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ORIGINAL CONTRIBUTION

Topological Analysis to Predict the Bonding Nature of Py-nM^+@H_2 (Py = Pyridazine, Pyrimidine, Pyrazine and M = Li, Na, K) compounds

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ABSTRACT

Energy decomposition analysis (EDA) of Py-M^+ (Py = Pyridazine, Pyrimidine, Pyridine & M=Li, Na, K) and pyrazine-2M^+ (M=Li, Na, K) building blocks have been carried out to evaluate the bonding nature after metal doping with $C_4H_4N_2$ (Pyridazine, Pyrimidine, Pyrazine) isomers. To show what type of interaction occurred between building blocks and adsorbed H_2 molecules, a topological analysis has been performed.

Keywords: Energy decomposition analysis (EDA), topological analysis, Multiwfn package

1. INTRODUCTION

The fact that atmospheric hydrogen can be an alternative source of energy to meet the energy needs of modern human civilization has already been tested and proven by the relentless efforts of scientists. But the finding of ideal hydrogen storage systems is a challenging task [1, 2]. Various materials have been reported as promising hydrogen storage materials [3-14]. Our research group has reported Li-decorated bi and tri heteroatomic six-membered aromatic isomers as ideal hydrogen storage materials which can bind molecular hydrogen in a quasi-molecular binding fashion [15, 16]. But the question for everyone is that what is the bonding interaction between rings and metals and also with which driving force can able to adsorb molecular hydrogen surround the metal. Thus in this article, we have tried to explain the bonding nature in $C_4H_4N_2$-M^+ [$C_4H_4N_2$ = Pyridazine, Pyrimidine, and Pyrazine&M=Li, Na, K] building blocks and in between metal and H_2 molecules after its H_2 adsorption.

2. THEORY AND COMPUTATIONAL DETAILS

We have optimized the three isomers of $C_4H_4N_2$ (Pyridazine, Pyrimidine, and Pyrazine), $C_4H_4N_2$-M^+(M=Li, Na, K) building blocks, and their H_2 trapped systems with the help of Gaussian-16W software package [17] at B3LYP/6-311+G(d,p) and ωB97X-D/6-311+G(d,p) level of theory [16] within a conceptual density functional theory (CDFT) [18] framework. To predict the bonding nature between $C_4H_4N_2$ isomers and M^+ in the $C_4H_4N_2$-M^+complexes we have carried out the energy decomposition analysis (EDA) [19-20] at the B3LYP-D3(BJ)/TZ2P level by taking optimized geometry at the ωB97X-D/6-311+G(d,p) level of theory. We have performed the topological analysis to get a clear idea about

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the bonding nature between the aromatic Py-rings and M^+as well as between 'M' center in the complexes with adsorbed H_2 molecules with the help of the Multiwfn package [21]. As a result, at the bond critical point (BCP), two crucial parameters, namely electron density ρ(r), its Laplacian ($\nabla^2\rho$), kinetic energy density, [G(r)] (always positive), potential energy density, [v(r)] (always negative) & electronic energy density [H(r)] have been determined [22]. Now from the ratio of [-G(r)/V(r)], we can predict the nature [16] of the bond –

(i) The interaction is said to be non-covalent if [-G(r)/V(r)] > 1.

(ii) The interaction is said to be partially covalent if 0.5 < -G(r)/V(r) < 1

and the strength of interaction can be known as stated below-

(i) The interactions are quite strong when both ∇^2 ρ and H(r) are negative.

(ii) Medium interaction is indicated by the negative value of H(r) and the positive value of $\nabla^2\rho$.

(iii) The interactions are weak when both ∇^2 ρ and H(r) are positive.

3. RESULTS AND DISCUSSION

All the optimized structures of $C_4H_4N_2$ isomers (Py) and Py-nM^+ (n = 1, 2) complexes have been given in Fig. 1, 2, 3 respectively [15]. From these figures, it is clear that among three isomers Pyrazine can able to bind mono and bi metallic cataions. Now we have split the total bonding energy (ΔE_{int}) of Py-M^+ and Py-2M^+ (Py = Pyrazine) into the following parts with the help of energy decomposition analysis (EDA).

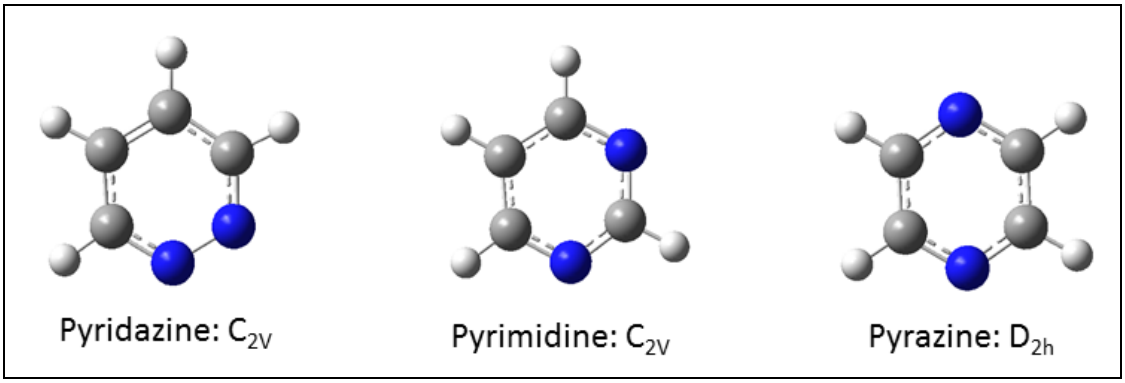


Fig. 1: Optimized geometries and point group of $C_4H_4N_2$ (Pyridazine, Pyrimidine, and Pyrazine) isomers at the ωB97X-D /6-311+G(d,p) level of theory [Adapted with permission from Ref.15; Copyright 2021. Elsevier]

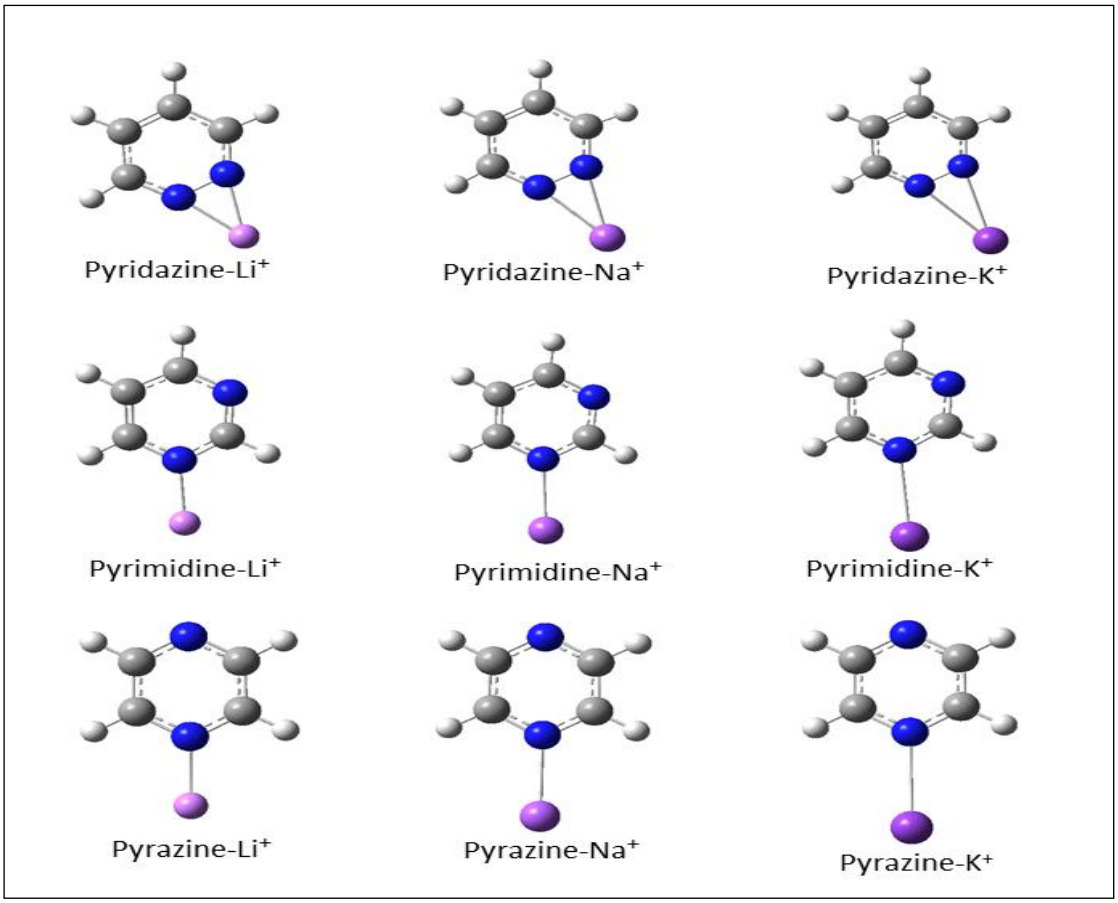


Fig. 2: Optimized geometries of $C_4H_4N_2$-M^+ ($C_4H_4N_2$ = Pyridazine, Pyrimidine, and Pyrazine & M=Li, Na, K) building blocks at the ωB97X-D /6-311+G(d,p) level of theory. [Adapted with permission from Ref.15; Copyright 2021. Elsevier]

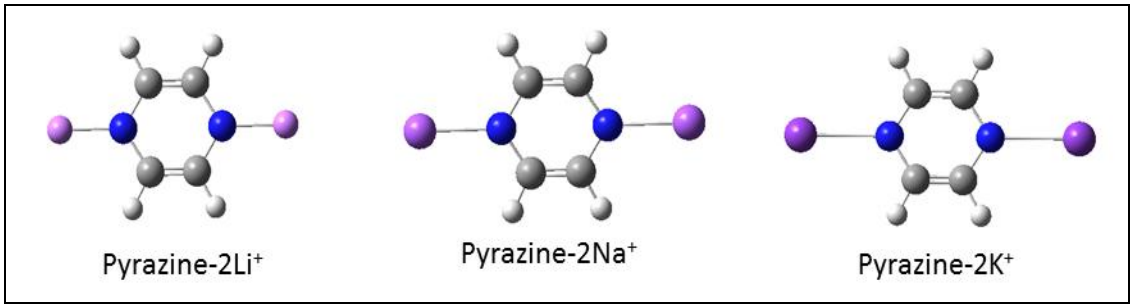


Fig. 3: Optimized geometries of Pyrazine-2M^+ (M=Li, Na, K) building blocks at the ωB97X-D /6-311+G(d,p) level of theory. [Adapted with permission from Ref.15; Copyright 2021. Elsevier]

Total bonding energy (ΔE_{int}) = Pauli repulsion (ΔE_{Pauli}) + electrostatic (ΔE_{elstat}) + orbital (ΔE_{orb}) + dispersion energy (ΔE_{disp}).

The calculated values (shown in Table-1) indicate that for all cases the N_{Py}-M^+ (M= Li, Na, K) bonds, the bonds are slightly greater in electrovalent nature than the covalent behaviour as the percentage of electrostatic interaction (ΔE_{elstat}) is greater than that of the percentage of orbital interaction (ΔE_{orb}), and as the no of metal increases the electrovalent nature also increases.

As well as N_{Py}-Na^+ bonding among the three metals (Li, Na, K) showed a higher percentage of electrostatic energy and follow the trend Na>K>Li in all cases. In case of orbital overlapping towards the covalent interactions for all complexes it follows the trend Li>Na>K.

Table-1: EDA Results of Py-M^+@ H_2[Py = Pyridazine, Pyrimidine, and Pyrazine] and Pyrazine-$2M^{2+}$@$2H_2$ [M=Li, Na, K] systems in eV at the ωB97X-D /6-311+G(d,p) // B3LYP-D3(BJ)/TZ2P level. The values given in parentheses are the percentage contributions toward the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$.

Building blocks	**ΔE_{int}**	**ΔE_{Pauli}**	**ΔE_{elstat}**	**ΔE_{orb}**	**ΔE_{disp}**
Pyridazine-Li^+	-2.60	0.52	-1.82(58.33%)	-1.23(39.42%)	-0.07(2.24%)
Pyridazine-Na^+	-1.89	0.42	-1.58(68.70%)	-0.64(27.83%)	-0.08(3.48%)
Pyridazine-K^+	-1.47	0.52	-1.37(68.5%)	-0.54(27%)	-0.09(4.5%)
Pyrimidine-Li^+	-1.88	0.68	-1.54(60.16%)	-0.94(36.72%)	-0.08(3.13%)
Pyrimidine-Na^+	-1.30	0.49	-1.18(65.92%)	-0.52(29.05%)	-0.09(5.03%)
Pyrimidine-K^+	-0.90	0.47	-0.89(64.49%)	-0.40(28.99%)	-0.09(6.52%)
Pyrazine-Li^+	-1.79	0.66	-1.45(59.18%)	-0.92(37.55%)	-0.08(3.27%)
Pyrazine-Na^+	-1.23	0.47	-1.10(64.70%)	-0.51(30%)	-0.09(5.30%)
Pyrazine-K^+	-0.84	0.46	-0.82(63.08%)	-0.39(30%)	-0.09(6.92%)
Pyrazine-$2Li^+$	-2.88	1.76	-3.18(68.53%)	-1.32(28.45%)	-0.14(3.02%)
Pyrazine-$2Na^+$	-1.92	1.35	-2.52(79.50%)	-0.58(15.30%)	-0.17(5.20%)
Pyrazine-$2K^+$	-1.18	1.56	-2.06(75.18%)	-0.53(19.34%)	-0.15(5.47%)

All the optimized structures of the highest molecular hydrogen trapped $C_4H_4N_2$-M^+ (M=Li, Na, K) complexes [15] have been shown in Fig. 4and Fig. 5. For the topological analysis, we have considered only$C_4H_4N_2$-M^+@H_2 (n = 1) and Pyrazine-$2M^+$@$2H_2$ systems. Fig. 6, 7, and 8 show the electron density between N_{py}-M^+ bonds and also the M^+….H_2 interactions.

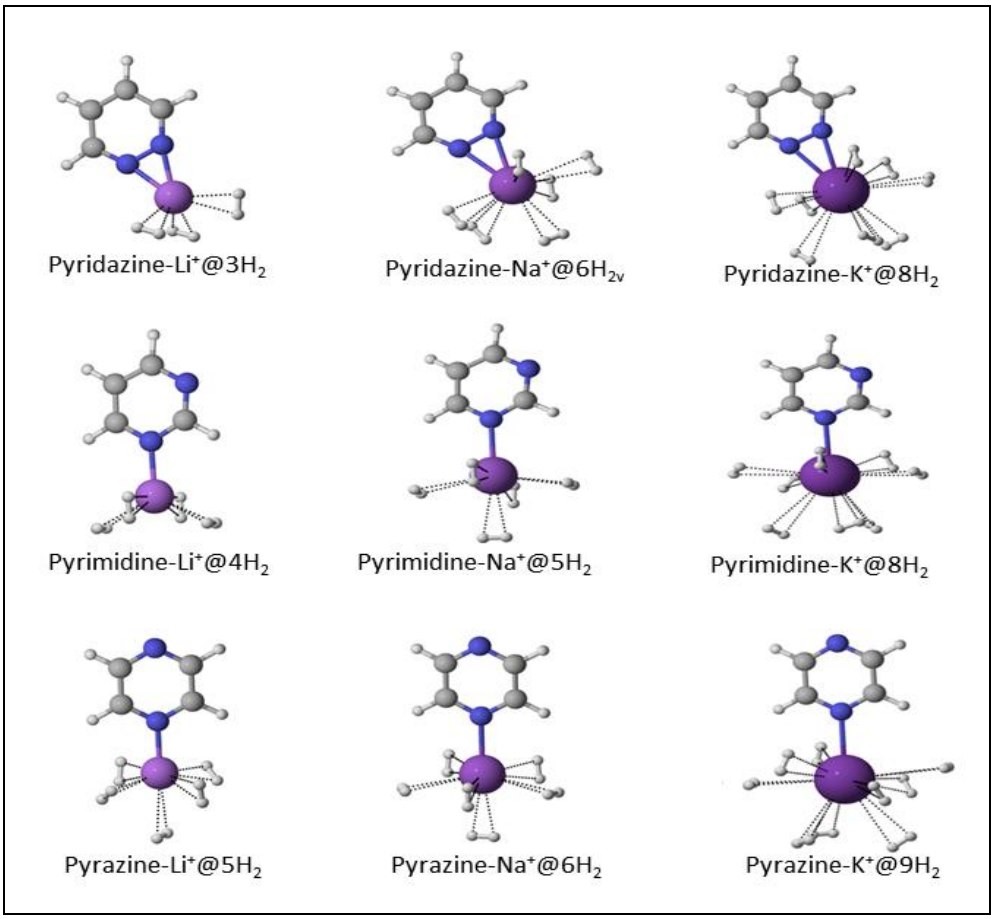


Fig. 4: The optimized geometries of the highest H_2 molecule absorbed Li/Na/K decorated $C_4H_4N_2$ (Pyridazine, Pyrimidine, and Pyrazine) isomers at the ωB97X-D /6-311+G(d,p) level of theory. [Adapted with permission from Ref.15; Copyright 2021. Elsevier]

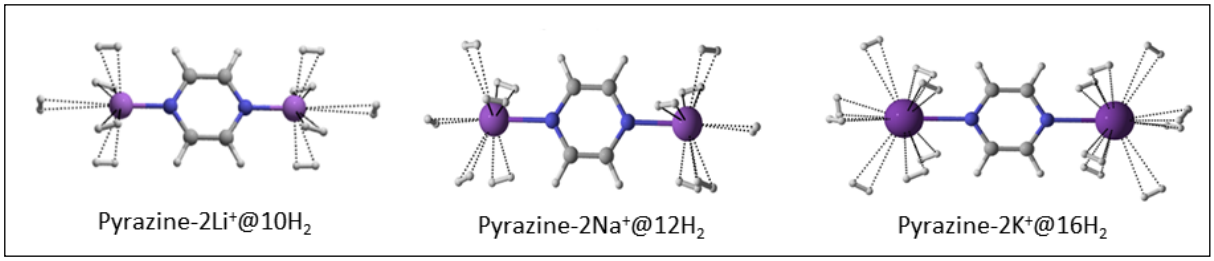
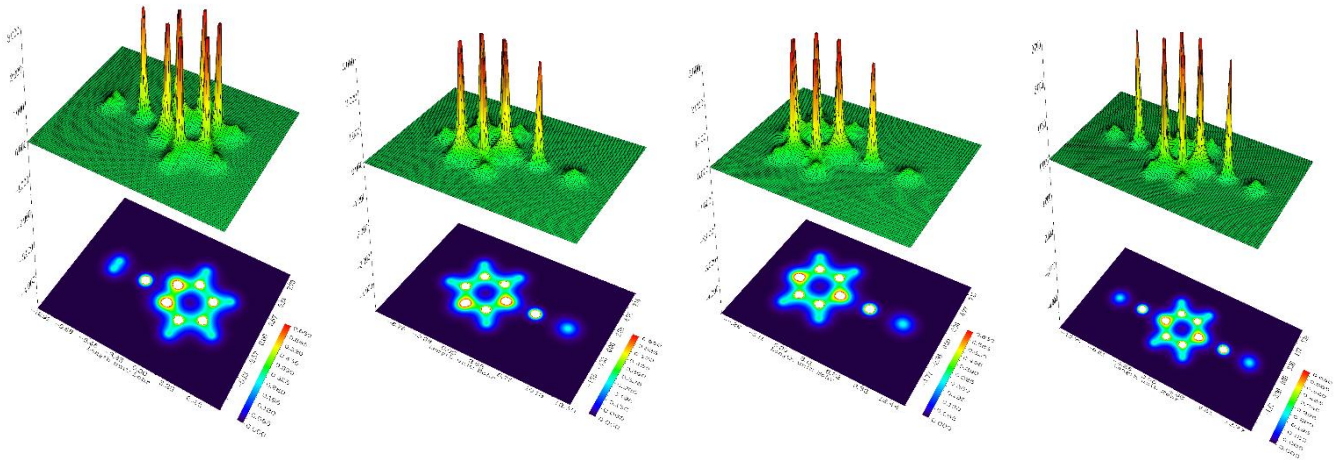


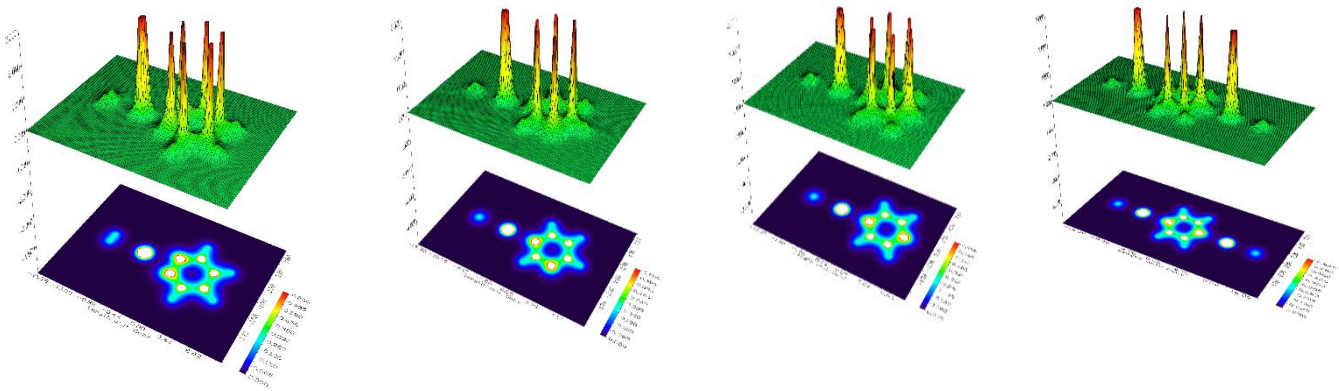
Fig. 5: The optimized geometries of the highest H_2 molecule absorbed 2 Li/Na/K decorated Pyrazine at the ωB97X-D/6-311+G(d,p) level of theory. [Adapted with permission from Ref.15; Copyright 2021. Elsevier]

The upper and lower part in Fig. 6 is the region of electron density. From these figures, we can correlate that the electron density is mostly accumulated on the high electronegative N atom of $C_4H_4N_2$ (Pyridazine, Pyrimidine, and Pyrazine) rings but there is no prominent electron density in between N-M bond & M···H_2 interaction is shown.



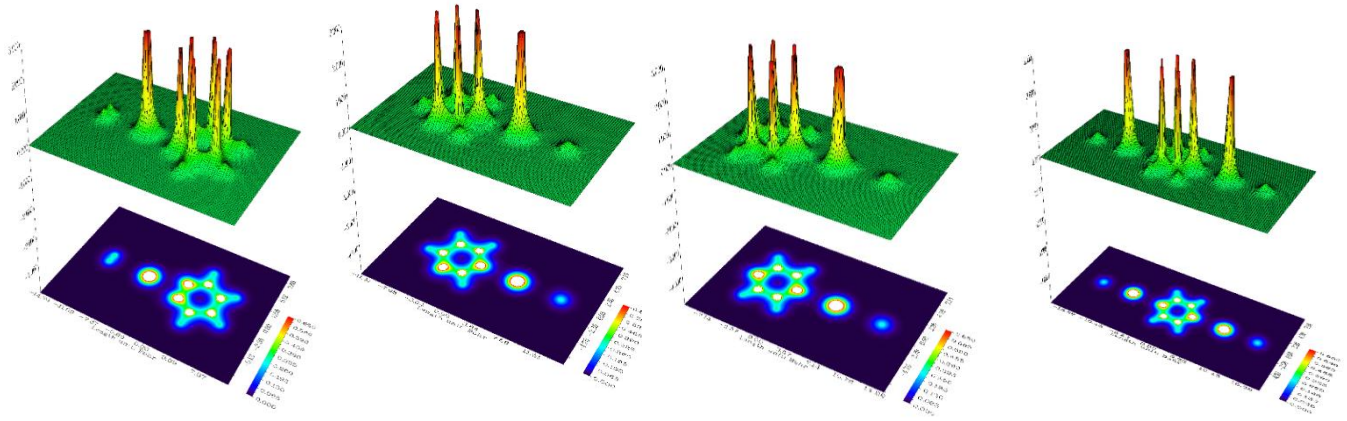
Pyridazine-$Li^+@1H_2$ Pyrimidine-$Li^+@1H_2$ Pyrazine-$Li^+@1H_2$ Pyrazine-$2Li^+@2H_2$

Fig. 6 (a): Py-$Li^+@nH_2$ systems



Pyridazine-$Na^+@1H_2$ Pyrimidine-$Na^+@1H_2$ Pyrazine-$Na^+@1H_2$ Pyrazine-$2Na^+@2H_2$

Fig. 6 (b): Py-$Na^+@nH_2$ systems

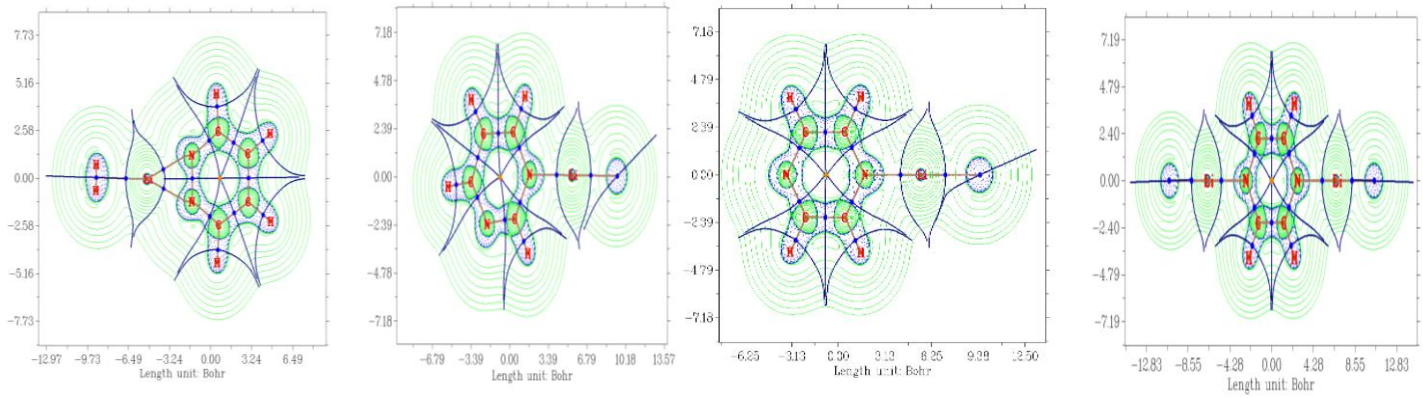


Pyridazine-K^+@$1H_2$ Pyrimidine-K^+@$1H_2$ Pyrazine-K^+@$1H_2$ Pyrazine-$2K^+$@$2H_2$

Fig. 6 (c): Py-K^+@nH_2 systems

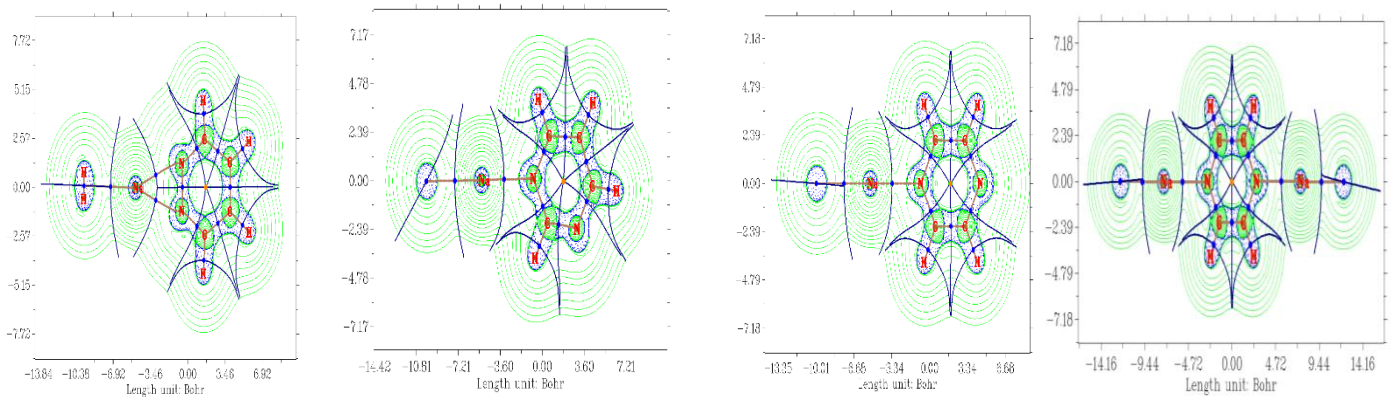
Fig. 6: Shaded surface map with the projection of the electron density of the Py-M^+@H_2 [Py = Pyridazine, Pyrimidine, and Pyrazine] and Pyrazine-$2M^{2+}$@$2H_2$ [M=Li, Na, K] systems generated at the ωB97X-D/6-311+G(d,p) level of theory. [6(a), Py-Li; 6(b), Py-Na; 6(c), Py-K complexes]

The green solid lines and the blue dotted lines in Fig. 7 indicate the charge depletion area ($\nabla^2\rho(r)>0$)and the charge concentration area ($\nabla^2\rho(r)<0$) [23] respectively. The brown solid lines and the solid bold blue lines in the same figure have been connected and separated the atomic nucleus respectively are known as bond paths and surfaces with zero-flux in the molecular plane. The bond critical points (BCPs) which are light blue spheres are the point where the bond paths and zero-flux surfaces cross each other. From this figures, we can say that the bond in between N-$M^+$is of noncovalent type and same is true for $M^+\cdots H_2$ interactions.



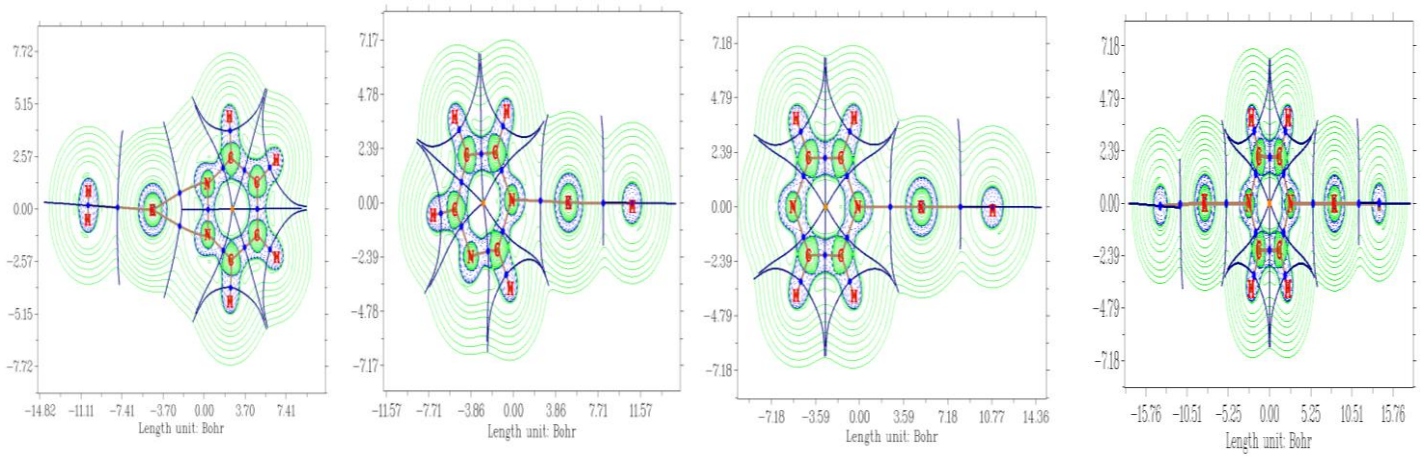
Pyridazine-Li^+@$1H_2$ Pyrimidine-Li^+@$1H_2$ Pyrazine-Li^+@$1H_2$ Pyrazine2Li^+@$2H_2$

Fig. 7 (a): Py-Li^+@nH_2 systems



Pyridazine-Na^+@$1H_2$ Pyrimidine-Na^+@$1H_2$ Pyrazine-Na^+@$1H_2$ Pyrazine-$2Na^+$@$2H_2$

Fig. 7 (b): Py-Na^+@nH_2 systems

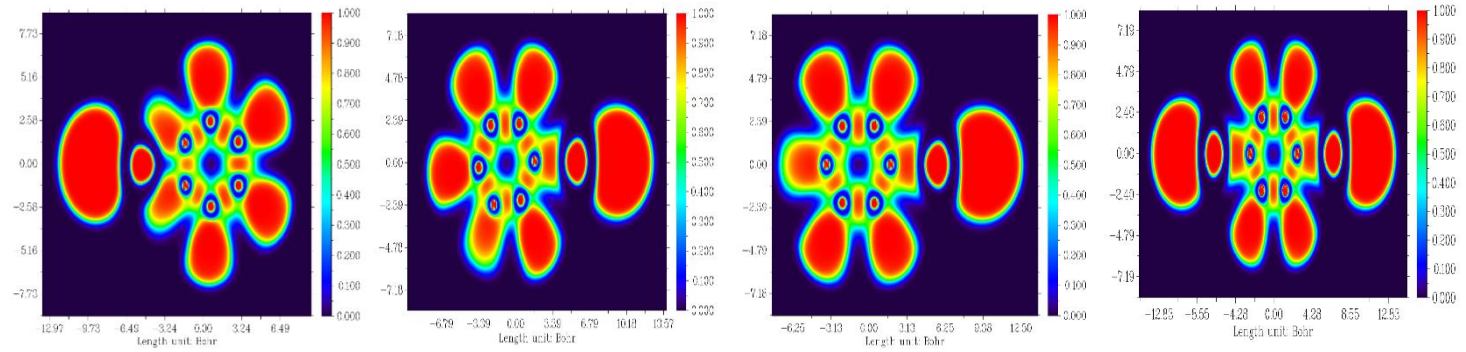


Pyridazine-K^+@$1H_2$ Pyrimidine-K^+@$1H_2$ Pyrazine-K^+@$1H_2$ Pyrazine-$2K^+$@$2H_2$

Fig. 7 (c): Py-K^+@nH_2 systems

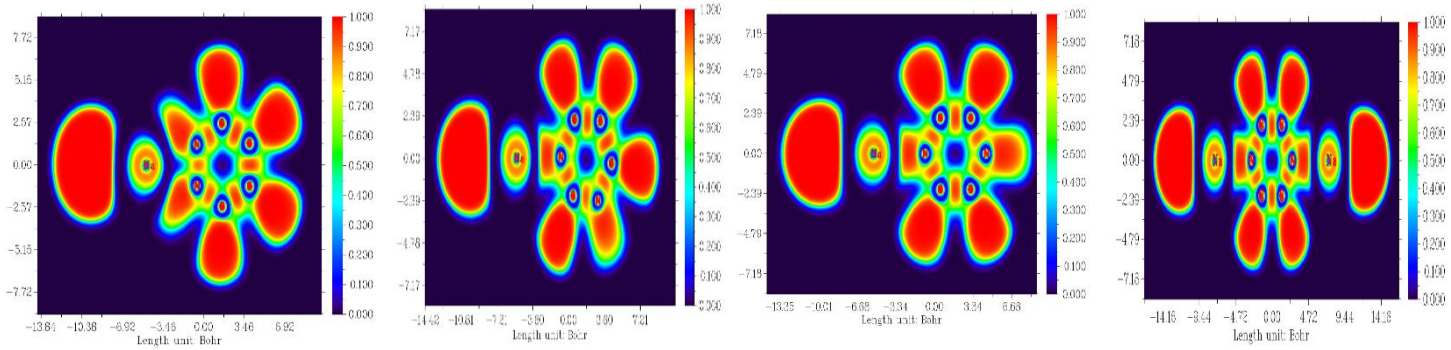
Fig. 7: Contour plot of the Laplacian of the electron density of the Py-M^+@H_2 [Py = Pyridazine, Pyrimidine, and Pyrazine] and Pyrazine-$2M^{2+}$@$2H_2$ [M=Li, Na, K] systems generated at the ωB97X-D/6-311+G(d,p) level of theory.

From Fig. 8 we can predict that the localized electrons in between the N-M^+ bond and $M^+\cdots H_2$ interaction is almost absent, which is another prove regarding the non-covalent type interaction in these bond formations.



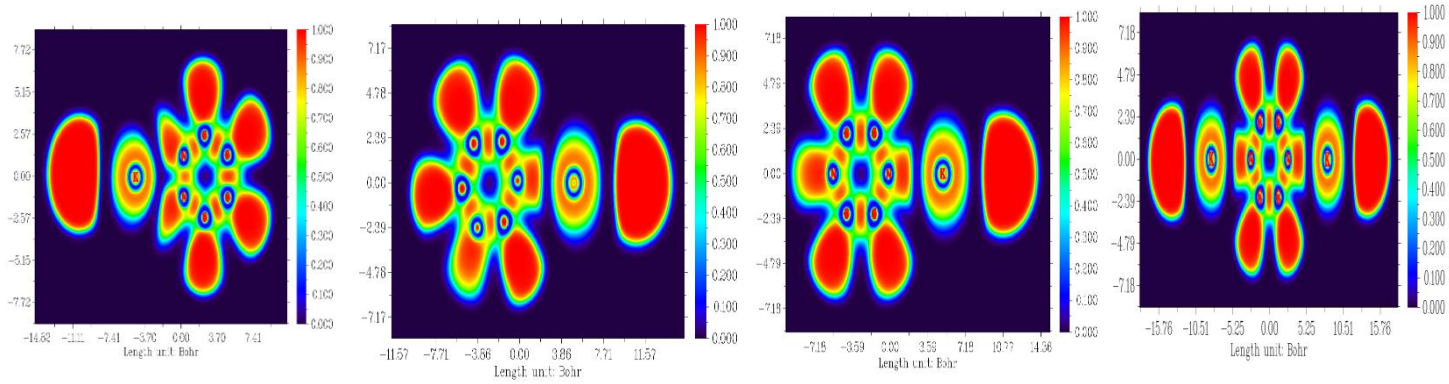
Pyridazine-Li^+@$1H_2$ Pyrimidine-Li^+@$1H_2$ Pyrazine-Li^+@$1H_2$ Pyrazine2Li^+@$2H_2$

Fig. 8 (a): Py-Li^+@nH_2 systems



Pyridazine-Na^+@$1H_2$ Pyrimidine-Na^+@$1H_2$ Pyrazine-Na^+@$1H_2$ Pyrazine-2Na^+@$2H_2$

Fig. 8 (b): Py-Na^+@nH_2 systems



Pyridazine-K^+@$1H_2$ Pyrimidine-K^+@$1H_2$ Pyrazine-K^+@$1H_2$ Pyrazine-2K^+@$2H_2$

Fig. 8 (c): Py-K^+@nH_2 systems

Fig. 8: The plot of the ELF of the Py-M^+@ H_2[Py = Pyridazine, Pyrimidine, and Pyrazine] and Pyrazine-2M^{2+}@$2H_2$ [M=Li, Na, K]systems generated at the ωB97X-D/6-311+G(d,p) level of theory.

Table-2: Electron Density Descriptors (au) at the BCPs of Py-M^+@H_2 [Py = Pyridazine, Pyrimidine, and Pyrazine] and Pyrazine-$2M^{2+}$@$2H_2$ [M=Li, Na, K] systems obtained from the wave functions generated at the ωB97X-D/6-311+G(d,p) level of theory.

BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$-G(r_c)/V(r_c)$
(Pyridazine−•− Li)$^+$ (H_2)	0.027, 0.027	0.200, 0.200	0.041, 0.041	-0.032, -0.032	0.009, 0.009	1.28, 1.28
(Pyridazine −Li)$^+$ −•− H_2	0.009	0.048	0.010	-0.007	0.002	1.43
(Pyridazine−•− Na)$^+$ (H_2)	0.020, 0.020	0.128, 0.127	0.026, 0.026	-0.021, -0.020	0.006, 0.006	1.24, 1.3
(Pyridazine −Na)$^+$ −•− H_2	0.006	0.031	0.006	-0.004	0.002	1.5
(Pyridazine−•− K)$^+$ (H_2)	0.019, 0.019	0.091, 0.091	0.019, 0.019	-0.016, -0.016	0.004, 0.004	1.19, 1.19
(Pyridazine −K)$^+$ −•− H_2	0.004	0.017	0.003	-0.002	0.001	1.5
(Pyrimidine −•− Li)$^+$ (H_2)	0.035	0.218	0.047	-0.039	0.008	1.21
(Pyrimidine −Li)$^+$ −•− H_2	0.010	0.049	0.010	-0.008	0.002	1.25
(Pyrimidine −•− Na)$^+$ (H_2)	0.025	0.143	0.030	-0.025	0.006	1.2
(Pyrimidine −Na)$^+$ −•− H_2	0.007	0.033	0.006	-0.005	0.002	1.2
(Pyrimidine −•− K)$^+$ (H_2)	0.021	0.085	0.018	-0.016	0.003	1.3
(Pyrimidine −K)$^+$ −•− H_2	0.004	0.017	0.003	-0.002	0.001	1.5
(Pyrazine −•− Li)$^+$ (H_2)	0.034	0.214	0.046	-0.038	0.008	1.21
(Pyrazine −Li)$^+$ −•− H_2	0.010	0.049	0.010	-0.008	0.002	1.25
(Pyrazine −•− Na)$^+$ (H_2)	0.025	0.140	0.030	-0.024	0.005	1.25
(Pyrazine −Na)$^+$ −•− H_2	0.007	0.033	0.006	-0.005	0.002	1.2
(Pyrazine −•− K)$^+$ (H_2)	0.021	0.083	0.018	-0.015	0.003	1.2
(Pyrazine −K)$^+$ −•− H_2	0.004	0.018	0.003	-0.002	0.001	1.5
(Pyrazine −•− 2Li)$^+$ ($2H_2$)	0.025,	0.148,	0.031,	-0.025,	0.006,	1.24,

	0.025	0.148	0.031	-0.025	0.006	1.24
(Pyrazine −2Li)$^+$ −•− $2H_2$	0.011, 0.011	0.052, 0.052	0.011, 0.011	-0.008, -0.008	0.002, 0.002	1.38, 1.38
(Pyrazine −•− 2Na)$^+$ ($2H_2$)	0.016, 0.016	0.088, 0.088	0.018, 0.018	-0.015, -0.015	0.004, 0.004	1.2, 1.2
(Pyrazine −2Na)$^+$ −•− $2H_2$	0.007, 0.007	0.035, 0.035	0.007, 0.007	-0.005, -0.005	0.002, 0.002	1.4, 1.4
(Pyrazine −•− 2K)$^+$ ($2H_2$)	0.013, 0.013	0.048, 0.048	0.010, 0.010	-0.008, -0.008	0.002, 0.002	1.25, 1.25
(Pyrazine −2K)$^+$ −•− $2H_2$	0.004, 0.004	0.019, 0.019	0.003, 0.003	-0.002, -0.002	0.001, 0.001	1.5, 1.5

Lastly to get a more accurate concept regarding interaction type we have calculated the electron density ($\rho(r_c)$), Laplacian of electron density ($\nabla^2\rho(r_c)$), local electron energy density [$H(r_c)$], kinetic energy density [$G(r_c)$], and potential energy density [$V(r_c)$] at the bond critical points (BCPs) [22] and results are tabulated in Table-2. As the values of both $\nabla^2\rho(r_c)$and $H(r_c)$ are positive for all systems thus the interaction between N_{py}-M^+ and $M^+\cdots H_2$are weak in nature and secondly as the values of $[-G(r_c)/V(r_c)]$ >1 for all cases so the interaction between N-M^+ and $M^+\cdots H_2$ is the electrovalent[24-26] in nature.

4. CONCLUSION

Both energy decomposition analysis (EDA) and topological analysis help us to make a conclusion that N_{py}-M^+ (M= Li, Na, K) bonds are non-covalent in nature rather the bonding interaction in $C_4H_4N_2$-M^+ complexes are slightly electrovalent in nature and after H_2 adsorption it has been observed that N_{py}-M^+ and $M^+\cdots H_2$ interaction is also maintaining the same bonding nature.

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