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The Proton Affinities of a Series of Heterocyclic Compounds Pyrrole, Furan, Thiophene and Pyridine in their Low-lying Excited Triplet State: A DFT-Based Comparative Study

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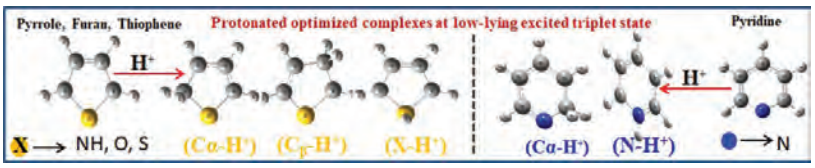
ABSTRACT Gas-phase proton affinities (PAs), basicities (ΔG) and transition energies ($^1S_0 \rightarrow T_1$) of a series of heterocyclic molecules (pyrrole, furan, thiophene, and pyridine) and their protonated counterparts have been investigated using density functional theory (Becke, Lee, yang, and parr [B3LYP]) method at 6-311G (d,p) basis set level with complete geometry optimization in their low-lying excited triplet state. The gas phase protonation has been found to be exothermic in each case. Geometry and electronic structures of the protonated complexes have been searched extensively. According to the calculated results, the PA is predicted to be 222.13 kcal/mol for pyridine. PAs have been obtained more due to protonation at Cα (C1) position of pyrrole, thiophene relative to the protonation at C_β and heteroatom sites. In furan, protonation at heteroatom (X = O) leads to O–C1 bond breaking where PA value is determined to be 206.45 kcal/mol. Computed PAs are sought to be correlated with the number of computed system parameters such as the net computed charge on the atoms (participating in protonation) of the free molecules and protonated species, charge on the proton of the protonated species and the computed hardness (η) of the unprotonated species in their relevant excited states. The proton induced shifts are in general redshifts for the lowest excited triplet states.



KEY WORDS B3LYP, Charge distribution, DFT, GAUSSIAN, Proton affinity, Proton induced shifts.

INTRODUCTION

The acid-base property of molecules is very functional and empirical thought. Definition of electron donor and acceptor provide a fundamental idea that there exists a close relation between the molecular electron density distribution and the acid-base properties. This also implies that this property may vary from one electronic state to another electronic state of the same molecule due to some electronic transitions which are accompanied by extensive reorganization of molecular electronic charge distribution. Gas-phase proton affinity (PA) or deprotonation energy of a molecule reflects their intrinsic acid-base properties in the absence of solvation. Absorption and fluorescence spectral data in conjunction with Forster cycle[1-4] are utilized for the experimental determination of acid-base properties of molecules in

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excited states in the presence of solvents. Gas-phase methods[5-7] have been successfully applied to determine the gas phase acid-base properties of molecules in excited states avoiding complicating effects of solvation. Absolute PA provides important information about electrophilic reactivity.[8] Intrinsic acid-base properties of a molecules or compounds may be reflected by their PA values. Gas-phase PA and basicity (ΔG) are of considerable interest in the field of theoretical chemistry research.[9] PA can be utilized to determine the stability of ion-molecule complexes.[10,11] Pyrrole, furan, and thiophene (C_4H_5N, C_4H_4O, and C_4H_4S) are planar five-membered (FM) aromatic heterocyclic molecules having C_{2v} point group. Pyridine (C_5H_5N) is a prototypical planar (C_{2v} point group) six-membered (SM) aromatic base. These heterocyclic molecules are widely known as basic units of different biological compounds.[12-14] The derivative of this five or SM heterocyclic compounds involved in various biomolecular and medicinal activities[15-20] such as anticancer, antitumor and so on. The present work deals with the effects of the change of electronic state (S_0 to T_1) on the PAs. Gas-phase basicities (ΔG) and geometrical parameters also have been investigated using quantum mechanical calculations. The PA values of furan and thiophene were determined theoretically[21] at the R1-MP2/aug-cc-pVDZ level of calculation. DFT/MRCI computational method was employed to explore the ground and low-lying excited states of thiophene.[22] Various computational methods have been applied to investigate the radiationless deactivation of photo-excited furan.[23] Geometries and some electronic properties of low-lying triplet states of aniline have been studied computationally.[24] So far, systematic and comprehensive studies on the ion-molecular reactions (protonation) of low-lying excited triplet state of a series of heterocyclic compounds (pyrrole, furan, thiophene, and pyridine) are rather scarce. We are, therefore, compelled to turn to theory to obtain some quantitative idea about the relative PAs of these heterocyclic compounds in this particular state employing DFT/B3LYP method[25,26] of calculation at 6-311G (d,p) basis set the level of Gaussian 09W program package.[27] In this manuscript, we have also discussed the physical properties (electronic and thermodynamic) and some geometrical parameters (bond distance, bond angles, and dihedral angles) in the gas phase of some important heterocyclic compounds (pyrrole, furan, thiophene, and pyridine) in their low-lying excited triplet state. Recently, the basicities of a series of substituted crotonaldehyde and acetophenone in their ground states and lowest excited triplet state have been theoretically calculated.[28-31] Ground state PAs of the same set of heterocyclic molecules have been studied[32] earlier. The ground state gas-phase PAs, basicities (ΔG) and some others physical properties of some N, S, O containing heterocyclic compounds have been studied earlier using various theoretical methods. The results are available in literature.[33] It has been seen that the results (PA and Gas-phase basicities) obtained theoretically shows good agreement with the values evaluated in an experimental procedure like Fourier transform ion cyclotron resonance mass spectrometry.[34-36] We have already investigated the gas-phase thermodynamic, electronic and some important structural parameters of pyrrole, furan, thiophene, and pyridine in the ground state (singlet, i.e., multiplicity = 1) applying same computational method. Gas-phase PAs, basicities value obtained in this investigation shows good agreement with the values present in literature (results have been provided in the tabular form [**Table 1a]** in result section). In low-lying excited state (multiplicity = 3), so far, detailed and comprehensive studies on the ion-molecule reactions in gaseous heterocyclic compounds are rather scarce. The results are also not available in literature. Therefore, we concentrate our research interest to investigate some important thermodynamic and electronic properties and also to find out geometrical features of the same heterocyclic compounds in their low-lying excited triplet state under DFT calculation. We have analyzed the PA values, transition energies of these molecules in various aspects, e.g., different protonation sites (Cα, C_β, and heteroatoms [N, O, or S]) have been considered to understand the most stable protonated complex in this electronic state. The natural charges of the atoms have been evaluated by means of natural population analysis (NPA). Finally, a comparison has been drawn between ground state and low-lying excited state molecular properties of the studied molecules. We have also analyzed the kind and extent of spectral shift caused by protonation. In a particular state, the possibility of correlating the PA values with the global hardness of the molecules is also explored.

COMPUTATIONAL DETAILS

All calculations were carried out using Gaussian O9W program package.[27] The molecular structures were optimized by the reliable DFT/B3LYP method at 6-311G (d,p) basis set level. In all calculations, complete geometry optimization has been carried out on the molecules both before and after protonation. Unscaled vibrational frequency calculations were performed (at 298.15 k) at the same level of theory. The optimized structures are used in these frequency calculations. PA has been calculated as $H_{BH}^{+} - H_B$ and gas-phase basicity (ΔG) = ($G_{BH}^{+} - G_B$), H= total enthalpy, and G = total Gibbs free energy.

Table 1: Different gas-phase proton affinities (ΔE) and basicities of pyrrole, furan, thiophene, and pyridine obtained from B3LYP/6-311G (d, p) method of calculation in low-lying triplet state

Compounds	Proton affinities (ΔE) (kcal/mol)	Gas-phase basicities (ΔG) kcal/mole
Pyrrole (X-H^+)	–209.96	–205.07
Pyrrole (C_β–H^+)	–226.9	–221.38
Pyrrole (C_α–H^+)	–223.14	–216.99
Furan (X-H^+)	–206.45	–207.07
Furan (C_β–H^+)	–208.96	–208.33
Furan (C_α–H^+)	–203.31	–203.94
Thiophene (X–H^+)	–193.27	–193.27
Thiophene(C_β–H^+)	–210.21	–210.21
Thiophene(C_α–H^+)	–215.23	–214.6
Pyridine (X–H^+)	–222.13	–222.13
Pyridine (C_α–H^+)	–220.88	–220.88

RESULTS AND DISCUSSION

The gas-phase basicity of a molecule defined as negative free energy change (ΔG) of a protonation reaction like B+ $H^+ \leftrightarrow$ [BH^+]. (1). PA is defined in terms of negative enthalpy change (ΔH) associated with the same reaction at 298.15k temperature. Where B represent the molecules studied in the present work. Gas-phase PAs have been calculated as $H_{B1H}^+ - H_{B1}$, $H_{B2H}^+ - H_{B2}$, $H_{B3H}^+ - H_{B3}$, and $H_{B4H}^+ - H_{B4}$. In the similar way, gas-phase basicities (ΔG) of the same molecules have been calculated as $G_{B1H}^+ - G_{B1}$, $G_{B2H}^+ - G_{B2}$ $G_{B3H}^+ - G_{B3}$, $G_{B4H}^+ - G_{B4}$. Where B1= pyrrole, B2= furan, B3= thiophene, B4 = pyridine, and G = Total Gibbs free energy. The molecules studied are listed in **Table 1** along with their respective names and their different PA and gas-phase basicity values obtained due to protonation occurred at different sites (Cα, C_β, and X heteroatoms) at the lowest excited triplet state. In case of pyridine, H^+ preferentially attacked at N atom and gives more PA value (–222.13 kcal/mol). Protonation at ^{1}Cα carbon of pyridine provides little less PA value (–220.88 kcal/mol). Five-membered heteroatomic systems, pyrrole, furan, and thiophene have two different carbon sites attracting the incoming proton. We observed that, protonation can also occurred at X hetero atoms (X = N [pyrrole], O [furan] and S [thiophene]). According to calculated results, it has been seen that PA values due to protonation at Cα and C_β position are differ only by ±3.76 kcal/mol. PA of thiophene is predicted to be −215.23 kcal/mol and −210.21 kcal/mol for Cα and C_β protonation. PA values are obtained little lower for pyrrole and thiophene in their X-protonated complexes. However, protonation of furan occurred at hetero oxygen atom accompanied with −206.45 kcal/mol PA and provide O-C1 bond opened optimized geometry (optimized geometry I of **Figure 1**). The PA values are predicted to be −203.31 and −208.96 kcal/mol, due to protonation at ^{1}Cα and $^2C_\beta$ sites of furan.

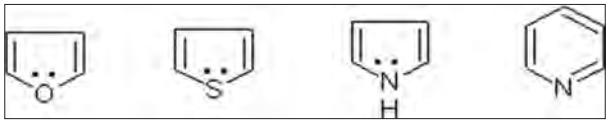


Figure 1: General chemical structure of studied molecules

Calculated gas-phase basicity (ΔG) results [**Table 1]** are found much closer to their PA values, in some cases two results are obtained almost identical. The ΔG values are obtained exactly same with their PA results for protonated complexes of pyridine, C_β and X- protonated complexes of thiophene. As per our results, PA and ΔG values are differs by ±4.89 to ±6.15 kcal/mol in pyrrole complexes. These differences are found to be much lower (±0.62–0.63 kcal/mol) in furan complexes and Cα complexes of thiophene.

In comparison to the ground state PA results, low-lying excited triplet state PA values of the studied FM heterocyclic molecules are obtained higher, in case of pyridine; PA value at this particular electronic state is predicted to be lower than the ground state result, which can be attributed to the phenomenon of redistribution of charges in the excited state.

In **Table 2**, we summarized the Mulliken atomic charges obtained on some specific atoms (protonation site) of the neutral and protonated complexes of the studied molecules. Partial atomic charges (natural charge) on added proton and ligand to proton charge transfer (q_{CT}) obtained from NPA procedure is tabulated in **Table 3**. The corresponding MPA values of charge transfer (Q_{CT}) are also included in **Table 2** for the sake of comparison. Both Q_{CT} and q_{CT} results indicate that there is a significant charge transfer from ligand to added proton. One might have expected the extent of charge transfer to parallel complex stability, but this not fulfilled in the present cases. The calculated charge transfer (Q_{CT} and q_{CT}) results provide same order of stability of the complexes of pyrrole, furan, and thiophene. It is Cα –H^+ ≥ C_β – H^+> X–H^+ for pyrrole and furan. In case of thiophene, we observed this order obtained as X–H^+> Cα –H^+ ≥ C_β – H^+.

Geometry of the five-member heteroatomic systems (pyrrole, furan, and thiophene) and SM heterocyclic pyridine have planar geometry at ground state with C_{2v} point group. The geometric parameters of all protonated complexes of the studied molecules have been tabulated in **Table 4a-c** and **5**. Protonation at heteroatom (X) of all the molecules provides [**Table 4a**] X–H^+ bond length 0.098Å to 1.39Å in the range. The < C–X–H^+ bond angle shows the variation in the range of 101.42–120.51° and dihedral angle τ (C_β–C_α-X–H^+) is observed 120.76 and 92.64° for pyrrole and thiophene

Table 1a: Different gas-phase proton affinities (ΔE) and basicities of pyrrole, furan, thiophene, and pyridine obtained from B3LYP/6-311G (d, p) method of calculation in ground state

Compounds	PA (kcal/mol)	Experimental PA values (kcal/mol)	Basicities (ΔG) kcal/mol	ExperimentalΔG values (kcal/mol)
Pyrrole (X–H^+)	–197.5	–209.98*	–190.09	–201.86*
Pyrrole (C_β–H^+)	–212.09		–205.82	
Pyrrole (C_α–H^+)	–217.7		–210.96	
Furan (X–H^+)	–173.8	–192.0*	–171.68	–187.22*
Furan (C_β–H^+)	–190.76		–189.75	
Furan (C_α–H^+)	–203.68		–189.75	
Thiophene (X–H^+)	–179.9	–194.97*	–177.39	–187.63*
Thiophene (C_β–H^+)	–194.15		–191.13	
Thiophene (C_α–H^+)	–204.8		–200.67	
Pyridine (X–H^+)	–232.8	–225.86*	–224.08	–218.25*

PA: Proton affinity

Table 2: Mulliken atomic charges (e) on some selected atoms of the free and protonated complexes of pyrrole, furan, thiophene, and pyridine in their low-lying triplet state and Charge transfer (Q_{CT}) obtained from MPA analysis.

Compounds	atom	Free molecule	(X- H^+) complex	Q_{CT}	Cα –H^+ complex	Q_{CT}	C_β- H^+ complex	Q_{CT}
Pyrrole	N	−0.424	−0.329		−0.279		−0.157	
	Cα	0.038			−0.03		-	
	$3C_\beta$	−0.143			-		−0.205	
	11_{H^+}	-	0.31	0.69	0.203	0.79	0.203	0.797
Furan	O	−0.293	−0.146		−0.162		−0.12	
	Cα	0.056			0.002		-	
	$2C_\beta$	−0.156			-		−0.187	
	10_{H^+}	-	0.3	0.7	0.217	0.78	0.22	0.78
Thiophene	S	0.172	0.562		0.571		0.556	
	Cα	−0.274			−0.373		-	
	$3C_\beta$	−0.067			-		−0.149	
	10_{H^+}	-	0.136	0.86	0.236	0.76	0.21	0.79
Pyridine	N	−0.201	−0.366				-	
	Cα	0.013					-	
	C_β	0.013					-	
	12_{H^+}	-	0.293	0.70			-	

*In case of pyridine, proton preferentially attacked at heteroatom (N) so charge on α or β carbon not given

Table 3: Partial atomic charges on H^+ion [qH^+] (in e unit) in different protonated complex obtained from NPA procedure and charge transfer (q_{CT}) from compound to added proton

Protonated complex	Charge on proton (qH^+)	Charge transfer (q_{CT})
Pyrrole (X–H^+)	0.237	0.763
Pyrrole (C_α–H^+)	0.145	0.855
Pyrrole (C_β–H^+)	0.168	0.832
Furan (X–H^+)	0.25	0.75
Furan (C_α–H^+)	0.143	0.857
Furan (C_β–H^+)	0.179	0.821
Thiophene (X–H^+)	0.142	0.858
Thiophene (C_α–H^+)	0.149	0.851
Thiophene (C_β–H^+)	0.168	0.832
Pyridine (X–H^+)	0.213	0.787

*Charge transfer calculated as normal charge of proton ([1] - qH^+)

which are found to be 179.99° and 179.97° in furan and pyridine, respectively. In Cα – H^+ complexes [**Table 4b**], the bond distance between Cα and excess proton (H^+) is found to be same (1.09Å) in each case. The <C-Cα-H^+ bond angle in all complexes remains in between 110.8 and 114.17°, and dihedral angle τ(C–C–Cα–H^+) has a variation in the range of 115.51–120.3°. **Table 4c** highlighted the structural parameters of C_β - protonated complexes. We observed, the C_β–H^+ bond length is identical (1.1Å) in each complex. Bond angle (<C–C_β–H^+) and dihedral angle (C–C–C_β–H^+) of these complexes vary within 110.65–112.03° and - 122.91–121.39°, respectively.

Comparison of the structural parameters of optimized unprotonated and various protonated complexes of the studied molecules demonstrate the large effects of protonation on geometry of the molecules. We observed, geometrical parameters are varies widely with the variation of the site of protonation [**Table 5**]. Optimized geometry of various protonated complexes is presented in **Figure 2**.

Optimized geometry of X– H^+ complexes

Protonation at X atom accompanied with the elongation of C4-X bond distance in pyrrole (0.07Å), large contraction is observed in furan (0.11Å) while it remains almost same in thiophene (±0.01Å). The C5-X bond distance in pyridine is also contracted by 0.07Å. C1-X bond length in pyrrole and pyridine protonated species is estimated 1.49Å and 1.46Å which are 0.07Å larger than the unprotonated molecules. Proton attacked at the O atom of furan leads to the O-C1 bond breaking mechanism, and C1-O bond length is observed enormously large 2.89Å.

In addition, C1-C2 bond length, in pyrrole and pyridine protonated systems, is increased by 0.03 and 0.1Å whereas, in furan and thiophene, this bond distance is decreased by 0.14 and 0.02Å. Concerning the bond angles (<C2–C2–C3), a larger alteration has been observed in furan (106° [neutral] to 125° [protonated]), in pyrrole, thiophene, and pyridine systems, minor alteration (0–3°) is found for this particular bond angle. Taking care of the (C1–X–C4) bond angle of three FM heterocyclic species, a huge contraction has been found in furan (105° [neutral] to 82° [complex]) whereas in pyrrole, thiophene, and pyridine, it remains almost equal (1–4° change observed).

Optimized geometry of Cα–H^+ complexes

In comparison with geometry parameters of optimized unprotonated molecules [**Figure 3**], C1-X bond distances are elongated by 0.06Å, 0.09Å, 0.07Å, and 0.02Å in

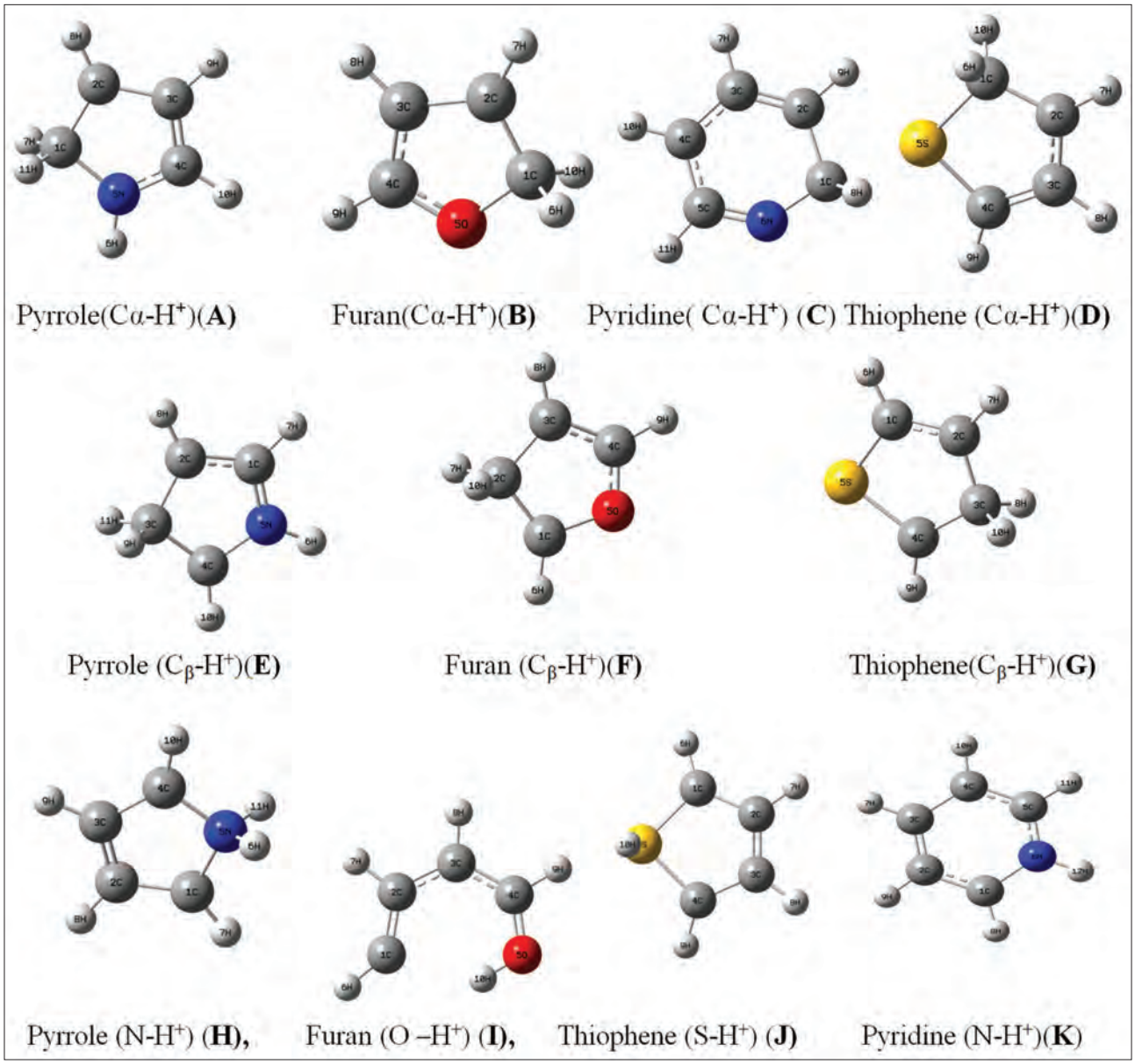


Figure 2: Various protonated optimized complexes of the studied heterocyclic molecules at low-lying excited triplet state

Table 4a: Some important geometrical features [bond length in Å, bond angle in degree (°), dihedral angle (τ) in degree] of the protonated complexes of pyrrole, furan, thiophene, and pyridine in the ground state

Complexes	X-H⁺ in Å	<Cᵅ-X-H⁺ in°	τ (C_β-C_α-X-H⁺)
Pyrrole (X-H⁺)	1.03	112.05	120.76
Furan (X-H⁺)	0.98	113.2	0.014 and 179.99
Thiophene (X-H⁺)	1.39	101.42	92.64
Pyridine (X-H⁺)	1.01	120.51	179.97

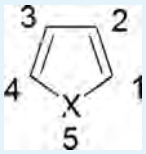
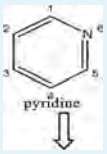
Table 4b: Some important geometrical features [bond length in Å, bond angle in degree (°), dihedral angle (τ) in degree] of the protonated complexes of pyrrole, furan, thiophene, and pyridine in the ground state

Complexes	C_α-H⁺ in Å	<C-C_α-H⁺ in°	τ (C-C-C_α-H⁺)
Pyrrole (C_α-H⁺)	1.09	114.17	117.69
Furan (C_α-H⁺)	1.09	115.45	115.51
Thiophene (C_α-H⁺)	1.09	113.9	−117.59
Pyridine (C_α-H⁺)	1.09	110.8	120.3

Table 4c: Some important geometrical features [bond length in Å, bond angle in degree (°), dihedral angle (τ) in degree] of the protonated complexes of pyrrole, furan, thiophene, and pyridine in the ground state

Complexes	C_β-H^+ in Å	<C-C_β-H^+ in°	τ (C-C-C_β-H^+)
Pyrrole (C_β-H^+)	1.1	112.03	−121.11
Furan (C_β-H^+)	1.1	111.71	121.39
Thiophene (C_β-H^+)	1.1	110.65	−122.91
Pyridine (C_β-H+)	-	-	-

Table 5: Low-lying excited triplet state optimized geometry parameters of unprotonated pyrrole, furan, thiophene, and pyridine and their protonated complexes. Calculated as B3LYP/6-311 (G) d, P level of theory. Bond lengths are given in angstrom unit (Å), bond angles are in degree (°)

	**B1 (X-H^+)**	**B2(X-H^+)**	**B3(X-H^+)**		B4(X-H^+)
C1-C2	1.47 (1.44)	1.35 (1.49)	1.44 (1.46)	C1-C2	1.46 (1.36)
C4-X	1.49 (1.42)	1.28 (1.39)	1.78 (1.79)	C5-X	1.32 (1.39)
C1-X	1.49 (1.42)	2.89* (1.41)	1.78 (1.79)	C1-X	1.46 (1.39)
<C1-C2-C3 109 (108)	125 (106)	113 (113)	<C1-C2-C3 122 (119)		
<C1-X-C4	103 (107)	82 (105)	89 (88)	<C1-X-C5	120 (117)
	B1 (Cα-H^+)	B2 (Cα-H^+)	B3 (Cα-H^+)		B4 (Cα-H^+)
C1-C2	1.50	1.48	1.43	C1-C2	1.52
C4-X	1.36	1.31	1.75	C5-X	1.27
C1-X	1.48	1.5	1.86	C1-X	1.41
<C1-C2-C3 108	106	114	<C1-C2-C3	122.4	
< C1-X-C4	114	111	94	<C1-X-C5	133.9
	B1 (C_β-H^+)	B2 (C_β-H^+)	B3 (C_β-H^+)		
C1-C2	1.43	1.49	1.39		
C2-C3	1.5 (1.34)	1.48 (1.34)	1.49 (1.34)		
C3-C4	1.5 (1.47)	1.42 (1.42)	1.49 (1.46)		
C4-X	1.43	1.28	1.81		
C1-X	1.31	1.43	1.68		
<C1-C2-C3	109	100	115		
<C1-X-C4	111	108	91		

*C1–5O bond opening, Bond distance observed 2.89Å. **Cα-H^+ complexes, protonation occurred at C1 and C_β-H^+ complexes, protonation occurred at C3. Values are in the parenthesis obtained from unprotonated optimized species. B1: Pyrrole, B2: Furan, B3: Thiophene, B4: Pyridine, X: N, O and S

protonated complexes of pyrrole, furan, thiophene, and pyridine, respectively. On the other hand, C5-X bond length is largely shortened (0.12Å) in pyridine and 0.04Å to 0.06Å contractions have been observed in three FM heterocyclic complexes. In addition, C1-C2 bond distance obtained higher in pyrrole (0.06Å), and pyridine (0.16Å) protonated systems, but in thiophene and furan complexes, C1-C2 bond distance is shortened by 0.03Å and 0.01Å, respectively. No such remarkable alteration has been found of C1-C2-C3 bond angles in all four heterocyclic protonated species relative to the unprotonated molecules. In contrary, large changes related to C1-X-C4 bond angle in FM heterocyclic protonated systems and C1-X-C5 bond angle of pyridine, which have been estimated to be 114°, 111°, 94°, and 133° in pyrrole, furan, thiophene, and pyridine, respectively.

Optimized geometry of C_β–H^+ complexes

We have estimated the C4-X bond length 1.43Å and 1.81Å in pyrrole and thiophene protonated complexes, which are slightly higher than a corresponding bond length in neutral systems. Large contraction (0.11Å) of this bond is found in furan complex compared to its unprotonated species (1.28Å). The C1-X bond length in both protonated pyrrole and thiophene is shortened by 0.11Å, and it is slightly elongated (0.02Å) in furan. Protonation at C_β do not effect effectively on C1-C2 bond distances of pyrrole and furan, but in case of thiophene complex, C1-C2 distance

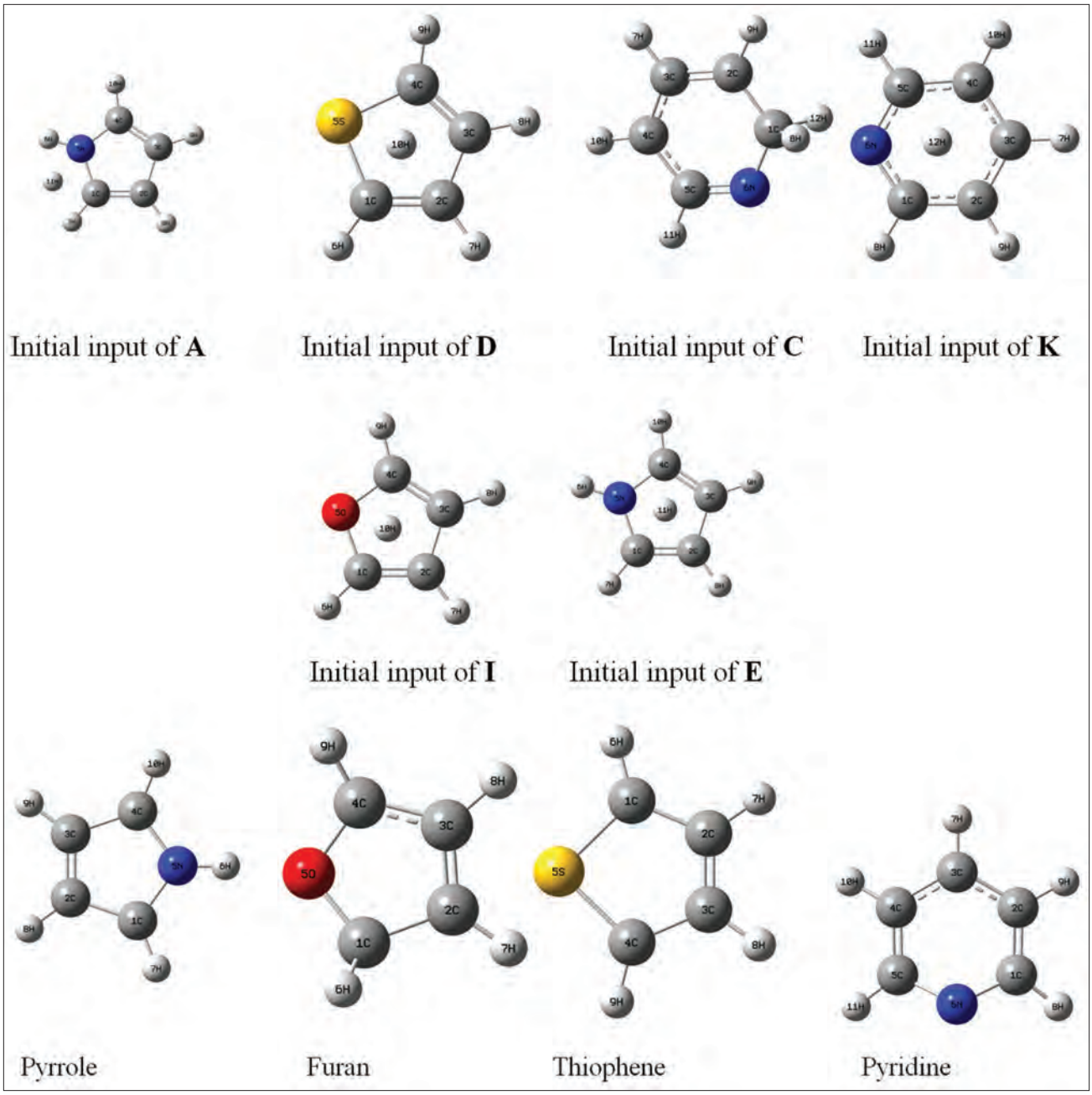


Figure 3: Un-protonated optimized geometries of the studied heterocyclic molecules (Optimized result are obtained from Gaussian 09 Programme)

decreased by 0.07Å. As per our estimated values, no large changes have been found in <C1-C2-C3 bond angles in C_{β}-H^{+} complexes of pyrrole and thiophene (1–2°), in furan complex, it shifted 106–100°. The <C1-X-C4 bond angles are in the range of 91–111° which are found 88–107° in optimized unprotonated molecules [**Figure 3**].

Electronic transition energies

There are plenty of reports[37-40] about different electronic transition energies of these five or SM heterocyclic molecules or their protonated complexes presented in literature. In this theoretical study, we have determined the adiabatic transition energies ($^1S_0 \rightarrow T_1$) as state energy difference. The results have been applied to find out the kind of shifts proton induced shifts (PIS) due to protonation. These results are tabulated in **Table 6a-c**. On the basis of our calculated results, the PIS are predicted to be redshift in all cases. These data refer to the gas-phase protonation of the isolated base molecules without any additional effects caused by solvation.

We have searched for the possibility of the existence of a correlation with a single global parameter of the entire molecule in the relevant state. As the global parameter, we have chosen the hardness (η). The absolute hardness (η) is defined by (I–A)/2. Where I is the vertical ionization energies and A mean the vertical electron affinity. According to Koopmans's theory, $I = -\epsilon_{HOMO}$ (HOMO energy) and $A = -\epsilon_{LUMO}$ (LUMO energies). Therefore, $\eta = (\varepsilon_{LUMO} \sim \varepsilon_{HOMO})/2$. **Table 7** contains the values

Table 6a: Computed adiabatic transition energies ($^1S_o \rightarrow T^1$) (hartree) and proton induced shifts (PIS, hartree) in the lowest excited triplet state of X – protonated complexes. (X=N, O, S)

Molecules ($^1S_o \rightarrow T^1$)	Transition energy		
	B	BH^+	PIS
B_1 (X=N)	0.1417	0.093	−0.0487
B_2 (X=O)	0.1254	0.06	−0.0654
B_3 (X=S)	0.1185	0.0864	−0.0321
B_4 (X=N)	0.1420	0.1389	−0.0031

Table 6b: Computed adiabatic transition energies ($^1S_o \rightarrow T^1$) (Hartree) and proton induced shifts (PIS in hartree) at the lowest excited triplet state of Cα-protonated complexes

Molecules ($^1S_o \rightarrow T^1$)	Transition energy		
	B	BH^+	PIS
B_1 (X=N)	0.1417	0.106	−0.0357
B_2 (X=O)	0.1254	0.113	−0.0124
B_3 (X=S)	0.1185	0.087	−0.0315
B_4 (X=N)	0.1420	0.0456	−0.096

Table 6c: Computed adiabatic transition energies ($^1S_o \rightarrow T^1$) (hartree) and proton induced shifts (PIS in hartree) in the lowest excited triplet state of Cβ-protonated complexes

Molecules ($^1S_o \rightarrow T^1$)	Transition energy		
	B	BH^+	PIS
B_1 (X=N)	0.1417	0.091	−0.0507
B_2 (X=O)	0.1254	0.086	−0.0394
B_3 (X=S)	0.1185	0.079	−0.0395
B_4 (X=N)	0.1420		

Table 7: Computed hardness (η) = (I–A)/2= (ε_{LUMO} ~ ε_{HOMO})/2 of the free molecules in the lowest excited triplet state

Molecules	ε_{HOMO} (hartree)	ε_{LUMO} (hartree)	η (ev)
B_1 (X=N)	−0.0722 (−0.2124)	0.0469 (0.0365)	1.62 (3.38)
B_2 (X=O)	−0.1341 (−0.2347)	0.0244 (0.0067)	2.15 (3.28)
B_3 (X=S)	−0.1228 (−0.2425)	0.0069 (−0.0182)	1.76 (3.05)
B_4 (X=N)	−0.1437 (−0.2609)	−0.01391 (−0.0348)	1.765 (3.07)

of HOMO and LUMO energies of the studied molecules and calculated hardness at lowest-excited triplet state along with the respective ground state values. From **Table 7**, it is seen that the triplet state η values are lower compared to their ground state which favor protonation, in general.

In comparison to the ground state singlet computed values, the net atomic charge on heteroatom of the neutral heterocyclic molecules little bit increased in three FM systems, while in case of B4 it decreases slightly (–0.292e–0.201e). This indicate that both pre- and post-protonation correlations with local charge densities in the immediate neighborhood of the protonation site are weak.

CONCLUSION

The PA and different electronic properties of pyrrole, furan, thiophene, and pyridine have been investigated extensively at low-lying excited triplet state. From the present theoretical study, it can be well concluded that the gas-phase PAs of the pyrrole, furan, thiophene, and pyridine are spontaneous. PA values are predicted to be higher in all three FM heterocyclic systems relative to their ground state. Little deviation has been observed in pyridine where PA value obtained little less (~10 kcal/mol) compared to the ground state. Protonation at Cα and C_β sites provides the more stable protonated complexes of pyrrole, thiophene than the N or S protonated. Proton attacked at O atom of neutral furan gives ring-opened (O-C1 bond breaking) planar structure (Torsion angle 179.99°). Protonation leads to loss of planarity for FM hetero systems (except O-protonated furan) whereas pyridine retained with planer geometry even after protonation (N-protonated). Protonation at any sites (C or X = N, O, S) inserts massive effect on geometrical features of the molecules. PIS are redshifts in all cases. The overall reactivity is fully explained by distant atom contribution in addition to the contribution from the heteroatoms of the free bases.

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