Theoretical Investigation of Hydrogen Adsorption Efficiency of [Oxadiazole-*x*Li⁺] Complexes (x = 1, 2); In Pursuit of Green Fuel Storage

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Abstract

In the current decade, all countries are going to launch their National Hydrogen Energy Mission with ambitious targets in the renewable energy sector and the push for hydrogen energy will steer the world in the promising direction toward green energy. Scientists, technologists, and industrialists are searching for a suitable hydrogen storage system. Influenced by our promising recent findings on Li-doped aromatic N-heterocyclic (ANH) six-membered Py-Li systems; (Py = Pyrazine, Pyrimidine, Pyridazine, and Triazine), here we have focused on isomeric oxadiazole-xLi⁺ (x = 1, 2) templates. The hydrogen trapping ability of the systems has been studied carefully with the density functional theory (DFT) approach. The aromaticity of the systems prevails even after hydrogen adsorption and the process is quasi-molecular in nature. It justifies these templates as potential hydrogen storage material. The charge on the Li atom decreases gradually with each successive H_2 adsorption, and a charge transfer type interaction occurs from the bonding orbital (BD) of H_2 molecules to the antibonding lone pair orbital (LP*) of lithium-ion (Li⁺). It is found that the molecular H_2 interacts with the oxadiazole-xLi⁺ template through ionic-type bonding. Gibbs free energy changes suggest that the H_2 adsorption process is spontaneous at or below 200 K.

1. Introduction

The ever-increasing demands for energy worldwide and the rapidly depleting fossil fuel resources necessitate looking for an alternative and sustainable energy resource. Fossil fuels also have a severe impact on the environment because of the emission of greenhouse gases when they generate useful energy. To save our planet from pollution, therefore, it is necessary to search for a renewable energy source in a greenway. In view of these points, hydrogen is considered to be a promising candidate for future fuel because of its tremendous energy density and near inexhaustibility.[1] However, the bottleneck problem of hydrogen-based energy sources is their storage; the storage system must be safe, economical, and reversible for practical use under ambient conditions.[2,3]

During the last couple of decades, many researchers have carried out both experimental and theoretical investigations to find suitable materials for storing H_2. For metal-based hydrides as examples,[4-8] metal hydrides form strong chemical connections with H_2 and have a high gravimetric wt%. However, the desorption of H_2 is problematic in practice due to its high binding energy. Carbon nanotubes (CNTs) have also been studied.[9-13] The huge specific surface area and significant porosities in the tube structure of carbon-based nanostructures make them potential H_2 storage materials theoretically, yet the experimental outcome does not meet expectations. As a consequence, several researchers are investigating metal-decorated carbon-based materials.[14] Metal-organic frameworks (MOFs) can also act as H_2 storage and have the advantage that their H_2 adsorption process is

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reversible and the relevant kinetics is fast.[15-18] But in some cases, quite low interaction energies between MOF and H_2 than that of the requirement, make them unfavorable for the actual purpose.[16-18]

It is clear from the preceding discussion that high H_2 storage capacity cannot be achieved by physisorption, although in this process desorption of H_2 can occur under ambient conditions. Chemisorption is a simple way to store a great amount of H_2. But since it's not a reversible process, it can't satisfy the storage criteria. It appears that for a material to possess promising storage, the H_2 adsorption process should be reversible and the concerned energy should lie in between that of physisorption and chemisorption (quasi-sorption).[19,20] We have explored the possibilities of light-weight materials, *i.e.*, oxadiazole isomers to fulfil the present target[21] with an expectation to follow the conditions of a better storage material.[22-24] Since it is well-known that metals do interact with H_2 molecules, it is worthwhile to investigate the adsorption capacity of a metal-doped organic host as this may enhance the H_2 adsorption capacity of the system. In recent years there is a number of literature reports on using transition metal atoms as dopants.[25-30] There is, however, a serious drawback of transition metal atoms as they have a tendency to aggregate and thereby form a cluster around the host because of their high cohesive energy. The cluster formation reduces the possibility of adsorption of H_2 on individual metal atoms. On the other hand, alkali metal cations have been reported to have high hydrogen binding capability.[31,32] We have already reported on H_2 storage efficacies of six-member di-nitrogen and tri-nitrogen heterocyclic compounds *viz*. pyridazine, pyrimidine, pyrazine isomers, and triazine isomers-based building blocks with encouraging results.[19,20] The astonishing theoretical findings of H_2 adsorption in a single lithium fluoride (LiF) molecule (gravimetric wt% 43.48; LiF@$10H_2$) substantiates this template to be a potential hydrogen storage material but the Gibbs free energy changes for spontaneous hydrogen adsorption process is at very low temperature (at or below 54 K).[33] The results promote us to find new templates to serve the purpose. Here in this article, we have judiciously chosen the isomers of a five-member di-nitrogen heterocyclic compound oxadiazole as the organic host and Li as doping material since this metal is reported to have good adsorption possibilities.[19-21,34-39] The effectiveness of oxadiazole isomers as a storage material was investigated. Any changes of aromaticity after the loading of lithium (Li) to oxadiazole, vis-à-vis loading H_2 on the [oxadiazole-nLi]$^+$ complexes were explored. The bonding type between Li and adsorbed H_2 and the spontaneous adsorption temperature were studied as well.

2. Theory and computational detail

Gaussian 16w program package[40] was used to optimize all electronic structures and to calculate frequencies within the framework of density functional theory (DFT)[41] by taking several functionals, namely B3LYP, CAM-B3LYP, ωB97X-D, and 6-311+G (d,p) basis sets.[20] The significance of the use of CAM-B3LYP and ωB97X-D is to account for the long-range interaction. By applying standard techniques, both hardness (η) and electrophilicity (ω) were calculated to have information regarding the stability and reactivity of the system after the doping of Li and H_2 trapping.[42-51] Nucleus-independent chemical shifts (NICS)[19] were calculated as an aromaticity criterion for all studied molecules. We computed energy decomposition analysis (EDA)[52-54] by applying optimized geometries of building blocks generated at the ωB97X-D/6-311+G(d,p) level to study and understand the type of bonding between N atoms of isomeric oxadiazole and Li$^+$ at the B3LYP-D3(BJ)/TZ2P level. Equations (1) and (2) were used to calculate the average binding energy (E_b) of each Li-decorated oxadiazole isomer and the binding energy per H_2 molecule (E_b/H_2) of the isomeric oxadiazole-xLi$^+$@nH_2.

$$E_b = [(E_{oxadiazole} + xE_{Li^+}) - E_{oxadiazole-xLi^+}]/x \qquad (1)$$

where $E_{(oxadiazole-xLi)^+}$, $E_{oxadiazole,}$ and E_{Li^+} stand for the energy of the lithium-doped oxadiazole isomers, oxadiazole isomers, and Li-ion, respectively, and x is the number of inserted Li atoms (x = 1 and 2).

$$E_b/H_2 = [(E_{oxadiazole-xLi^+} + nE_{H2}) - E_{oxadiazole-xLi^+ @nH2}]/n \quad (2)$$

where $E_{(oxadiazole-xLi)^+}$, E_{H2}, and $E_{(oxadiazole-xLi)^+ @nH2}$ are energies of the Li dopped oxadiazole isomers, H_2 molecule, and H_2 adsorbed complexes, respectively, and n = no. of adsorbed H_2 molecules. To see the effect of temperature on Gibbs's free energy of adsorption, we started with room temperature (298 K). Since all the energy values became positive, we scanned the system starting from 250 K to 210 K with a 20K interval. In this temperature span also; all the Gibbs free energy values turned positive. We then calculated Gibbs free energy change from 210 K to 200 K at every 5 K interval, and at 200K we got the negative Gibbs free energy value for each studied system. To validate this observation, we additionally performed the calculation at 201 K where some of the systems gave positive free energy values. Details are given in Table ST-6. The influence of basis-set superposition error (BSSE) was taken into consideration using the counterpoise process (CP)[55] in order to produce the correct binding energy per H_2 according to the equation E_b/H_2 (BSSE) = E_b/H_2 - $\frac{1}{n}$ BSSE.

Aromaticity is an important factor that offers stability to the system and so to check this property before and after Li doping and H_2 adsorption we studied NICS (0,1) (nucleus independent chemical shift)[20,56-61] and we also determined NBO (natural bonding orbital) charges[19,20] to know the order of changes of charge after gradual H_2 adsorption. Calculations were made on gravimetric wt%[19-21] to cross-check with the U.S.DOE target[22] by considering the following Equation (3):

$$Gravimetric\ wt\% = \frac{Molecular\ weight\ of\ trapped\ H_2}{Molecular\ weight\ of\ (oxadiazole-xLi)^+@nH_2\ complex} \times 100 \qquad (3)$$

The nature of the interaction was investigated using second-order perturbation theory[62] with the help of relations (4) and (5) below. The delocalization correction energy (ΔE_{CT}) was tabulated for each donor natural bonding orbital NBO(i) and acceptor NBO(j) to scrutinize the donor-acceptor (bonding–antibonding) charge-transfer interaction.[63]

$$\Delta E_{CT} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (4)$$

$$\Delta E_{CT}^{av} = \frac{1}{n} \Delta E_{CT} \quad (5)$$

In Equation (4), q_i is the donor orbital occupancy, $F(i,j)$ is the off-diagonal NBO Fock matrix element and ε_i and ε_j are diagonal elements (orbital energies). The average delocalization correction energy is represented by Equation (5), where n is the number of adsorbed molecular hydrogen (1, 2, 3......). To get an idea about the bonding nature of this trapping process we evaluated the atoms in molecules (AIM) analysis[64] with the assistance of the Multiwfn package.[65] Lastly, the temperature-dependent spontaneity of this storing process was verified by deriving the Gibbs free energy change values at different temperatures following Equation (6).

$$\Delta G_{oxadiazole\text{-}xLi^+@nH2} = G_{oxadiazoe\text{-}xLi^+@nH2} - G_{oxadiazole\text{-}xLi^+} - nG_{H2} \quad (6)$$

Here $G_{oxadiazole\text{-}xLi^+@nH2}$, $G_{oxadiazole\text{-}xLi^+}$, and nG_{H2} indicate Gibbs free energy of the H_2 adsorbed complexes, Li doped oxadiazole isomers, and molecular hydrogen, respectively. Next atom centered density matrix propagation (ADMP)[66-68]

study was performed to know about the kinetic stability of the H_2-trapped systems of the isomeric oxadiazole-xLi$^+$(x = 1, 2) building blocks.

3. Results and discussion

3.1. Oxadiazole isomers: a study of Stability, Reactivity, and Aromaticity

All the ground state optimized geometries of oxadiazole isomers and their Cartesian coordinates are shown in SF-1 and SF–2 of supplementary information (SI) file. The stability, reactivity, and aromaticity of these isomers are presented in Table 1 and Table ST-1 (reported in SI). From these tables, it can be seen that hardness is greater for 124 oxadiazoles and electrophilicity is greater for 125 oxadiazoles, implying the fact that 124 oxadiazole has higher stability and 125 oxadiazoles has more reactivity. Very good 'σ', as well as 'Π' aromaticity of all the isomers, are concluded from the negative values of NICS (0,1) in ppm.

3.2. Li-doped oxadiazole isomers: Stability, Reactivity, Aromaticity, Energy Decomposition Analysis (EDA) and NBO

By placing the Li atom on the top and side of the oxadiazole ring, a building block for H_2 adsorption has been created. Li connected in a linear fashion via nitrogen (N) atom is more stable than the other fashion and we have taken that for our

Table 1. Hardness (η; eV), Electrophilicity (ω; eV) of Oxadiazole and its lithiated isomers at the ωB97X-D /6-311+G(d,p) level of theory and NICS (0,1) [ppm] values calculated at the CAM-B3LYP/6-311+G(d, p) level of theory. The value within the '()' represents the hardness/atom and electrophilicity/atom (eV).

Systems	η (eV)	ω (eV)	E_b(eV)	NICS (0) [ppm]	NICS (1) [ppm]	NBO
123 Oxadiazole	10.794 (1.542)	1.129 (0.161)	-	-13.15	-11.83	-
123 Oxadiazole -Li$^+$	10.460 (1.307)	4.408 (0.551)	1.573	-13.50	-12.24	0.975
123 Oxadiazole-2Li$^+$	10.287 (1.143)	9.214 (1.024)	- 0.233	-13.91	-12.37	0.986
124 Oxadiazole	11.579 (1.654)	1.111 (0.159)	-	-11.54	-10.60	-
124 Oxadiazole-Li$^+$	11.396 (1.424)	4.165 (0.521)	1.400	-11.94	-10.47	0.980
124 Oxadiazole-2Li$^+$	11.831 (1.314)	8.210 (0.912)	0.013	-12.34	-10.32	0.986
125 Oxadiazole	10.406 (1.486)	1.528 (0.218)	-	-13.05	-12.27	-
125 Oxadiazole-Li$^+$	11.185 (1.398)	4.569 (0.571)	1.922	-13.48	-12.11	0.980
125 Oxadiazole-2Li$^+$	11.265 (1.252)	9.054 (1.006)	0.189	-13.62	-11.82	0.986
134 Oxadiazole	11.554 (1.651)	0.961 (0.137)	-	-10.74	-10.21	-
134 Oxadiazole-Li$^+$	11.854 (1.482)	3.943 (0.493)	1.948	-11.20	-10.19	0.971
134 Oxadiazole-2Li$^+$	12.161 (1.351)	7.531 (0.837)	-0.085	-11.78	-10.12	0.983

further study. Figs. SF-3, SF-4, and SF-5 (reported in SI) represent the optimized geometry and corresponding Cartesian coordinates of all Li-doped oxadiazole isomers. Looking at chemical reactivity parameters in Table 1 and Table ST-1 (reported in SI) it is observed that, among all four mono-lithiated isomers, hardness (η)[34] is greater for 134 oxadiazole-Li$^+$ system and electrophilicity (ω)[36] is lesser for 134 oxadiazole-Li$^+$ system, which describes their corresponding greater stability and lesser reactivity among other mono-lithiated systems according to maximum hardness minimum electrophilicity principle. Again, among four bi-lithiated systems, hardness (η)[34] is greater for 134 oxadiazole-2Li$^+$ systems, and electrophilicity (ω)[36] is lesser for 134 oxadiazole-2Li$^+$ systems, which relates to their stability and reactivity among other bi-lithiated systems. The variation in hardness values within the isomers may be due to the position of N atoms within the Li-inserted ring. When we look into the general trend of hardness values upon gradual addition of Li$^+$ (mono- and bi-lithium) the lithiated-124 isomer shows irregularity. However, to address the anomaly, the per-atom hardness quantity for all the systems has been calculated and the values for all the systems show a gradually decreasing trend upon Li incorporation (shown in Table 1). This also supports the increasing reactivity of the Li-incorporated systems upon H$_2$ adsorption.

To determine the type of bonding between Li and the N atoms of the oxadiazole ring we calculated the total bonding energy for all isomers as follow Equation (7).

Total bonding energy (ΔE_{bon}) = Pauli repulsion (ΔE_{Pauli}) + electrostatic energy (ΔE_{elstat}) + orbital interaction (ΔE_{orb}) + dispersion energy (ΔE_{disp}).   (7)

As seen from Table 2, the percentage of electrostatic energy is greater than that of the orbital contribution for all the mono- and bi-lithiated building blocks, suggesting that electrovalent interaction occurs between Li and N atoms of the oxadiazole ring. Average binding energy (E_b) values are reported in Table 1, which clearly show that mono-lithiated oxadiazoles are more stable than the corresponding bi-lithiated isomers; as the E_b values are larger for the former. All the lithiated isomers have negative values for both NICS (0) and

NICS (1), indicating that all the systems retain their 'σ' and 'Π' aromaticity even after lithiation. The 123 isomer of oxadiazole-xLi$^+$(x = 1, 2) exhibits greater aromaticity. The calculated positive NBO charge on the Li center (Table 1) implies that a strong electric field is formed surrounding the Li center which strongly polarises the H$_2$ molecules and exerts an influence on their better adsorption.
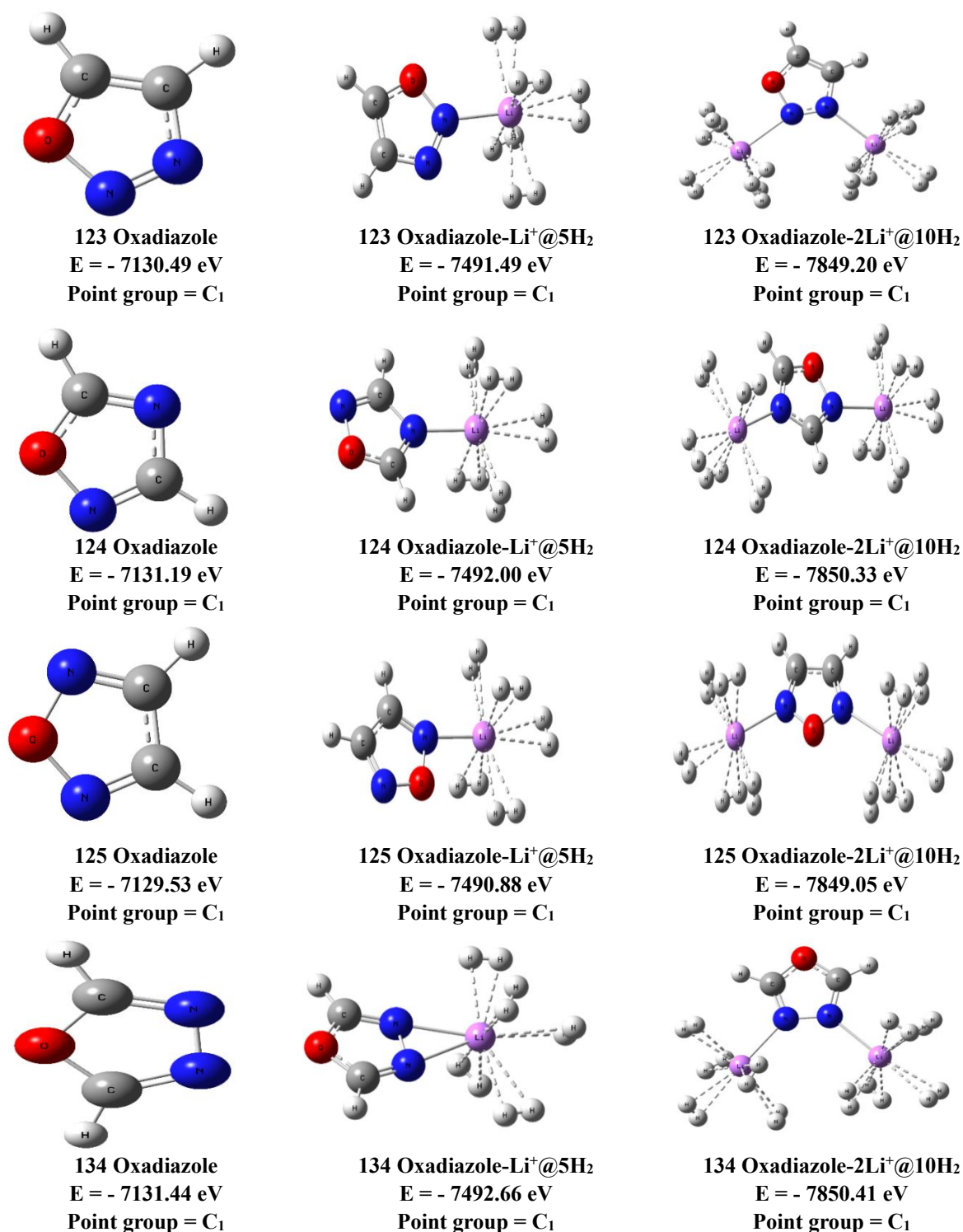
3.3 Isomeric oxadiazole-xLi$^+$@nH$_2$ complexes: Stability, Reactivity, and Aromaticity

After getting the building blocks, we focused on how many H$_2$ molecules may get adsorbed surrounding the Li center. The result shows that up to a maximum of five H$_2$ molecules can be adsorbed on all the mono-lithiated oxadiazole isomers and consequently a maximum of ten H$_2$ molecules can be adsorbed on bi-lithiated isomers, whereas for optimized structures the imaginary frequency turns out to be zero in its ground state potential energy surface. All the maximally H$_2$-trapped optimized structures of the isomeric oxadiazole-xLi$^+$ (x = 1, 2) complexes with Cartesian coordinates are given in Fig. 1 and Fig. SF-(6-7). Others are portrayed in Fig. SF-8.

We have calculated hardness (η), electronegativity (χ), and electrophilicity (ω) [Table ST-1] with the help of ionization energy (IE) and electron affinity (EA). From Table ST-1 (reported in SI), we can see that ionization energy (IE), electron affinity (EA), and electronegativity (χ) gradually decreases upon successive H$_2$ adsorption. Again, the hardness (η) of the lithiated heterocyclic systems increases, and electrophilicity (ω) decreases with an increase in the number of the trapped H$_2$ molecules, which is shown in Table ST-1 (reported in SI) and Figs. SF-9, SF-10 (reported in SI). To know if there is any change of aromaticity after H$_2$ trapping, we have done NICS (0,1) calculation. The negative values of NICS (0,1) for all systems reflect that both 'σ' and 'Π' aromaticity have been maintained throughout the H$_2$ adsorption process [Table ST-2 (reported in SI)]. The basis-set superposition error (BSSE) corrected binding energy per H$_2$ molecule (Fig. 2) on Li-decorated oxadiazole isomers (detail given in Table ST-3 of SI] goes on to decrease as the number of adsorbed H$_2$ molecules increases. This can be attributed to

Table 2. Energy decomposition analysis (EDA; eV) results of isomeric lithiated Oxadiazole templates at the ωB97X-D/6-311+G(d,p)//B3LYP-D3(BJ)/TZ2P level of theory. The values given in parentheses are the percentage contributions toward the total attractive interaction ΔE_{elstat} + ΔE_{orb} + ΔE_{disp}.

Building blocks	ΔE_{bon}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{disp}
123 Oxadiazole-Li$^+$	-1.76	0.42	-1.29(59.17%)	-0.83(38.07%)	-0.06(2.75%)
124 Oxadiazole -Li$^+$	-1.60	0.59	-1.31(59.81%)	-0.81(36.98%)	-0.07(3.20%)
125 Oxadiazole -Li$^+$	-1.57	0.45	-1.14(56.44%)	-0.82(40.59%)	-0.06(2.97%)
134 Oxadiazole -Li$^+$	-2.13	0.39	-1.43(56.74%)	-1.03(40.87%)	-0.06(2.38%)
123 Oxadiazole -2Li$^+$	-2.61	0.40	-1.91(63.46%)	-1.09(36.21%)	-0.01(0.33%)
124 Oxadiazole -2Li$^+$	-2.50	0.60	-2.17(70.00%)	-0.80(25.80%)	-0.13(4.19%)
125 Oxadiazole -2Li$^+$	-2.45	0.48	-1.96(66.89%)	-0.88(30.03%)	-0.09(3.07%)
134 Oxadiazole -2Li$^+$	-3.29	0.64	-2.59(65.90%)	-1.29(32.82%)	-0.05(1.27%)

123 Oxadiazole
E = - 7130.49 eV
Point group = C_1

123 Oxadiazole-Li$^+$@5H$_2$
E = - 7491.49 eV
Point group = C_1

123 Oxadiazole-2Li$^+$@10H$_2$
E = - 7849.20 eV
Point group = C_1

124 Oxadiazole
E = - 7131.19 eV
Point group = C_1

124 Oxadiazole-Li$^+$@5H$_2$
E = - 7492.00 eV
Point group = C_1

124 Oxadiazole-2Li$^+$@10H$_2$
E = - 7850.33 eV
Point group = C_1

125 Oxadiazole
E = - 7129.53 eV
Point group = C_1

125 Oxadiazole-Li$^+$@5H$_2$
E = - 7490.88 eV
Point group = C_1

125 Oxadiazole-2Li$^+$@10H$_2$
E = - 7849.05 eV
Point group = C_1

134 Oxadiazole
E = - 7131.44 eV
Point group = C_1

134 Oxadiazole-Li$^+$@5H$_2$
E = - 7492.66 eV
Point group = C_1

134 Oxadiazole-2Li$^+$@10H$_2$
E = - 7850.41 eV
Point group = C_1

Fig. 1 Optimized geometries, their corresponding ground state energy (eV), and point group of isomeric Oxadiazole, isomeric Oxadiazole-Li$^+$@5H$_2$, isomeric Oxadiazole-2Li$^+$@10H$_2$ at the ωB97X-D/6-311+G(d,p) level of theory.

the fact that, with increasing the number of adsorbed H$_2$, the interaction between Li and individual H$_2$ decreases which leads to a reduction in the NBO charges on the Li center. This causes a lowering of binding energy per H$_2$ molecule. It is also found from Table ST-4 (reported in SI) that, as the number of trapped H$_2$ molecules around the Li center increases, the Li−N bond distance increases. This supports the observation that the charge on the Li center decreases on gradual H$_2$ adsorption on lithiated-oxadiazole systems. The gravimetric wt% for maximum adsorbed H$_2$ molecules on Li-decorated oxadiazole systems are found at 11.49 and 19.93 [Table ST-5 (reported in SI)] for mono-lithiated and bi-lithiated systems, respectively. And undoubtedly, this is a promising finding in comparison to the target set by the Department of Energy (DOE), United States.[22]
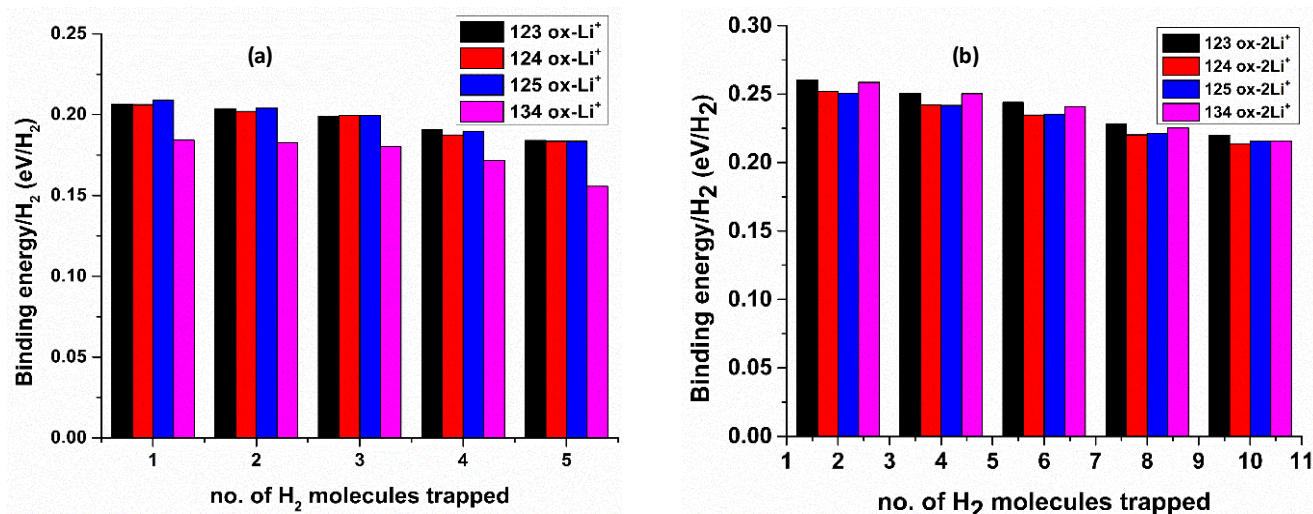
Fig. 2 Plot of basis-set superposition error (BSSE) corrected binding energy/H_2 (eV/H_2) vs no. of H_2 molecules trapped on isomeric Oxadiazole-xLi$^+$@ nH_2 complexes at the ωB97X-D/6-311+G(d,p) level of theory. (2.a.) a mono-lithiated system with 1-5 H_2 adsorption, (2.b.) a bi-lithiated system with 2,4,6,8, and 10 H_2 adsorption.

3.3.1. Bonding nature

The delocalization correction energy (ΔE_{CT}) and it's average (ΔE_{CT}^{av}) values displayed in Fig. 3 and Table ST-6 (reported in SI) imply that a charge transfer interaction takes place from the bonding orbital (BD) of the trapped H_2 molecules to the anti-bonding lone pair orbital (LP*) of Li$^+$ ions. As the number of trapped H_2 molecules increases, the value of ΔE_{CT}^{av} increases (some anomalous trends were also observed due to steric crowding among the trapped H_2 molecules around the Li-ion).
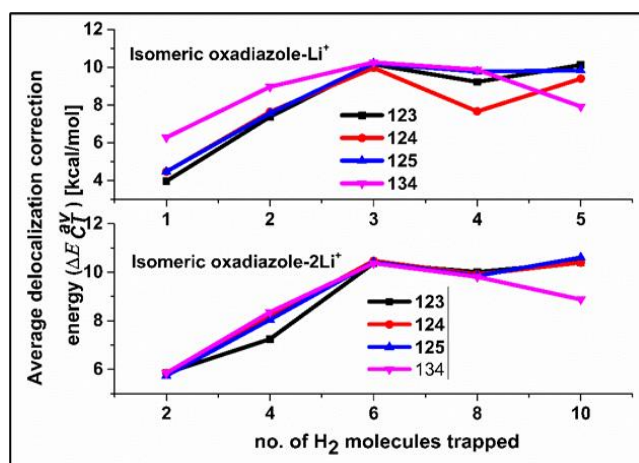

Fig. 3 Plot of average delocalization correction energy (kcal/mol) vs the number of H_2 molecules trapped on isomeric Oxadiazole-xLi$^+$@nH_2 systems at ωB97X-D/6-311+G(d,p) level of theory.

To address the most common question, what form of bonding occurs during adsorption between the Li$^+$ and the entering H_2 molecules, we have studied the topological analysis at the bond critical point (BCP). We calculated bonding nature controlling parameters like, 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 [$v(r_c)$] of the oxadiazole-xLi$^+$@nH_2 [n = 1, 2] isomers. We have drawn three types of figures [representative figures are shown in the main text (Fig. 4) and detail available in the supplementary file as Fig. SF- (11-15)] by considering isomeric oxadiazole-Li$^+$@H_2 to visualize the clear image of the bonding nature with the help of the multi-win software package.[62]

The upper and lower section of Fig. 4 (for mono-lithiated isomers) shows the variation of electron densities on different atoms throughout the systems. We can see that the electron cloud exists on the highly electronegative N atom, but not between N and Li centers and between the Li center and H_2 molecule. This supports electrovalent interactions between the N and Li centers, as well as between the Li center and the adsorbed molecular hydrogen. Bi- lithiated isomers are shown in Fig. SF-13.

From Fig. SF-11, the area of charge depletion ($\nabla^2\rho(r) > 0$) and the area of charge concentration ($\nabla^2\rho(r) < 0$) are shown as green solid lines and blue dotted lines, respectively. The brown solid lines indicate bond pathways. The solid bold blue lines which separate the atomic nuclei represent the zero-flux molecular plane surfaces. Bond critical points (BCPs) which are represented by the light blue dots are the points where the bond path and zero-flux surfaces cross with each other.[69] This figure also suggests the existence of electrovalent bonding between the N and Li centers, as well as between Li and the H_2 molecule as no electron density is found between them. Fig. SF-11 represents mono-lithiated isomers and the bi-lithiated isomers are shown in Fig. SF-14 (reported in SI). The graphical plot for the electron localization function (ELF) of the systems (mono-lithiated isomers) is given in Fig. SF-12 (reported in SI). From this figure, it is evident that there are no localized electrons in between N and the Li center and also in between Li and the adsorbed H_2 molecule. In addition, $\nabla^2\rho(r_c)$, $H(r_c)$, and [$-G(r_c)/V(r_c)$] data have also been computed at the
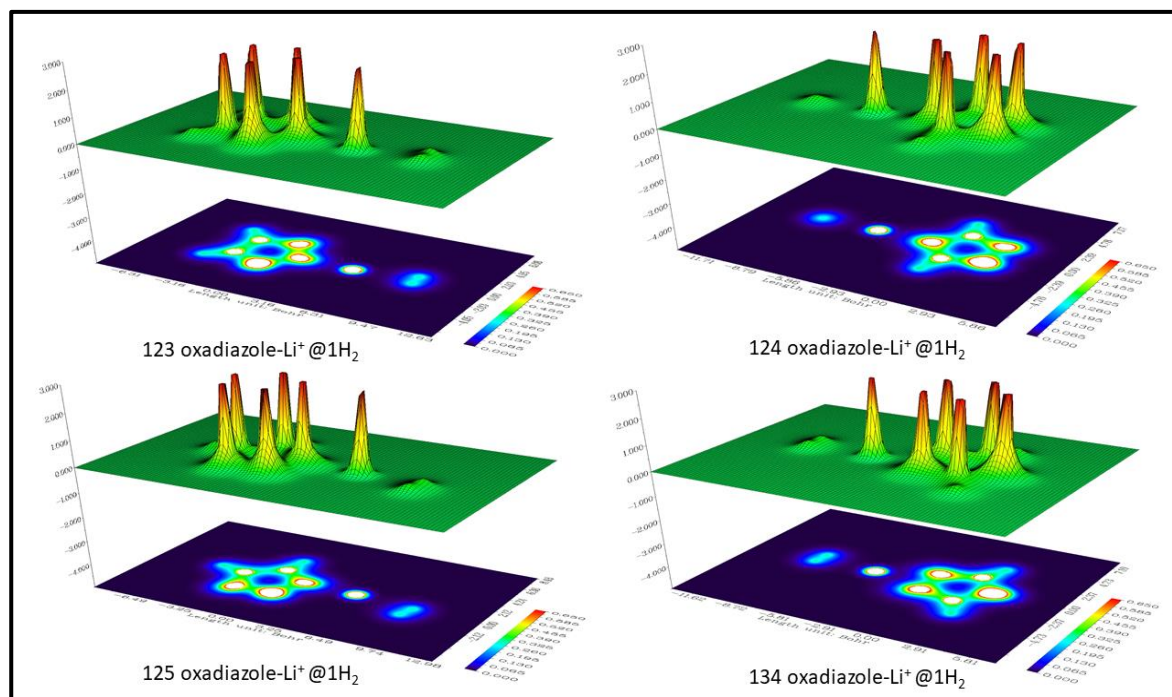
Fig. 4 Shaded surface map with the projection of the electron density of the isomeric oxadiazole−Li+−(H₂) complexes generated at the ωB97X-D/6-311+G(d,p) level of theory.

bond critical point (BCP) to get a clear idea of the bonding type (Table 3). As the values of both $\nabla^2\rho(r_c)$ and $H(r_c)$ are positive and the ratio of $-G(r_c)$ to $V(r_c)$ is greater than 1. From the theoretical consideration, we can conclude that both (isomeric oxadiazole…Li)$^+$ (H₂) and (isomeric oxadiazole −Li)$^+$··H₂ interactions are mostly ionic type.[70-72] The same inference is also true for bi-lithiated oxadiazole isomers regarding bonding type which have been represented in Fig. SF-15.

3.3.2 Effect of Temperature on H₂ Adsorption

To know the temperature at which the H₂ adsorption process becomes spontaneous, we have calculated Gibbs free energy change at different temperatures in the range from 200 K to 298K. The results of which have been presented in Fig. SF-16 and Table ST-7 (reported in SI). From the observation, it is found that the H₂ trapping process will be spontaneous at 200

K for all studied systems.

3.3.3 Atom-centered density matrix propagation (ADMP) study

To determine the kinetic stability of the isomeric oxadiazole-xLi$^+$@nH₂ (x = 1, 2 & n = 5, 10) complexes, ADMP investigations were conducted at two different temperatures (*i.e.* at 50 K & 300 K). As a result, we chose a time period of 1 fs and employed a thermostat to maintain the temperature velocity scaling throughout the experiment. The relation between potential energy (E, au) with time (t, fs) is shown in Fig. 5 by taking 125 oxadiazole isomer as a reference (detail given in supporting information file, Figs. SF-17 to SF-22), and corresponding time *vs.* temperature-dependent simulated structures of isomeric oxadiazole-xLi$^+$@nH₂ (x = 1, 2 & n = 5, 10) complexes at 300 K, at the 500 fs time is shown in Fig. SF–23 to SF-28 (supporting information file). From

Table 3. Electron density descriptors (au) at the bond critical points (BCP) of hydrogen and the isomeric Oxadiazole−Li$^+$ complex obtained from the wave functions generated at the ωB97X-D/6-311+G (d,p) level of theory.

BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$-G(r_c)/V(r_c)$
123 Oxadiazole−•− Li+ (H₂)	0.03	0.198	0.041	-0.033	0.008	1.24
123 Oxadiazole−Li+ −•− H₂	0.009	0.05	0.01	-0.007	0.002	1.42
124 Oxadiazole−•− Li$^+$ (H₂)	0.03	0.205	0.043	-0.035	0.008	1.22
124 Oxadiazole−Li$^+$ −•− H₂	0.009	0.05	0.01	-0.007	0.002	1.42
125 Oxadiazole−•− Li$^+$ (H₂)	0.03	0.19	0.039	-0.031	0.008	1.26
125 Oxadiazole−Li$^+$ −•− H₂	0.009	0.05	0.01	-0.007	0.002	1.42
134 Oxadiazole−•− Li$^+$ (H₂)	0.02	0.165, 0.166	0.033, 0.033	-0.025, -0.026	0.008, 0.008	1.32 1.27
134 Oxadiazole−Li$^+$ −•− H₂	0.009	0.05	0.01	-0.007	0.002	1.42
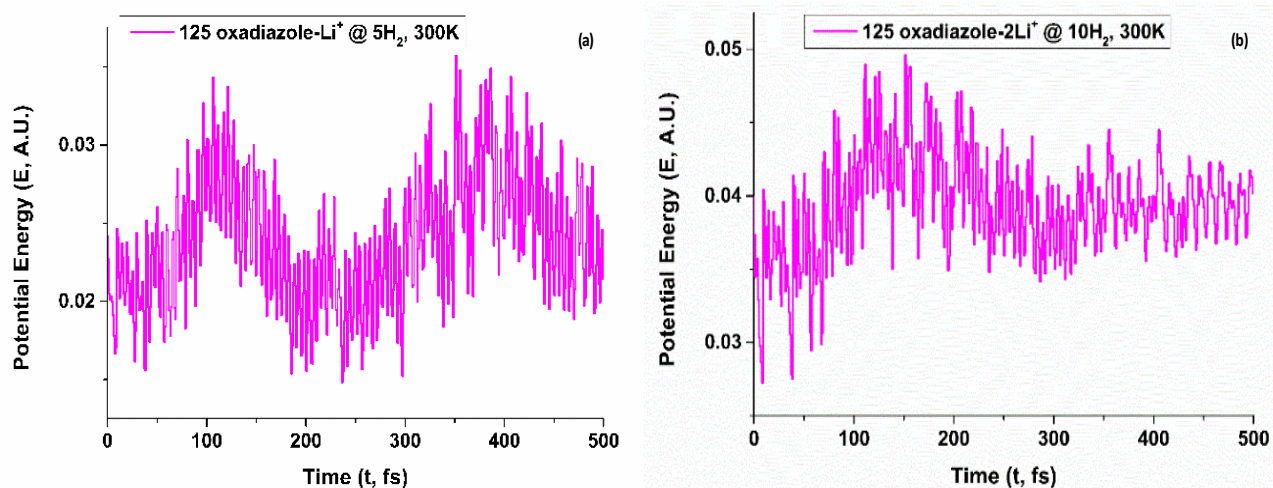
Fig. 5 Potential Energy (E, au) vs Time (t, fs) of Isomeric 125 Oxadiazole-xLi$^+$@nH$_2$ (x = 1, 2 & n= 5,10) complexes at 300 K at 500 fs obtained at the ωB97X-D/6-311+G(d,p) level of theory; (5. a) [125 Oxadiazole-Li]$^+$@5H$_2$ and (5. b) [125 Oxadiazole-2Li]$^+$ @10H$_2$.

these figures, it is clear that Li-oxadiazole complexes are able to retain all trapped H$_2$ molecules at 50 K for up to 1500 fs. But the desorption starts at 300 K, from our starting measured time (500 fs) and the desorption rate increases as time intervals have increased [Fig. SF-(23-28)]. This implies that a low temperature is necessary for H$_2$ molecule capture and a higher temperature is required for H$_2$ molecule release.

4. Conclusion

The isomeric oxadiazole-xLi$^+$ building blocks have been found to be promising H$_2$ storage materials as the binding energy per H$_2$ support the quasi-molecular adsorption process. The high gravimetric wt% (11.49 and 19.93 % for mono-lithiated and bi-lithiated systems respectively) grants a satisfactory result which supports that, these organometallic templates are a new group of promised H$_2$ storage material. According to NBO analysis, the charge on the Li atom decreases gradually with each successive H$_2$ adsorption, and a charge transfer interaction occurs from the bonding orbital of H$_2$ molecules to the antibonding orbital of Li-ion. From AIM (atoms in molecules) analysis we can say that trapped H$_2$ molecules interact with building blocks through electrovalent interactions. Gibbs free energy change, suggests that the H$_2$ adsorption process is spontaneous at or below 200 K. The results are highly promising and exciting imputes for the synthetic chemists and chemical industries for the possible synthesis of this material as a suitable H$_2$ storage candidate in the quest of green fuel storage.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

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