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Electronic effects on 1H-azepines valance tautomerization: an ab initio comparative study

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Abstract

Ab initio HF/6–31G*, B3LYP/6–31G* and MP2/6–31G*//HF/6–31G are employed for calculations of equilibrium constants (K_{eq}), rate constants (k_r), activation electronic energies ($\Delta E^{\#}$), enthalpies ($\Delta H^{\#}$), and Gibbs free energies ($\Delta G^{\#}$) for conversions of 3(X)-1H-azepine, **1** (where X=H, NH_2, OCH_3, CH_3, CF_3, F, Cl, Br, NO_2 and CN) to their corresponding 2(X)-benzene imines, **2** (Series 1). The same calculations are carried out for conversions of 4(X)-1H-azepines, **1′**, to analogous 3(X)-benzene imines, **2′** (Series 2). Equilibriums related to Series 1 with different (X) substitutions occur with $K_{eqs}=1.4\times10^7$ (H), 4.8×10^4 (NH_2), 5.6×10^3 (OCH_3), 9.7×10^5 (CH_3), 1.1×10^7 (CF_3), 3.1×10^5 (F), 7.6×10^5 (Cl), 1.2×10^6 (Br), 2.4×10^8 (NO_2) and 2.4×10^6 (CN). Similarly, for Series 2, the K_{eqs} are: 1.4×10^7 (H), 7.1×10^7 (NH_2), 9.7×10^6 (OCH_3), 9.4×10^6 (CH_3), 3.0×10^7 (CF_3), 9.6×10^7 (F), 7.1×10^7 (Cl), 9.3×10^7 (Br), 1.0×10^9 (NO_2) and 1.2×10^8 (CN). A Hammet ρ value of 1.70 is obtained for Series 2. Due to steric effects, meaningful ρ is not fond for Series 1.

Keywords: Valence tautomerizations; Electronic effects; 1H-azepine; Benzene imine; Ab initio; HF and DFT methods

1. Introduction

Reaching for tautomerization of 1H-azepine, $\mathbf{1_H}$, to benzene imines, $\mathbf{2_H}$, via calculations is interesting, since it is mostly unreachable through experiment (Scheme 1). This is for the instability of $\mathbf{1_H}$ due to its rapid tautomerization to 3H-azepine, $\mathbf{3_H}$. Only *N*-substituted derivatives of **1** exist in the 1H-tautomeric form. A reason set forward is a possible encountering of the formation of a planar antiaromatic 8π-electron system anticipated for $\mathbf{1_H}$. This polyene nature of the ring system of $\mathbf{1_H}$ is characterized by cycloaddition reactions and metal complex chemistry normally associated with homocyclic and acyclic polyene systems [1]. X-ray of *N*-substituted derivatives of 1H-azepine confirms that these molecules have a boat conformation with substantial sp^2 character for the nitrogen atom [2]. Theoretical studies have indicated that $\mathbf{1_H}$ possesses a boat configuration with 22% chair character. This permits π-delocalization of the cyclic double bond system to a level comparable to that of a linear polyene [3,4]. The chemistry of azapines has been well served by a number of excellent reviews [5].

The binary valence tautomerization system of **1** is a reminiscent of cyclozheptatriene (**4**)/norcaradiene (**5**); oxepin (**6**)/benzene oxepine (**7**) [6–12] and 1H-azepine ($\mathbf{1_H}$)/benzene imine ($\mathbf{2_H}$) (Scheme 1). These valance tautomerizations occur through simultaneous shift of σ and/or π electrons without the intervention of ionic or free radical intermediates, or the migration of atoms or groups [6,7,13–16]. There is a significant difference in the chemical properties of 1H-azepines, oxepins and cycloheptatrienes. Whereas cyclozheptatrienes [17–20] and oxepines [21] are capable of ready disrotatory cyclization to the corresponding norcaradienes and arene oxids, respectively (especially in the course of chemical reactions), 1H-azepines derivatives are particularly reluctant to form their related benzene imine counterparts and will do so only as a last resort [13,22–26]. A large number of 1H-azepine derivatives have been obtained through the work on nitrene chemistry [27–29]. There remains the question of electronic effects on 1H-azepine valance tautomerization which is addressed in this manuscript.

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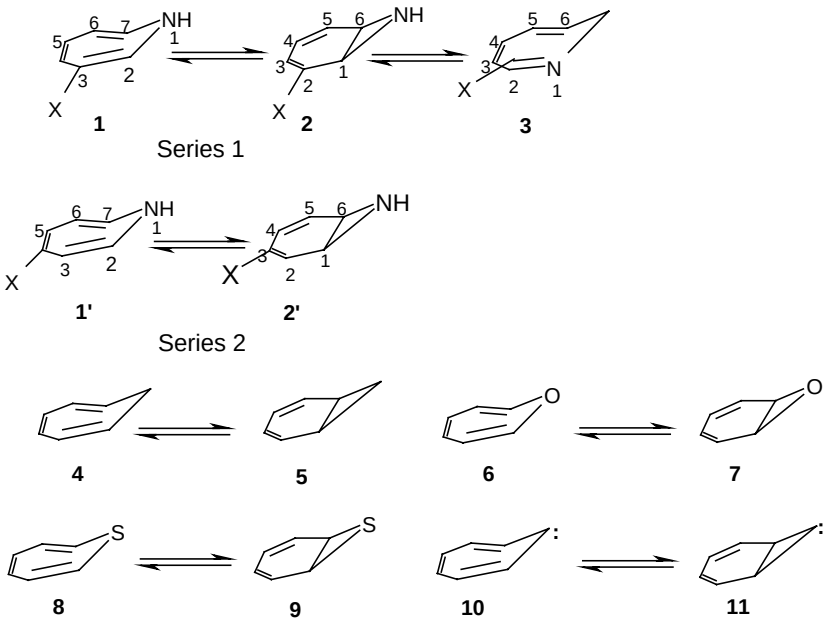

Scheme 1. Binary valence tautomerizations in seven memberd ring systems. Ab initio studies are carried out for electronic effects on conversions of 3-(X)-Azepines to their corresponding 2-(X)-benzene imines, Series 1; as well as 4-(X)-Azepines to their analogous 3-(X)-benzene imines, Series 2; for X = H, Me, NH_2, OCH_3, F, Cl, Br, CF_3, CN and NO_2.

2. Computational methods

Geometry optimizations are carried out by ab initio HF and B3LYP [30–31] methods using 6–31G* basis set of the GAUSSIAN 98 system of programs [32]. The HF/6–31G* optimized geometrical outputs are used as inputs for the B3LYB/6–31G* calculations. This is for obtaining more accurate values of activation electronic energies ($\Delta E^{\#}$), enthalpies ($\Delta H^{\#}$) and Gibbs free energies ($\Delta G^{\#}$). MP2/6–31G*//HF/6–31G calculation are done. In order to find energy minima, keyword 'FOPT' and for transition states keyword 'FOPT (QST3)' are used. To confirm the nature of the stationary species and evaluate the activation energy barriers for valence tautomerization, frequency calculations (keyword: FREQ = NORAMAN) are carried out. This is for ground and transition states, at both HF and DFT levels. For minimum state structures, only real frequency values, and for the transition states, only a single imaginary frequency value is accepted. Thermodynamic functions obtained through frequency calculations, are multiplied by the scaling factors. This is to account for the difference between the harmonic vibrational calculations and the anharmonic oscillations of the actual bonds.

3. Results and discussion

1H-azepine and its derivatives (**1**) are analogues of the unstable, 8π-electron cycloheptatrienide anion which are scrutinized in this manuscript (Scheme 1). Ab initio calculations are employed for conversions of 3(X)-1H-azepine, **1**, (where X = H, NH_2, OCH_3, CH_3, CF_3, F, Cl, Br, NO_2 and CN) to their corresponding 2(X)-benzene imines, **2** (Series 1). The same calculations are carried out for conversions of 4(X)-1H-azepines, **1′**, to analogous 3(X)-benzene imines, **2′** (Series 2).

Thermodynamic data of Series 1 (Table 1) and Series 2 (Table 2), are calculated via HF/6–31G* and B3LYP/6–31G*. These data include: sum of electronic and thermal energies (E), sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G), for the ground state of benzene imines, **2** (or **2′**), and 1H-azepines, **1** (or **1′**), as well as their corresponding transition states (TS)[1] which are obtained by the FREQUENCY option of the GAUSSIAN 98 program [24].

Using the above data changes of activation electronic energies ($\Delta E^{\#}$), enthalpies of activation ($\Delta H^{\#}$), Gibbs activation free energies ($\Delta G^{\#}$), and equilibrium constants (K_{eq})[2] are calculated for Series 1 (Tables 3) and Series 2 (Tables 4).

Relative energies (E_r), enthalpies (H_r) and free energies (G_r) relating all substituents (X) are presented in a way to facilitate comparisons between ground state as well as

[1] $G = H - TS = (E + RT) - TS = [(E_0 + E_{vib} + E_{rot} + E_{trans}) + RT] - TS$, where $E_0 = E_{elec} + ZPE$.

[2] According to the transition state theory, the rate constant (k_r), is calculated as shown by the following equation: $K_r = (K_B T/h)K^{\#} = (K_B T/h)e - \Delta G^{\#}/RT$.