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THE COMPARATIVE BASICITIES, Li^+AND Na^+CATION AFFINITIES WITH A SERIES OF HETEROCYCLIC MOLECULES: A DFT STUDY

Biswarup Mandal[1], Umasankar Senapati[2,*]and Kalipada Bankura[3]
[1]Department of Chemistry, Sitananda College, Nandigram,
Purba Medinipur, 721631, West Bengal, India.
[2]Department of Chemistry, Belda College, Belda,
Paschim Medinipur, 721424, West Bengal, India.
[3]Department of Chemistry,TamraliptaMahavidyalaya,
Tamluk, Purba Medinipur, West Bengal., India.
*E-mail: senapatiumasankar@gmail.com

ABSTRACT

Ground state gas phase proton affinities, alkali metal cation (Li^+, Na^+) affinities and basicities of pyrrole, furan, thiophene and pyridine have been calculated computationally with the help of DFT /B3LYP method of calculation at hybrid triple zeta 6-311G(d,p) basis set level. Different binding sites of pyrrole, furan and thiophene for protonation are observed. Proton affinity (PA) value of $C\alpha$–H^+ complexes of pyrrole, furan and thiophene are found to be higher compared to C_β–H^+ and X–H^+ complexes (X= N, O, S). In case of pyridine, protonation is found to occur at heteroatom (N) and the most stable protonated complex is formed. Results obtained in this calculation ~~shows~~ good agreement with the experimental values. Alkali metal cation (Li^+, Na^+) affinity and basicity of the same molecules have been calculated at the same level of theory. Pyridine exhibits the highest affinity for Li^+ and Na^+ cation. The electronic properties of the complexes indicate that polar co-valent sigma bond is formed by a proton with the binding site of the corresponding molecule whereas alkali metal cation (Li^+,Na^+) –free molecule interactions are predominantly of an ion-dipole attraction and the ion-induced dipole interaction as well rather than a covalent interaction.Calculated proton and metal cation affinities are sought to be correlated with some of the computed system parameters like the calculated net charge on the binding atom of the free molecules and with the net charge on proton, Li^+ and Na^+ of the protonated, lithium and sodium complexes.

Keywords: DFT B3LYP, computationally, gas phase, proton affinity, alkali metal cation

INTRODUCTION

Acid-base interactions are of prodigious importance in chemistry. Quantitative studies in the gas phase provide the inherent acid-base properties free from interference due to solvent molecules and counter ions. The majority of the extensive studies concern about different gas phase proton transfer equilibria.[1]Protonation reactions are very important in a various organic reaction mechanism and it plays significant roles in bio-molecular processes.[2] Though mass spectrometric studies can explain easily the thermodynamic and kinetic properties of protonation and deprotonation process but it is difficult to recognize the structural behavior, sometimes more than one results are obtained.[3]The heterocyclic molecules have very recently drawn much attention due to their “shifted PKa values” upon complexation to metal ions, because it can rationalize the existence of nucleobases of differing protonation state at physiologicalP^H.[4]The reactivity and positional selectivity for electrophilic substitution reactions of five-membered N, O and S heterocyclic compounds were studied quantitatively.[5,6] It is also known that heterocyclic compounds containing N, O or S hetero atoms (X) increase the reactivity of α–carbon (next to hetero atom) and usually form stable complexes. It was also seen[5, 6] that the order of the reactivity (N–hetero > O–hetero > S–hetero) does not maintain the sequence of positional selectivity (product ratio of α andβ substituted complexes), it appears as O–hetero > S–hetero > N–heterocyclic compounds. In the

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present work we have optimized the H^+– heterocyclic (pyrrole, furan, thiophene) complexes thrice (by changing the position of the proton in initial input) to investigate proper binding sites for protonation and the most stable protonated complexes. Interestingly, in each heterocyclic molecule, more than one protonation sites (heteroatom, $C_\alpha$and C_β) are found. Lithium and sodium complexes of these molecules are optimized in two different ways. At first, lithium and sodium are directly bonded to X atom and secondly, they are non-bonded in the initial input. We observethat,Li^+ and Na^+have two possible positions relative to hetero cyclic molecules (pyrrole, furan, thiopheneand pyridine).A number of experimental and theoretical studies were performed[7-10] with different heterocyclic molecules. To the best of our knowledge, a systematic and comprehensive comparative theoretical investigation on gas-phase basicity, proton affinity (PA), alkali metal cation affinity and basicity of the above-mentioned molecules is still lacking. OttoDopferet al[11]have reported on protonation of heterocyclic molecules. Interaction of hydrogen molecules with complexes of lithium cation and N-containing heterocyclic anions have been studied earlier.[12]Some electronic properties of pyridine, pyrimidine, pyrazineandpyridazine have been studied[13] before by the DFT method. $LiNH_2$ interaction with pyridine, furan and thiophene havebeen reportedrecently.[14]Stabilities and structures of five membered heterocyclic molecules containing N, O and S hetero atom were investigated by Hikora et al.[15]In an effort to comprehend the nature of bonding and origin of variation in the relative magnitude of the basicities, lithium cation affinities, basicities (LCA, LCB) and sodium cation affinities, basicities (SCA, SCB) to be expected in a series of heterocyclic compounds (pyrrole, furan, thiophene and pyridine), the most biologically important and deadly poisons, we havecomputationally studied the gas phase basicities, LCA, LCBand SCA, SCB of the above said molecules.The comparative studies of proton affinity, Li^+, Na^+ affinity and basicity of these heterocyclic compounds in the ground state have been performed by the DFT/ B3LYP method using 6-311G(d,p) basis set.

Alkali metal ions were the first metal cations to be considered in the gas phase for their coordination properties. Because of their relatively easier production under vacuum. On the contrary with the transition metal ions, their reactivity towards ligands is rather simple, in general, they form adducts, or clusters that can be considered as ions “solvated” by one or several ligands.[16] In recent times, the basicities of a series of substituted crotonaldehyde and acetophenone in their ground state were reported.[17,18]The gas phase Li^+ and Na^+ affinities of a series of substituted crotonaldehyde and acetophenone in their ground state were also reported in previous studies.[19-21] Gas phase methods[22-30]have the advantage for determining the intrinsic ground state, acid-base properties in the absence of complicating effect of solvation. Therefore the present study has been undertaken to evaluate few important data in the gas phase.

The intention of the present work is not only to assemble information of the basicities, proton affinities, Li^+ and Na^+ affinities of the above said heterocyclic molecules by means of computational calculation but also to observe the geometrical features of their protonated, lithium, and sodium complexes.We also report more than one result about protonation and alkali metal cation interaction site(s) observed in our study.

Here we have analyzed the PA, LCA and SCA values to understand whether the pre-complex charge distribution local to the molecules or post-complex relaxation of charge density or both are important for explaining the overall gas phase basicity and affinities of the molecules in the ground state.

Since the ion-molecule complexes are involved in molecular recognition process[32]and help in removing metal cations from contaminated media. These studies may be used to gain insight into many important biological processes,[33-36] electron transfer process[37, 38]and more complicated biological system.

In this work, we have looked into the possible origin of the small shift in the proton, Li^+ and Na^+ affinities on the heterocyclic molecules and also focus our attention on the nature of bonding in protonated and alkali metal complexes.

EXPERIMENTAL

Standard quantum mechanical calculations (DFT)were performed at B3LYP/6-311G(d,p) level[39] using Gaussian O9W program package.[31] In all calculations, complete geometry optimization has been carried out on the free molecules and on their protonated, $Li^+$and Na^+ complexes. It has been shown[40] that the B3LYP triple zeta calculations well reproduce the thermodynamic values of ion-molecule interactions with higher accuracy with respect to the experimental results. So this method is appropriate as an alternative to the traditional *ab initio* method for studying these types of interactions. Frequencies were calculated at same levels. No scaling was applied to obtain DFT frequencies for the calculation of thermodynamic parameters (at 298.15°K) using standard procedures. Natural population analysis (NPA) has been applied to evaluate the partial atomic charge on atoms.

Furan ThiophenePyrrole Pyridine

Fig.-1: General chemical structure of studied molecules

RESULTS AND DISCUSSION

Gas phase proton affinity(PA), Lithium cation affinity (LCA) and Sodium cation affinity (SCA) is defined as negative value of enthalpy change (ΔH) of the following reactions:

$B + H^{+} \leftrightarrow [BH^{+}]$ (1)
$B + Li^{+} \leftrightarrow [BLi^{+}]$ (2)
$B + Na^{+} \leftrightarrow [BNa^{+}]$ (3)

Where, B represents the corresponding hetero cyclic molecule.

Gas phase basicity, Lithium cation basicity (LCB), Sodium cation basicity (SCB) is the negative value of free energy change (ΔG) of the same reaction 1, 2 and 3.Gas phase proton affinities have been calculated as $[H_{B1H}^{+} - H_{B1}]$, $[H_{B2H}^{+} - H_{B2}]$, $[H_{B3H}^{+} - H_{B3}]$, $[H_{B4H}^{+} - H_{B4}]$.
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. H= Total enthalpy and G = Total Gibbs free energy at 298.15k.
Gas phase alkali metal cation affinities (LCA and SCA) and basicities (LCB and SCB) have been calculated as:

$MCA = [H_{BM}^{+} - (H_{B} + H_{M}^{+})]$ (4)
$MCB = [G_{BM}^{+} - (GB + G_{M}^{+})$ (5)

MCA = Metal cation affinity and MCB = Metal cation basicity. M^{+} = Lithium and sodium. B represents the hetero cyclic molecules B1, B2, B3 and B4. Table-1 summarises the proton affinity and basicity values of the studied molecules obtained in this theoretical calculation.
In the present work, a significant incident is arisen with more than one protonation sites for the 3 five-membered heterocyclic molecules, protonation occurred at heteroatom and also at C_{α} and C_{β} position. C_{α}–H^{+} complexes of pyrrole, furan and thiophene are obtained as most stable compared to C_{β}–H^{+} and X–H^{+} complexes (X= N, O and S).In case of pyridine we observe that H^{+} prefers to bind with heteroatom (N) to form a stable protonated complex. That means C_{α} protonated complexes (for B1, B2, B3) have reached to the global minima potential energy surface (PES) whereas C_{β} and X–protonated complexes corresponds to the comparatively higher energy local minima. For B4, X–protonated species corresponds to the global minima PES. From Table-1 we observe that, both PA and ΔG results of C_{α} and C_{β} protonated species are seen to be much closer to each other. The difference of PA values between C_{α} and C_{β} for pyrrole is <5 kcal/mole. It is slightly higher in case of furan (≈ 13kcal/mole) and thiophene (<10 kcal/mole). Very interestingly we have observed, PA values obtained in $C_{\beta} - H^{+}$ complexes are nearer to the reported results, the difference are only ± 2.11, ± 1.24 and ± 0.82 kcal/mole for pyrrole, furan and thiophene

respectively. Gas phase PA value of pyridine (–232.8 kcal/mole) is also found to be well agreed with the experimental data (–225.86 kcal/mole, Calculated gas phase basicities are in ~~a~~ good correspondence to the experimental ones (Table-1). In respect to the obtained ΔG values of the $C_α$–H^+ complexes, the differences are ±9.1, ±2.53, ± 13.04 kcal/mole for B1, B2 and B3 respectively and it is ± 5.83 kcal/mole for B4. The calculated difference in gas phase basicities for protonation at $C_α$ and $C_β$ site(s) are ± 5.14, ± 0.0 and ± 9.14 kcal/mole for B1, B2 and B3 respectively.

Considering all PA values of different protonated complexes of pyrrole, furan and thiophene, PA order can be written as $C_α$– H^+> $C_β$– H^+> X– H^+. With the inclusion of pyridine in the series, PA order of the molecules ranked as pyridine > pyrrole > thiophene > furan. This order of stability (PA) of the $C_α$, $C_β$and X protonated complexes are well supported by NPA results. Partial NPA charges on binding proton in the complexes obtained from NPA procedure are summarised in Table-3.

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

Compounds	ΔE (kcal/mole)	Experimental ΔE values (kcal/mole)	ΔG kcal/mole	Experimental ΔG values (kcal/mole)
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*
Thipohene ($C_β$- H^+)	–194.15		–191.13	
Thiophene ($C_α$ – H^+)	–204.8		–200.67	
Pyridine(X-H^+)	–232.8	–225.86*	–224.08	–218.25*

X= N, O, S. * Ref. Hunter, E. P.; Lias, S. G. 1998, *J. Phy. Chem.* 27(3), 413-656.

Table-2: Mulliken atomic charges (e) on some selected atoms of the free and protonated complexes of pyrrole, furan, thiophene and pyridine.

Compound	atom	Free compound	(X- H^+) complex	Cα –H^+ complex	$C_β$- H^+ complex
Pyrrole	N	–0.327	–0.331	–0.304	–0.258
	Cα	0.042	0.0321	–0.0479	----
	$3C_β$	–0.174	–0.0615	----	–0.251
	11_{H+}	--	0.3202	0.223	0.22
Furan	O	–0.229	–0.2787	–0.152	–0.102
	Cα	0.065	0.161	–0.0143	----
	$2C_β$	–0.165	–0.114	----	–0.256
	10_{H+}	--	0.392	0.237	0.244
Thiophene	S	0.263	0.552	0.49	0.573
	Cα	–0.289	–0.269	–0.38	----
	$3C_β$	–0.082	–0.0094	----	–0.187
	10_{H+}	--	0.1839	0.251	0.234
Pyridine	N	– 0.292	–0.316	----	----
	Cα	----	0.213	----	----
	$C_β$	–0.177	–0.198	----	----
	12_{H+}	----	0.294	----	----

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

The values of q_{CT} indicate that there is a significant transfer of charge from ligand to interacting proton. The extent of charge transfer is quite similar to the complex stability for pyrrole and furan. A minor discrepancy is observed in case of thiophene where q_{CT} values obtained are little higher (0.798e) in X–

H^+complex compared to C_α–H^+ complex. The q_{CT} values for pyrrole protonated complexes (C_α, C_β and N) are 0.729e, 0.694e and 0.544e. It is 0.724e, 0.678e and 0.413e in furan complexes and 0.701e, 0.682e and 0.798e in thiophene complexes. The origin of such discrepancy needs a further exploration in case of thiophene complexes. Table-2 summarised the Mullikan charges on some specific atom of the free molecules and their different protonated complexes. It is seen that,the charge on proton binding atom is slightly increased in complexes relative to their corresponding free molecules, that means they favor~~s~~ protonation according to this particular point of view.Mullikan charge (e) on hetero atom (X) in the X-H^+ complexes vary in the range of 0.552e to –0.331e, Charge on C_α in C_α-H^+ complexes has a variation in the range of –0.0143e to –0.38e, in case of C_β–H^+ complexes, –0.187e to –0.256e of Mullikan charges are obtained on$C_\beta$atom. These Mullikan charges obtained in this calculation do not correlate properly with the complex stability or PA value of the corresponding complex. Our results suggest that,results obtained in Mullikan population analysis (MPA) are not very reliable to predict the exact protonation site(s) of the molecules.

The gas phase lithium and sodium cation affinity and basicity values of studied molecules are collected in Table-4. LCA and SCA's are calculated following equation 4, and LCB and SCB values are calculated with the help of equation 5.Calculated DFT results show~~s~~ that, both LCA (–48.25kcal /mole) and SCA (–33.82 kcal/mole) values are observed highest for pyridine then it followed by pyrrole (LCA = –42.79 kcal/mole, SCA= –28.17 kcal/mole), thiophene (LCA = –39.79 kcal/mole, SCA= –25.85 kcal/mole) and furan (LCA = – 32.37kcal/mole, SCA= –21.64 kcal/mole). On the basis of calculated LCA and SCA values, lithium and sodium complex stability of the studied heterocyclic molecules stand in the order N– hetero > S– hetero > O– hetero. In the present study it is pyridine > pyrrole > thiophene > furan.As per result obtained in this work, the metal cation affinities or metal cation basicities are much lower than proton affinities and gas phase basicities. But the order of metal cation affinity and basicity of the molecules are observed same as PA order.

Table-3: Partial atomic charges on H^+ ion [q_{H^+}] (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 (q_{H^+})	Charge transfer (q_{CT})
Pyrrole (X– H^+)	0.456	0.544
Pyrrole (C_α– H^+)	0.271	0.729
Pyrrole (C_β– H^+)	0.306	0.694
Furan (X–H^+)	0.587	0.413
Furan (C_α–H^+)	0.276	0.724
Furan (C_β- H^+)	0.322	0.678
Thiophene (X– H^+)	0.202	0.798
Thiophene (C_α– H^+)	0.299	0.701
Thiophene (C_β– H^+)	0.318	0.682
Pyridine (X– H^+)	0.44	0.56

*Charge transfer calculated as [Normal charge of a proton (1) – q_{H^+}]

Table-4: Ground state gas phase lithium cation affinities (LCA), basicities (LCB) and sodium cation affinities (SCA), basicities (SCB) of pyrrole, furan, thiophene and pyridine obtained from B3LYP/ 6-311G (d,p) method of calculation.

Compounds	LCA	LCB	SCA	SCB
	Kcal/mole	Kcal/mole	Kcal/mole	Kcal/mole
Pyrrole	–42.79	–35.2	–28.17	–21.38 (–14.4)
Furan	–32.37	–28.8	–21.64	–18.51
Thiophene	–39.59	–31.24	–25.85	–18.32
Pyridine	–48.25	–40.97	–33.82	–26.79 (–20.4)

*Values noted in the parenthesis are experimental results

Partial NPA charges on alkali metal cation (q_{Li+} and q_{Na+})of the metal complexes are summarised in Table-5. ΔQ_{Li}^{+} and ΔQ_{Na}^{+}valuesindicate the fact of a significant charge transfer from ligand to the metal cation. It may also be expected that, there will be a good correlation between the extent of charge transfer and complex stability or metal cation affinity, but this is not found properly, instead, the NPA results produce stability order as pyrrole> thiophene > pyridine > furan for lithium complexes. In case of sodium complexes, this order appears as pyrrole ≥ pyridine > thiophene > furan.

Charges on the atom obtained from both MPA and NPA procedure tend to suggest that, two different Lewis acids H^+ and alkali metal cation (Li^+ and Na^+) shows to the contrary in nature of bonding with the ligand. Proton adds to the molecules gives a covalent sigma(σ) bondwith extensive charge transfer where H^+ retains with 0.202 to 0.587 unit of NPA charge. On the other hand ,thebond formed by alkali cations (with its filled 1S shell) is largely ionic in nature. Thus the interactions are ion-dipole and ion induced dipole rather than covalent where Li^+ cation retains with 0.896 to 0.975 e and Na^+ contain 0.95e to 0.98e of positive charge in the complexes.

Some geometrical parameters for protonated and alkali metal (Li^+ and Na^+) complexes of the heterocyclic compounds are summarised in Table-6.

Table-5: Partial atomic charges on metal cation [q_{Li}^{+} and q_{Na}^{+}] (in e unit) in different alkali metal complexes and ligand to metal charge transfer ($\Delta Q_{Li}^{+}$and(ΔQ_{Na}^{+}) obtained from NPA procedure.

Compounds	Li^+ complex	Charge transfer (ΔQ_{Li}^{+})	Na^+ complex	Charge transfer (ΔQ_{Na}^{+})
	q_{Li}^{+}		q_{Na}^{+}	
Pyrrole	0.896	0.104	0.965	0.035
Furan	0.975	0.025	0.98	0.02
Thiophene	0.93	0.07	0.95	0.05
Pyridine	0.96	0.04	0.967	0.033

*Charge transfer calculated as [Normal charge of a metal cation (1) – q_M^{+}] M = Lithium and Sodium.

Table-:6 Some important geometrical features [bond length in Å , the bond angle in degree, dihedral angle (τ) in degree] of the protonated and alkali metal (Li^+ and Na^+) complexes of pyrrole, furan, thiophene and pyridine in the ground state.

6a: ($X–H^+$) complexes

Complexes	$X–H^+$	$< C_\alpha–X–H^+$	$\tau\ (C_\beta–C_\alpha–X–H^+)$
Pyrrole ($X–H^+$)	1.028	111.19	+120.53, – 120.52
Furan ($X–H^+$)	0.976	119.92	+ 146.38, –146.34
Thiophene ($X–H^+$)	1.362	99.70	+105.85, –105.92
Pyridine ($X–H^+$)	1.10	118.37	+180.01, – 180.0

6b: (C_α -H^+) complexes:

Complexes	$C_\alpha–H^+$	$< C–C_\alpha–H^+$	$\tau\ (C–C–C_\alpha–H^+)$
Pyrrole ($C_\alpha–H^+$)	1.09	113.0	118.6
Furan ($C_\alpha–H^+$)	1.09	114.7	116.8
Thiophene ($C_\alpha–H^+$)	1.09	112.7	–119.4
Pyridine ($C_\alpha–H^+$)	1.11	110.0	126.7

6c: (C_β–H) Complexes:

Complexes	$C_\beta–H^+$	$< C– C_\beta –H^+$	$\tau\ (C–C– C_\beta –H^+)$
Pyrrole ($C_\beta –H^+$)	1.10	113.6	–120.01
Furan ($C_\beta–H^+$)	1.102	114.7	119.58
Thiophene ($C_\beta –H^+$)	1.103	112.8	–124.5
Pyridine ($C_\beta –H^+$)	----	---	----

6d: ($X–Li^+$) complexes:

Lithium complexes	$X–Li^+$	$< C–X–Li^+$	$\tau\ (C–C– X–Li^+)$

Pyrrole	2.19	73.67	62.97
Furan (In-plane)	1.84	126.87	179.7
Furan (out-of-plane	2.16	75.15	66.47
Thiophene (out of plane)	2.46	64.11	61.74
Thiophene (in-plane)	2.33	133.38	179.99
Pyridine	1.91	121.12	179.99

6e: ($X–Na^+$) complexes:

Sodium complexes	$X–Na^+$	$< C–X–Na^+$	τ ($C–C– X–Na^+$)
Pyrrole	2.87	73.16	– 63.14
Furan	2.23	126.89	179.99
Thiophene	2.92	67.76	66.80
Pyridine	2.3	121.27	180.0

Protonated complexes of pyrrole, furan, thiophene and pyridine

Pyrrole, furan, thiophene are planar 5-membered heterocyclic molecules. They have three possible protonation sites X, $C_\alpha$and C_β. Pyridine is a planar 6-membered heterocyclic molecule.Single protonation site (N) has been found for pyridine in our study. Geometrical optimized structures obtained in B3LYP/6-311G (d,p) optimization process of all possible protonated complexes of these heterocyclic molecules are shown in Fig.-2. From the data tabulated in **6a** part of Table-6, we observe~~d~~ that, $X–H^+$ bond distance is largest in thiophene (1.362Å) and it is found shortest in furan (0.976Å). The $<C_\alpha–X–H^+$ bond angle varies in the range 99.7° to 118.37°. Torsion angle (τ) $< C_\beta–C\alpha–X–H^+$ of the complexes revealed that,five-membered heterocyclic compounds lost their planarity due to the protonation at X atom, but pyridine remain planar even after $X–H^+$ complex formation.Comparison of the geometrical parameters of $C_\alpha–H^+$ and $C_\beta–H^+$complexes (except pyridine) of all four heterocyclic molecules (Table-6b and6c) clears that, the geometry of the complexes strongly affected by H^+ interaction. Both 5 and 6 membered heterocyclic molecules become non-planar after protonation. Ther($C_\alpha–H^+$) and r($C_\beta–H^+$) bond length remains almost same (1.09 to 1.1Å) and 1.1Å) in each case. It has been seen in the present work, protonation at all three (X, Cα, C_β) sites leads to elongation of $C_\alpha–X$ bond length for pyrrole, furan and thiophene, it remains almost same in pyridine ($X–H^+$)complex. Due to protonation at the C_α position of these three molecules,$C_1–X$ bond length elongated by 0.09Å, it is 0.06 to 0.11Å for X–protonated complexes. In case of C_β protonation, $C_1–X$ bond distance increased by 0.05Å and 0.04Åfor pyrrole and thiophene while it is decreased by 0.1Å for furan.Little contractions are observed in $C_1–C_2$ of X- protonated species whereas $C_1– C_2$bond length elongated by 0.11 to 0.12Å for C_α protonation. C_β protonation induces small contractions of $C_1– C_2$ in pyrrole, thiophene (0.03 to 0.04Å) and large elongation (0.11Å) in furan. We have observed, $C_2 – C_3$ bond length increases 0.02 to 0.04Å and 0.06 to 0.07 Å due to protonation at X and C_β position, while 0.06 to 0.07 Å contraction is observed due to C_α protonation.

Figure-3 shows the optimized structures of lithium and sodium complexes of four studied heterocyclic molecules. Lithium and sodium have different position (in the plane, out of plane)depend on the types of heterocyclic molecules. For furan and pyridine, lithium complexes are found in plain (structure b, d)where a bond is formed between lithium cation and X heteroatom. The $X– Li^+$ bond distance is 1.84Å and 1.91Å for furan and pyridine respectively. Dihedral angle (τ) $<C-C-X-Li^+$ is found 179.7° and 179.99° in furan and pyridine complex. The out of plane structures are formed for pyrrole (a) and thiophene (c) where lithium remain above the ring but inclined to the heteroatom (N and S). The distance between X and Li^+ is 2.19Å and 2.46Å for pyrrole and thiophene respectively. Out of plane structures are well supported by obtained $< C-C-X-Li^+$ dihedral angle data of Table-6d (62.97°in pyrrole and 61.74° in thiophene). An in-plane structure of thiophene–Li^+ complex (c1) is also formed by bonding between S and lithium. The $S–Li^+$ bond distance and $\tau < C-C-S-Li^+$ angle are found 2.33Å and 179.99° respectively.An out-of-plane structure of the furan-Li^+ complex is also obtained (b1) with same optimization energy (– 231.418 hartree) where lithium is inside the ring with the distance 2.16Å and 2.24Å from O and $C_\alpha$atom. The $\tau< C-C-O-Li^+$ angle (66.47°) reveals the non-planarity of the complex.

Table-6e summarised the geometrical parameters of sodium complexes of the same heterocyclic molecules. It is obvious from the results, furan and pyridine form in-plane structures (dihedral angle <C-C-X-Na^+= 179.99° and 180.0°) while out-of-plane structures are obtained for pyrrole and thiophene (τ = –66.14° and 66.8°). The X– Na^+ bond distances are found little higher in all complexes relative to X–Li^+ distances. The bond distance between sodium and X atom is 2.23Å and 2.3Å in furan and pyridine. In pyrrole and thiophene complexes, X–Na^+ distances are found larger; it is 2.87Å in pyrrole and 2.92Å in thiophene.

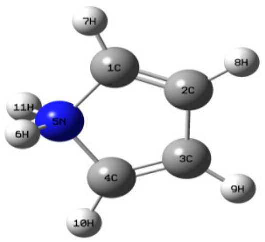
It is known that, isomers having lowest potential energies are most stable. But there is some exception with the conjugated cyclic planar ring systems. In these cases stability of the molecules depends on their resonance stabilization energy. DFT method provides some important parameters like hardness (η), the chemical potential (μ), electrophilic index(ω) which helps to predict the molecular stability and reactivity.[41]The absolute hardness (η) is defined by (I –A)/2. Where I is the vertical ionisation energies and A mean the vertical electron affinity. According to Koopman'stheory ,I= $-\varepsilon_{HOMO}$ (HOMO energy) and A = $-\varepsilon_{LUMO}$ (LUMO energies). Therefore $\eta = (\varepsilon_{LUMO} \sim \varepsilon_{HOMO})/2$. Table-7 contain the values of HOMO and LUMO energies of the studied molecules and their hardness also. In order to understand the stability of the protonated complexes, we also summarized the hardness for thedifferent protonated complexes in the same Table. The higher HOMO energy is expected for a more reactive molecule in a reaction with electrophile[42]. The calculated HOMO energies are obtained in this work as pyridine (–7.09ev)< thiophene (– 6.6ev) < furan (–6.38ev)< pyrrole (–5.75ev). The HOMO–LUMO energy gap is lower in the protonated complexes relative to the unprotonated species in each case. In an effort to estimate the reactivity of these molecules computationally, we calculate the chemical potential (μ) andelectrophilicity index (ω) of each molecule (Table-8). The calculated μ and ω values are seen lowest for pyrrole (-2.39 ev and 0.840 ev) then followed by furan (–3.09 and 1.46 ev), thiophene (–3.05 and 2.05 ev) and pyridine (–4.02 and 2.61 ev).

Table-7:Computed hardness (η) = (I –A)/2= $(\varepsilon_{LUMO} \sim \varepsilon_{HOMO})/2$ of the protonated complexes in the ground state. $\in_{HOMO}$ and $\in_{LUMO}$ energies are in hartree unit. (1 hartree = 27.21ev)

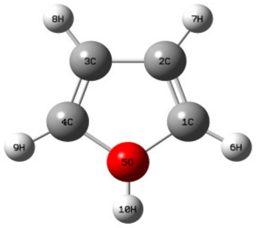
Free molecules	$\in_{HOMO}$	$\in_{LUMO}$	η (ev)
Pyrrole	–0.2124	0.0365	3.38
Furan	–0.2347	0.00676	3.28
Thiophene	–0.2425	–0.0182	3.05
Pyridine	–0.2609	–0.0348	3.07
Protonated complexes	$\in_{HOMO}$	$\in_{LUMO}$	η (ev)
Pyrrole (C_α- H^+)	–0.4898	–0.2849	2.78
Pyrrole (C_β- H^+)	–0.4693	–0.2781	2.60
Furan (C_α- H^+)	–0.5298	–0.3211	2.83
Furan (C_β- H^+)	–0.4982	–0.3171	2.46
Thiophene (C_α- H^+)	–0.4893	–0.3183	2.32
Thiophene (C_β- H^+)	–0.4803	–0.3142	2.25
Pyridine (X- H^+)	–0.4845	–0.2648	2.98

Table-8:Calculated chemical potential (μ) = $(\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$ and electrophilicity (ω) = $\mu^2/ 2\eta$ of the heterocyclic molecules in the ground state. Unit in ev).

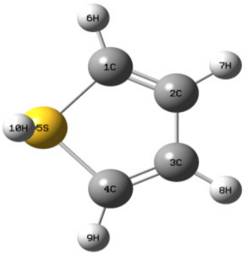
Molecules	μ (ev)	ω (ev)	η (ev)
Pyrrole	–2.39	0.840	3.38
Furan	–3.09	1.46	3.28
Thiophene	–3.54	2.05	3.05
Pyridine	–4.02	2.61	3.07



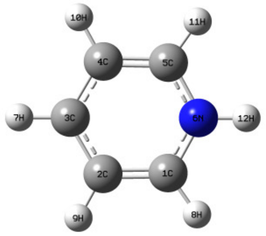
Pyrrole (X-H$^+$)



Furan (X-H$^+$)

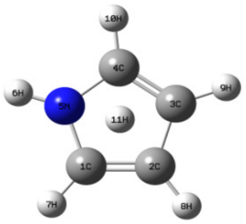
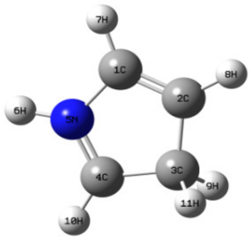
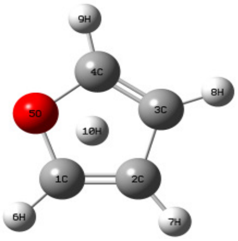
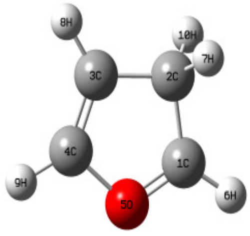
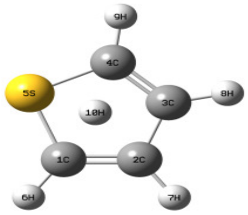
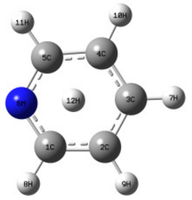
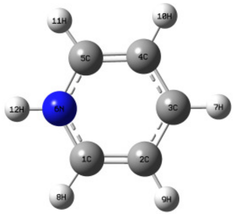


Thiophene (X-H$^+$)

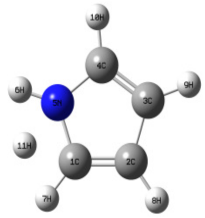
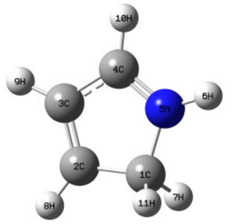
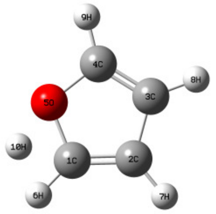
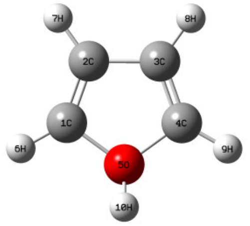
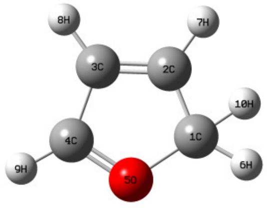
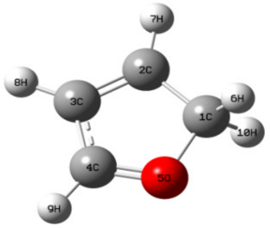
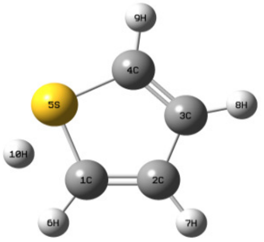
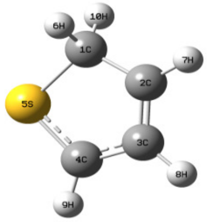
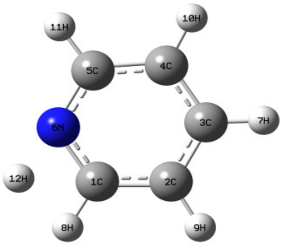
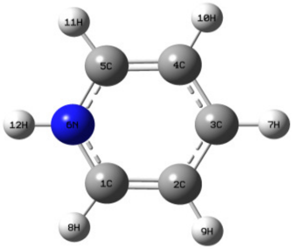


Pyridine (X-H$^+$)

Path –I: Gas phase optimized structures (Proton directly bonded with hetero[X] atom in initial input. X= N, O, S

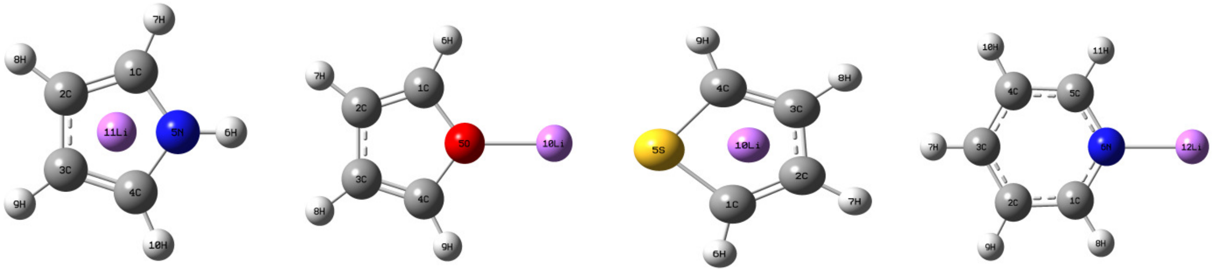
Input Structures	Output Structures
	
[Pyrrole-H$^+$]	Pyrrole (C_β– H$^+$) complex
	
[Furan-H$^+$]	Furan (C_β– H$^+$) complex
	
[Thiophene-H$^+$]	Thiophene (C_β–H$^+$) complex
	
[Pyridine-H$^+$]	Pyridine (N–H$^+$) complex

Path –II: Gas phase optimized structures (Proton placed inside the ring in initial input).

Input structure	Output optimized structure
	
Pyrrole –H$^+$	Pyrrole (Cα–H$^+$) complex
	
Furan-H$^+$	Furan (O-H$^+$) complex
	
Furan-H$^+$	Furan (Cα–H$^+$) complex
	
Thiophene-H$^+$	Thiophene (Cα–H$^+$) complex
	
Pyridine-H$^+$	Pyridine (N-H$^+$) complex

Path –III: Gas phase optimized structures (Proton placed outside the ring in between X and α-C in initial input).

Fig.-2: Optimized structures of the protonated complexes (different sites of protonation) pyrrole, furan,

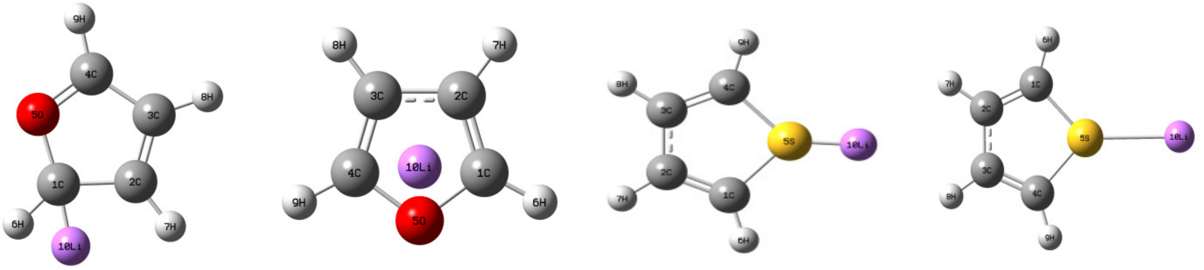


a
Pyrrole–Li$^+$

b
Furan (O–Li$^+$)

c
Thiophene–Li$^+$

d
Pyridine (N–Li$^+$)

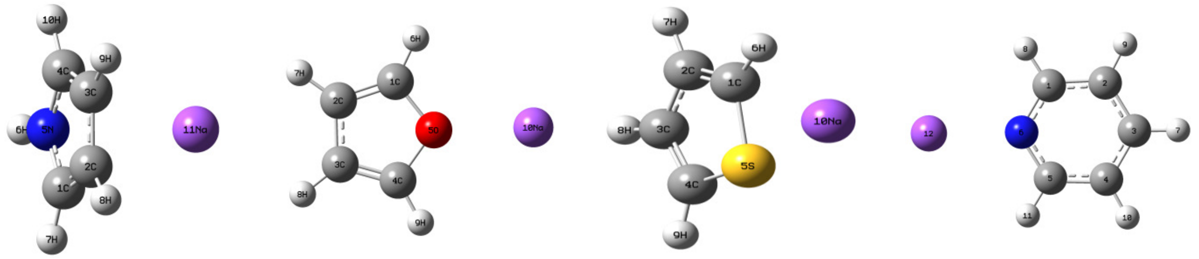


Input Furan–Li$^+$

b1
Optimized furan–Li$^+$

Input Thiophene (S–Li$^+$)

c1
Optimized (S–Li$^+$)



e
Pyrrole–Na$^+$

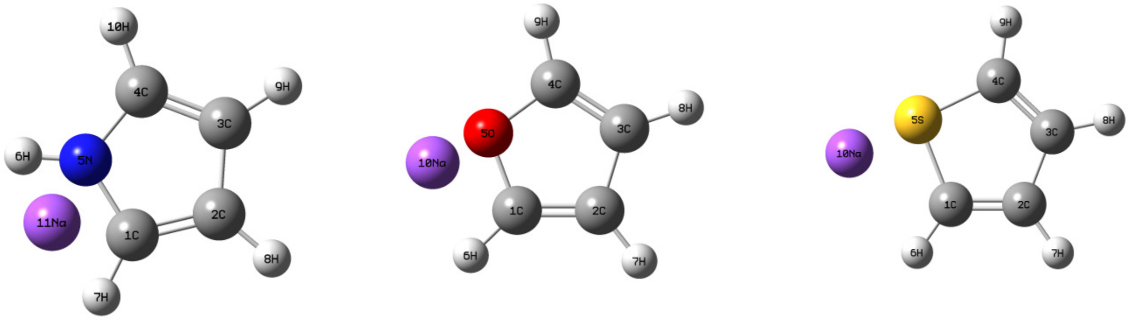
f
Furan–Na$^+$

g
Thiophene–Na$^+$

h
Pyridine–Na$^+$

thiophene and pyridine.

Fig.-3: Optimized structures of Li$^+$ and Na$^+$ complexes of pyrrole, furan, thiophene and pyridine.
a: out-of-plane, b: In-plane, b1: out-of-plane, c: out-of-plane, c1: In-plane d: In-plane, e: out-of-plan, f: out-of-plane, g: In-plane, h: out-of-plane, i: In-plane.



f

Pyrrole-Na$^+$

g

Furan-Na$^+$

h

Thiophene-Na$^+$

Fig.-4: Geometry of sodium complexes before optimization.

CONCLUSION

From the above theoretical analysis, it can be well concluded that,pyrrole, furan andthiopheneexhibit highest PA values when proton attacked at the C_α position of the free molecules. Proton preferentially attacked at hetero atom (N) and formed a most stable protonated complex of pyridine. C_β– protonated complexes are also formed for three five-membered heterocyclic molecules [which can be rationalized by kinetic factor [42]]. PA and basicity results obtained in this study show~~s~~ good agreement with the results found in the literature. Protonation at all three position (Cα, C_β, X= N, O, S) leads to form non-planar structures of pyrrole, furan and thiophene. The only pyridine retains with planar form. N-hetero molecules (pyridine and pyrrole) exhibit more affinity and basicity as well for alkali metal cations (Li^+ and Na^+) compared to O and S- heterocyclic molecules. Furan and thiophene can form lithium complex with two different geometries. One is in-plane and another is out-of-plane structure. Alkali-metal complexes of pyridine are found to exist~~s~~ with planar structures. Comparing three 5-membered heterocyclic molecules, the only furan-sodium complex is planar. Pyrrole-lithium or pyrrole- sodium and thiophene-sodium complexes are found non-planar. The lower value of μ andω is characterised by the more reactivity of the molecule. In the present study reactivity order of the molecules are pyrrole> furan > thiophene > pyridine.

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