

# H<sub>2</sub>-Anion Interactions and Energy Calculations for Imidazolium-based Ionic Liquids as Hydrogen Storage Materials

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**Abstract**-The aims of this study are to explore the molecular hydrogen-anion interactions and assess the energy calculations in imidazolium-based compounds. The stable modes were structurally discussed after the achieving optimizations by density functional theory. It is concluded that the interaction energies were very weak against the strong interaction lengths. The impacts of the loaded molecular hydrogen to the imidazolium-based structure were discussed by the frontier molecular orbital analysis. While the amounts of H<sub>2</sub> involved to the interaction increased, the changes in the energy gap were calculated. The bonding interactions on the cation-anion and molecular nH<sub>2</sub>-anion were compared.

**Keywords:** Hydrogen storage materials, ionic liquids, imidazolium, molecular H<sub>2</sub> interactions.

## 1. Introduction

Hydrogen, being alternative to conventional energy sources such as natural and fossil fuels in recent years, is an important research topic to prevent global climate change and continuously meet the increasing energy demand [1]. The development of hydrogen fuel cells is also increased the activities on high-capacity hydrogen-containing materials aimed hydrogen storage [2].

Hydrogen storage-based studies have certain disadvantages such as continuous boil-off for liquid hydrogen, low capacity in use of compressed hydrogen gas and lack of safety concerns under high pressures [3]. So, materials-based scientific studies for hydrogen storage have been focused on composite materials, metal hydrides, ammonia borane, amides, metal organic structures and organic liquids [1]. Metal borohydrides with a high hydrogen capacity also has been the subject of many researchers [4-6]. Ammonium borane (AB) and derivatives are also structures comprising the high hydrogen, ~19 wt%, and this value is reduced to ~14 wt% in partial dehydrogenation of AB because of that the full dehydrogenation occurs at higher temperatures than 500 °C [7]. Ionic liquids (ILs) are eco-friendly solvent widely used in green energy applications to avoid environmental concerns and attract attention with the chemical-electrochemical characteristics in fields such as

better thermal stability, lithium batteries and electrochemical capacitors [8-10]. Besides, ILs are more special structures about ionic, covalent interactions, pi-stacking and hydrogen bonding according solvents [11-14].

Newly researches on the role of imidazolium ILs, hydrogen storage materials, for H<sub>2</sub> generation from AB derivatives [15], thermal dehydrogenation of ethylene diamine bisborane [16, 17] and physicochemical properties of the several synthesized imidazolium ILs [3, 18-20] are available. In addition, quantum calculations on imidazolium-derivative ILs are enriched to the literature such as hydrogen bond interactions among the ion pairs [21-23], structural and spectral analysis etc. [24]. We wish to investigate the interaction energy between BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> anions and molecular H<sub>2</sub> for the 1-butyl-3-methylimidazolium structures in this study. 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup>), 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup>) and 1-butyl-3-methylimidazolium hydrogen carbonate ([BMIM]<sup>+</sup>HCO<sub>3</sub><sup>-</sup>) structures have been selected. In the first part, the lowest energy conformers have been studied in order to highlight the anions-nH<sub>2</sub> interactions. Interaction energies, frontier orbitals and spectral data have been calculated and interpreted for the anions subjected to interact with nH<sub>2</sub> in the next stage.

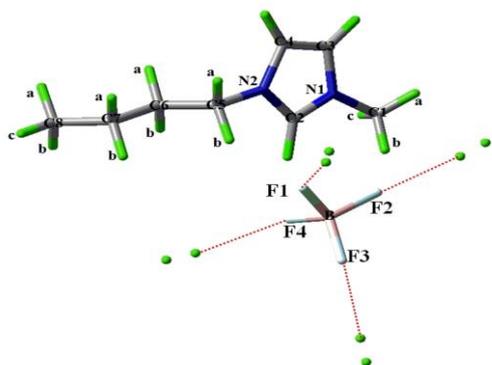
## 2. Computational details

In this work, all the quantum calculations on the structural optimizations, theoretical spectral characteristics, interaction energies with  $n\text{H}_2$  and molecular orbitals have been performed using density functional theory (DFT) [25] and Becke's three-parameter exchange function [26] combined with the exchange functional component of Perdew and Wang (B3PW91) [27], 6-31G (d) basis set level. Datta and Pati have reported that the PW91 function provided more successful outcomes than B3LYP related physical adsorption of molecular hydrogen for circulene derivatives [28]. Inputs on the atomic coordinates and the identification of redundant coordinates for all geometry optimizations and potential surface scans, respectively, have been formed by Gauss View software database [29]. All the optimizations on geometries of ion pairs and molecular  $\text{H}_2$  interactions have been performed by using Gaussian 09W program package [30]. Basis set superposition error (BSSE) corrections and interaction energies between fluorides with molecular  $\text{H}_2$  have been calculated by the counterpoise correction procedure (CP) [31]. The partial densities of states (PDOS) spectral analysis for each of the groups of atoms and contributions of the molecular orbitals have been performed by the agency of GaussSum Version 3.0 [32].

## 3. Results and discussion

### 3.1. Structural investigations on interactions

Firstly, we focused on exploring of the most stable conformation for  $n\text{H}_2$  interactions. Taking into account molecular  $\text{H}_2$  interactions, it is obvious that the clustering dihydrogen structures around anions ( $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{HCO}_3^-$ ) have minimum energies due to the strong electronegative effects. An imidazolium-based structure involving the interaction with  $+4\text{H}_2$  is shown in Fig.1.

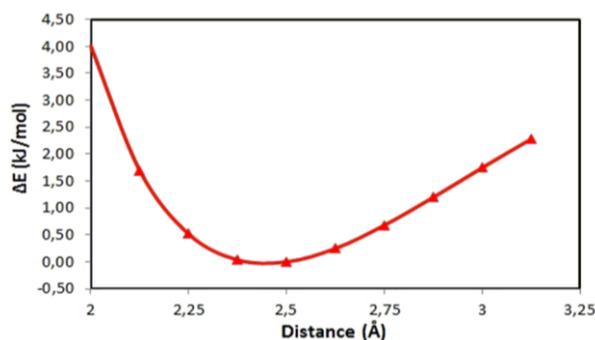


**Fig. 1.** Optimized structure of  $[\text{BMIM}]\text{BF}_4$  that emphasizes the interaction between  $\text{BF}_4^-$  and molecular  $\text{H}_2$

Total SCF energy, relative energy, structural properties of a single  $\text{H}_2$  interaction and the impacts on  $[\text{BMIM}]\text{BF}_4^-$  such as fluorine-dihydrogen distance are interpreted in the first section. For the single  $\text{H}_2$  interaction, the most stable conformations have been determined in  $\text{F1}\cdots\text{H}_2$  interaction and, total energy value for the whole structure,  $[\text{BMIM}]\text{BF}_4\cdots\text{H}_2$ , is equal  $-848.68806$  a.u. in quantum chemistry calculations. In other single  $\text{H}_2$  interactions,

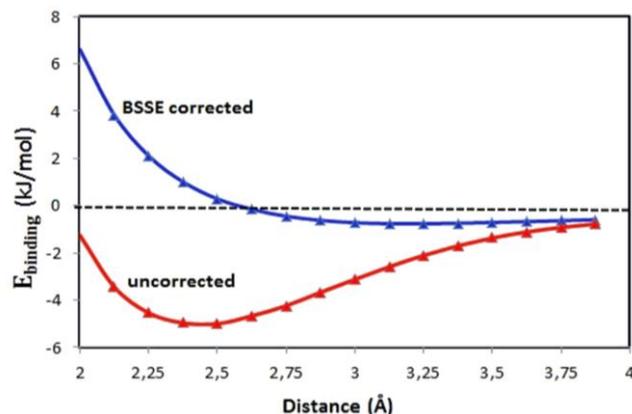
$\text{F2}\cdots\text{H}_2$ ,  $\text{F3}\cdots\text{H}_2$  and  $\text{F4}\cdots\text{H}_2$ , relative energies of  $[\text{BMIM}]\text{BF}_4\cdots\text{H}_2$  are at very small values of 0.09, 0.30 and 3.37 kJ/mol, respectively.  $\text{F1}\cdots\text{H}_2$  distance is approximately 2.449 Å and others are increased in the range of 2.449–2.480 Å.

The graphic obtained by data of optimized potential surface scan is given as Fig. 2. Potential energy surface (PES) computation is performed to determine the position of  $\text{H}_2$  molecule in stability of the  $\text{BF}_4-\text{H}_2$  interaction. Total energies of  $[\text{BMIM}]\text{BF}_4\cdots\text{H}_2$  structure are obtained by 0.125 Å increments of the each interaction distance from 2.000 Å to 3.125 Å in total step numbers of 10. Scan coordinates selected as  $\text{F1}-\text{H}_2$  interaction distances are variables of the x-axis and y-axis represents relative energies,  $\Delta E$ , to the total energy of  $[\text{BMIM}]\text{BF}_4\cdots\text{H}_2$  structure ( $\text{F1}-\text{H}_2$  interaction) in Fig. 2. Minimal relative energies are in the range of 2.375–2.500 Å. These results support the optimizations in the conformation analysis regarding molecular  $\text{H}_2$  positioning.



**Fig. 2.** Variation graph of relative energy with to  $\text{F1}-\text{H}_2$  interaction distances for  $[\text{BMIM}]\text{BF}_4\cdots n\text{H}_2$  structure

Fig. 3 shows the variations of BSSE corrected and uncorrected binding energies by the  $\text{F1}\cdots\text{H}_2$  distances in single molecular  $\text{H}_2$  interaction. Even though uncorrected binding energy between fluorine ( $\text{F1}$ ) and  $\text{H}_2$  is the minimal value in  $\sim 2.500$  Å, minimal interaction energy is in  $\sim 3.125$  Å in BSSE corrected calculation. While the anion- $\text{H}_2$  distances increase, interaction energies are closer to zero in both calculations (BSSE corrected and uncorrected). Also, it is remarkable that the BSSE corrected binding energy passes through negative value in 2.500–2.625 Å.



**Fig. 3.** BSSE corrected and uncorrected interaction energies of the molecular  $\text{H}_2$  (single) corresponds to  $\text{F1}-\text{H}_2$  interaction distances

Total energies and interaction energies in the anion-H<sub>2</sub> interactions for the various imidazolium-based structures have been listed in Table 1. While the numbers of hydrogen molecules included to anion interactions increases, the average interaction energies per H<sub>2</sub> mostly decreases in uncorrected and BSSE corrected calculations. For the zero point energy (ZPE) corrected calculations, the interaction per H<sub>2</sub> is stronger except for the PF<sub>6</sub><sup>-</sup>-H<sub>2</sub> interaction, while the amount of H<sub>2</sub> increases. In a previous study, the averaged adsorption energies (ZPE corrected) between a lithium functionalized naphthalene and +3H<sub>2</sub>, +6H<sub>2</sub> are calculated as 0.04, 0.02 eV (respectively), and these results are evaluated as the weak interactions with H<sub>2</sub> molecule [33]. Also, the fluorine-hydrogen distances (average values) for BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and oxygen-hydrogen distances for HCO<sub>3</sub><sup>-</sup> anion have been listed in Table 1. The average lengths have been calculated within the range 2.449–2.538 Å from the added single H<sub>2</sub> up to 8H<sub>2</sub> for the [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> complex. Similarly, structural parameters have resulted as 2.618, 2.656 Å and 2.432, 2.524 Å in [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and [BMIM]<sup>+</sup>HCO<sub>3</sub><sup>-</sup>, respectively. While the amounts of H<sub>2</sub> molecules added to the system increased, the binding abilities have decreased for all investigated compounds. The BSSE corrected interaction energies per H<sub>2</sub> have decreased

and, anion-H<sub>2</sub> distances have increased depending on the increase in the amount of H<sub>2</sub> molecules for [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> and [BMIM]<sup>+</sup>HCO<sub>3</sub><sup>-</sup> complexes. The calculations on the uncorrected interaction energies per H<sub>2</sub> contain these results for all complexes. Binding energies of up to loading 10 H<sub>2</sub> molecules to octathio[8]circulene are within the range -0.70 kcal/mol (+H<sub>2</sub>) and -4.5 kcal/mol (+10H<sub>2</sub>) and the distance between single H<sub>2</sub> molecule (vertically) and thiophene ring is 3.2 Å [28]. In a study of the H<sub>2</sub> adsorption on pure carbon nanotubes, the calculated binding energy for adsorbed H<sub>2</sub> molecule are ~57 meV and this results are assessed as the weak physical adsorption [34].

In the present work, the uncorrected interaction energies are close to the binding energies for these complexes with physisorption property. However, distances between the H<sub>2</sub> and anions are smaller. The small distance in H<sub>2</sub> interactions makes it difficult to store the hydrogen molecules whereas planar structures providing large surface areas are also effective for molecular hydrogen storage according to Datta and Pati [28]. For reasons highlighted above, despite of reasonable interaction energies, it is thought that the investigated ionic liquids are structurally unfavorable in terms of hydrogen storage.

**Table 1.** Energy values in the interactions and distances between imidazolium structures with the hydrogen molecules by ab initio calculations

Complex	Total SCF Energy (a.u.)	Interaction energy -uncorrected- (kJ/mol)	Interaction energy -BSSE corrected- (kJ/mol)	Interaction energy -ZPE corrected*- (kJ/mol)	Δd** (Å)
[BMIM] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>					
+H <sub>2</sub>	-848.688	-4.997	0.553	-1.321	2.449
+2H <sub>2</sub>	-849.864	-9.568 (-4.784)	1.013 (0.507)	-3.067 (-1.534)	2.468
+4H <sub>2</sub>	-852.216	-18.938 (-4.735)	1.829 (0.457)	-7.506 (-1.877)	2.469
+8H <sub>2</sub>	-856.919	-35.045 (-4.381)	3.114 (0.389)	-16.289 (-2.036)	2.538
[BMIM] <sup>+</sup> PF <sub>6</sub> <sup>-</sup>					
+H <sub>2</sub>	-1364.714	-2.979	0.227	-1.861	2.618
+6H <sub>2</sub>	-1370.592	-17.345 (-2.891)	2.164 (0.361)	-10.730 (-1.788)	2.656
[BMIM] <sup>+</sup> HCO <sub>3</sub> <sup>-</sup>					
+H <sub>2</sub>	-688.693	-6.555	-1.581	-0.549	2.432
+3H <sub>2</sub>	-691.046	-15.352 (-5.117)	-2.138 (1.069)	-4.096 (-1.365)	2.524

\* The interaction energy with zero point energy correction.

\*\* d[F<sup>-</sup>⋯H<sub>2</sub>] average values are for [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> and [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup>.

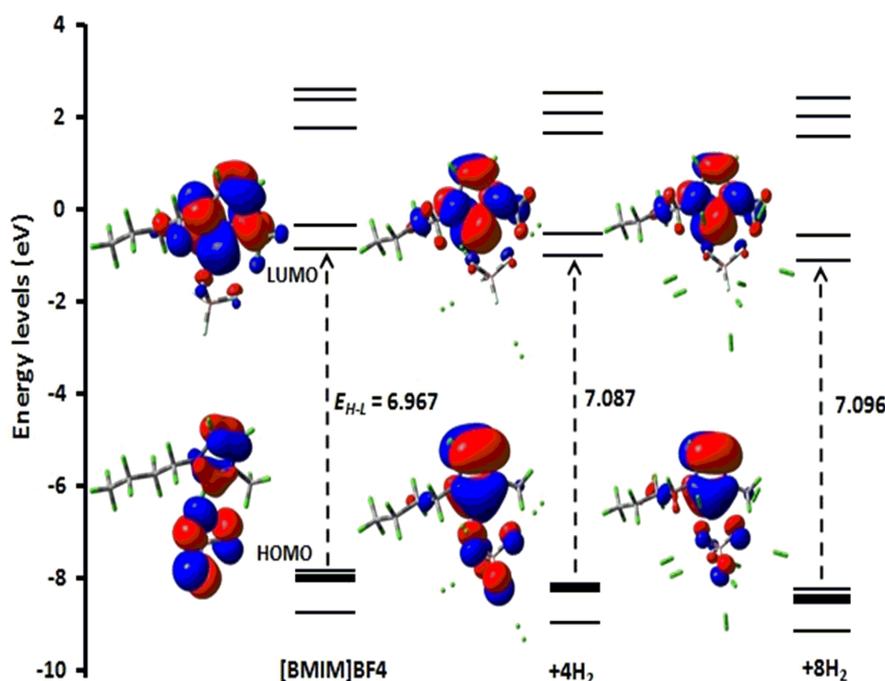
d[O<sup>-</sup>⋯H<sub>2</sub>] average values are for [BMIM]<sup>+</sup>HCO<sub>3</sub><sup>-</sup>.

The values in parentheses are average interaction energies per H<sub>2</sub>.

### 3.2. Molecular orbital analysis

HOMO and LUMO energies as frontier molecular orbitals (FMO's) are important to define the optical, electrical properties of compounds in quantum chemistry calculations, and act as electron donor and acceptor, respectively. [35–37]. The frontier molecular orbitals and energy diagrams of [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> and +nH<sub>2</sub> have been shown in Fig. 4. The positive and negative wave functions for the

molecular orbitals are shown in red and blue tones, respectively. Although the HOMO plot is scattered over the imidazolium moiety in cation and anion, LUMO is over the imidazolium structure, entirely. While the amounts of H<sub>2</sub> involved to the interaction increase, HOMO plot on BF<sub>4</sub><sup>-</sup> anion decreases and the energy gap between the FMO's also increases.



**Fig. 4.** Molecular orbital energy levels, boundary ranges and HOMO-LUMO visuals for [BMIM]BF<sub>4</sub>...nH<sub>2</sub> structures

The energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the selected IL's...nH<sub>2</sub> are given in Table 2. While the amounts of H<sub>2</sub> subjected to interaction increases, it is noteworthy that the differences in HOMO-LUMO energy gap are much higher than the BSSE corrected interaction energies. The changes of HOMO-LUMO energy gaps are much less than the adsorption energies, and this result has been interpreted as associated with the H<sub>2</sub> adsorption property of sumanene in a previous study [38]. Also, the HOMO-LUMO energy gaps in complexes (excepting [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup>...H<sub>2</sub>) that interact with the hydrogen molecules are higher than the gaps of pure [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and [BMIM]<sup>+</sup>HCO<sub>3</sub><sup>-</sup> structures in this study.

**Table 2.** Energy gaps of the frontier molecular orbitals obtained by ab initio computing

Complex	$\Delta E_{H-L}$ * (kJ/mol)	Relative values in $\Delta E_{H-L}$ (kJ/mol)
[BMIM] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	672.192	0.000
+H <sub>2</sub>	676.070	3.878
+2H <sub>2</sub>	677.807	5.615
+4H <sub>2</sub>	683.789	11.597
+8H <sub>2</sub>	684.658	12.466
[BMIM] <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	685.478	0.000
+H <sub>2</sub>	685.333	-0.145
+6H <sub>2</sub>	691.508	6.030
[BMIM] <sup>+</sup> HCO <sub>3</sub> <sup>-</sup>	447.208	0.00
+H <sub>2</sub>	453.480	6.272
+3H <sub>2</sub>	461.005	13.797

\* Energy gap between highest occupied molecular orbital and lowest unoccupied molecular orbital for the complex.

### 3.3. Spectral properties

The calculated <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (with respect to TMS) for [BMIM]BF<sub>4</sub> and the changes in [BMIM]BF<sub>4</sub>...nH<sub>2</sub> interactions have been listed in Table 3. When the results are compared with the experimental data [8] obtained from the literature, it can be said that the mean absolute errors (MAE) have reasonable values. The carbon and hydrogen atoms in the table are numbered according to the model in Fig. 1.

The chemical shifts in C2 (138.8 ppm), C3 (113.2 ppm), C4 (114.8 ppm) and H2 (10.86 ppm), H3 (6.49 ppm), H4 (6.52 ppm) are higher, compared with the ones of the other carbons. The high chemical shifts can be attributed to its proximity to the nitrogen atoms own electronegative property. The chemical shift values of carbon and hydrogen atoms in the methyl and methylene groups are also small as expected. The most significant changes in the chemical shifts of [BMIM]BF<sub>4</sub>...nH<sub>2</sub> are computed for the C5, C6 and H5b, H6b (see Table 3). <sup>1</sup>H chemical shift changes between [BMIM]BF<sub>4</sub> and [BMIM]BF<sub>4</sub>-acetonitrile (CH<sub>3</sub>CN) interaction have been computed as 0.64 (for H2), 0.44 (H3) and 0.45 ppm (H4) by DFT (B3LYP functional) calculations in a previous study [39]. In this study, the changes ( $\Delta\delta'$  and  $\Delta\delta''$ ) in <sup>1</sup>H and <sup>13</sup>C chemical shifts for the [BMIM]BF<sub>4</sub>...4H<sub>2</sub> and +8H<sub>2</sub> are associated that the electron-withdrawing groups (the attaching of the H<sub>2</sub> molecules) can decrease the shielding [40].

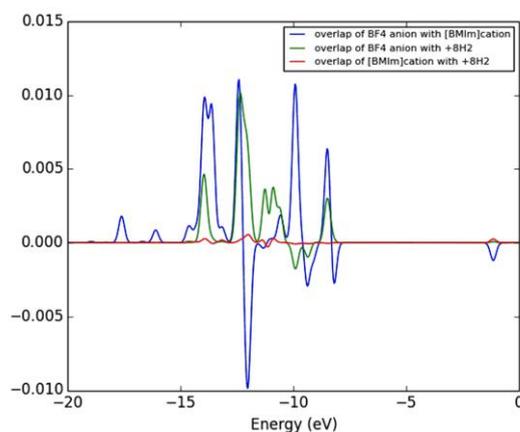
**Table 3.** Chemical shift values of [BMIM]BF<sub>4</sub> and the changes of [BMIM]BF<sub>4</sub>···*n*H<sub>2</sub> interactions in parts per million (ppm) relative to tetramethylsilane by ab initio calculations

Atom	Exp.**	[BMIM]BF <sub>4</sub>	$\Delta\delta'$ (in [BMIM]BF <sub>4</sub> + 4H <sub>2</sub> )	$\Delta\delta''$ (in [BMIM]BF <sub>4</sub> + 8H <sub>2</sub> )
C1	36.04	35.08	0.209	0.251
C2	135.99	138.82	0.167	0.732
C3	123.80	113.23	1.398	1.845
C4	126.50	114.83	0.474	0.364
C5	49.57	52.21	2.135	2.126
C6	31.86	30.53	4.886	4.894
C7	19.25	22.28	0.179	0.237
C8	13.27	15.54	0.003	0.020
	<i>MAE</i> =	<i>4.413</i>		
H1_a	3.962	3.173	0.035	0.078
H1_b		5.247	0.013	0.075
H1_c		3.277	0.063	0.113
H2	8.857	10.860	0.001	0.162
H3	7.417	6.490	0.068	0.108
H4	7.257	6.524	0.081	0.120
H5_a	4.191	3.248	0.158	0.225
H5_b		4.662	0.614	0.524
H6_a	1.864	1.422	0.204	0.217
H6_b		3.272	1.437	1.435
H7_a	1.358	1.242	0.136	0.149
H7_b		1.698	0.041	0.052
H8_a	0.959	0.898	0.012	0.006
H8_b		1.298	0.250	0.252
H8_c		1.183	0.083	0.095
+H <sub>2</sub> *		5.070, 3.864		
	<i>MAE</i> =	<i>0.752</i>		

\* Chemical shift value in [BMIM]BF<sub>4</sub>+H<sub>2</sub> and 5.070 ppm is for H close to F1. \*\* Taken from Ref. [8].

The COOP diagrams are defined as a multiplication of the density of states (DOS) spectrum and the overlap population in the form of positive or negative between two different groups expressed as bonding–antibonding with respect to each of the molecular orbitals [32]. In overlap population analysis, the positive, negative regions and zero line represent the bonding, anti-bonding and nonbonding interactions, respectively [41, 42]. The overlap between BF<sub>4</sub> anion with [BMIM] cation is more intense than ones of BF<sub>4</sub> anion with +8H<sub>2</sub> as illustrated in Fig. 5. The bonding interactions on BF<sub>4</sub><sup>-</sup>···8H<sub>2</sub> are effective, but weaker than BF<sub>4</sub><sup>-</sup>···[BMIM]<sup>+</sup> bonding interactions. The interaction energies between anion–cation have been computed in the range of -345.10 and -300.01 kJ/mol for the different four optimized conformers of [BMIM]<sup>+</sup>···BF<sub>4</sub><sup>-</sup> complex in a previous study [43]. These results too higher according to the interactions on BF<sub>4</sub><sup>-</sup>···8H<sub>2</sub>, and support the remarks obtained by the overlap population analysis. The interaction between [BMIM] cation and +8H<sub>2</sub> have been also interpreted as nonbonding

interactions. In addition, the anti-bonding interactions remain lower than bonding interactions.



**Fig. 5.** COOP diagrams between atoms groups in [BMIM]BF<sub>4</sub>···8H<sub>2</sub>

#### 4. Conclusions

In this work, a detailed analysis on interactions between the anions of several imidazolium-based compounds and loading molecular hydrogen has been presented with the aid of computational quantum mechanical modelling methods. The BSSE corrected, ZPE corrected and uncorrected interaction energies have been calculated for comparison. It was concluded that the interaction energies are very weak against the strong interaction lengths. It was also seen that the averaged interaction lengths increase while the number of the loading H<sub>2</sub> molecules have increased. The frontier molecular orbitals and energy diagrams are also remarkable on the anion-H<sub>2</sub> interactions. While the amounts of H<sub>2</sub> involved to the interaction increase, the HOMO plots surrounding the anion have decreased, markedly. In the spectral analysis section, the NMR calculations and overlap population diagrams have been reviewed. The significant variation of the chemical shifts in cation have been obtained by NMR calculations and compared with the studies in the literature. We have also found that the bonding interactions on the BF<sub>4</sub><sup>-</sup>...8H<sub>2</sub> are effective, but weaker than BF<sub>4</sub><sup>-</sup>...[BMIM]<sup>+</sup> bonding interactions. Consequently, it is believed that this study will contribute to green energy applications.

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