore the evolution of structures along the distinguish co-ordinate does not obey the MPP.

On the other hand our computed chemical hardness (Fig. 6) along the proton transfer co-ordinate (O–H distance) shows a decreasing trend while passing from enol to keto tautomer without showing minimum at TS. Since chemical hardness is used as global reactivity descriptor it must show, minimum value at TS and

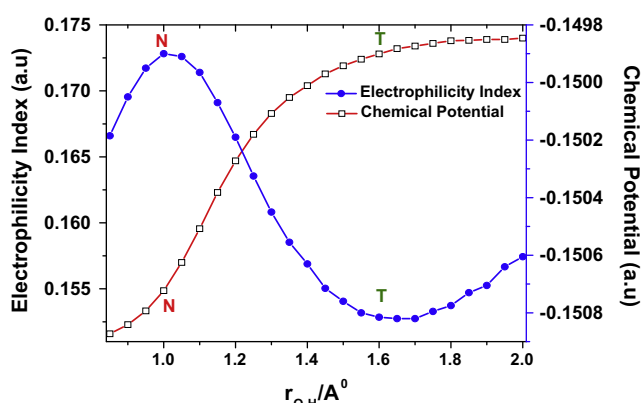


Fig. 7. Variation of electrophilicity index (ω) and chemical potential (μ) with $r_{\text{O-H}}$ bond distance as proton transfer co-ordinate of 1H2AN as obtained using DFT-B3LYP/6-31+G(d,p) level of theory.

maximum value for product according to maximum chemical hardness (η) principle (MHP).

Again the variation of electrophilicity index (Fig. 7) along the O–H distance shows a decreasing trend while passing from enol to keto tautomer without showing any optimum value at the transition state. And the variation of chemical potential (Fig. 7) along the O–H distance illustrates an increasing trend while passing from enol to keto form without showing any optimum value at TS.

Therefore according to both of these principles (MPP and MHP), transition state of keto enol tautomer can hardly be defined, if one uses O–H distance as proton transfer co-ordinate. Thus we believe the use of O–H distance (distinguished co-ordinate) is not the right choice of proton transfer co-ordinate instead of IRC.

4. Conclusion

This is for the first time that average polarizability, chemical hardness, electrophilicity index and chemical potential are being used as global descriptor to locate the transition state as well as the product for intramolecular proton transfer processes. We also raised the decade old issue of using O–H distance of enol tautomer as proton transfer co-ordinate instead of intrinsic reaction co-ordinate (IRC). A comparison of IRC and distinguished co-ordinate to compute ground as well as excited state proton transfer processes of the titled compound, 1H2AN is being made in the light of global reaction descriptors e.g. average polarizability, chemical hardness, electrophilicity index and chemical potential. Computation of PE curve using both IRC and distinguished co-ordinate suggest the viability of ESIPT processes in 1H2AN. This is in conformity with the earlier experimental observation. Again the computation of global reactivity descriptor along the IRC co-ordinates shows optimum values for TS and is the product side both the minimum polarizability principle (MPP) and maximum hardness principle (MHP) are obeyed. But the computations of all the global parameter along the distinguished co-ordinate do not obey these principles. Therefore we believe that the use of distinguished co-ordinate is in no way a substitute of IRC for intramolecular proton transfer processes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2014.01.010>.

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