



## Research Article

# Theoretical Exploration of the Role of CO<sub>2</sub> in an Imidazolium Cation-Based Ionic Liquid

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### Abstract

Optimized structures of imidazolium cation-based ionic liquids (ILs) and CO<sub>2</sub> were obtained using the Gaussian 09 software package and density functional theory (B3LYP/6-31+G(d,p)) with dispersion correction. The interaction energy between cation and anion for imidazolium cation-based ILs, as well as that between ILs and CO<sub>2</sub>, were estimated to investigate specific interactions. The presence of CO<sub>2</sub> highly impacts the formation of the optimized geometry of imidazolium-based IL. The wavenumber of the C2-H stretching frequency in the imidazolium cation was calculated. The shift of the C2-H stretching wavenumber verified the strong interaction of CO<sub>2</sub> with imidazolium and halogen based ILs.

### Keywords

Carbon dioxide; Ab Initio calculation; Lewis acid and base; Interaction energy

## Introduction

The unique nature of ionic liquids (ILs) has allowed their usage to be extended to reactions, cellulose processing, and gas handling [1]. In particular, CO<sub>2</sub> capture with ILs has yielded several advantages over conventionally applied technology. Not only the minimal environmental impact of ILs, but also their physical properties (e.g., almost negligible vapor pressure) have made them able to assist power plant to discharge CO<sub>2</sub> at a controlled level.

There are several detailed explanations [2-4] as to how ILs considerably enhance CO<sub>2</sub> solubility. The essential factor in the higher solubility of CO<sub>2</sub> in ILs was the alkyl chain length on the cation. Further increasing the concentration of fluoroalkyl chains had much larger effect on the CO<sub>2</sub> solubility [5]. However, a much more important contribution of ILs to CO<sub>2</sub> solubility comes from anion counterparts. For example, increasing the fluorination of the anion boosts the CO<sub>2</sub>-philicity, causing higher CO<sub>2</sub> solubility [6].

In parallel with research on ILs, there has been substantial accomplishment in theoretical computation [7-11]. Density functional theory (DFT) calculations illustrated that vibrations of the imidazolium C-H group can be used as a fingerprint to gauge the interaction energy in ILs [12]. Dhumal et al. [9] showed that strong C-H...O interactions can serve to determine which among several conformers were the most

stable. Therefore being able to determine the optimized structure of a complex, as well as vibrational spectra, would be quite useful tools to determine the interaction between ILs and CO<sub>2</sub>.

Many researchers have reported CO<sub>2</sub> solubility data for ILs and looked into the reason why CO<sub>2</sub> has strong affinity with certain functional groups in ILs from a rigorous theoretical approach. Even so, the fundamental reason why the solubility of CO<sub>2</sub> is so high in certain type of ILs was still indistinct. In this study, we chose 1-ethyl-3-methylimidazolium as a cation, and fluorine, chloride, bromide, and tetrafluoroborate as anions. First, we found optimized geometry of four ILs, calculated both interaction energy and vibrational spectra of each, and carried out natural bond orbital (NBO) analysis to prove the existence of intermolecular hydrogen bonds. Second, we repeated the work in the presence of CO<sub>2</sub> to investigate the role of CO<sub>2</sub> in CO<sub>2</sub>-philic species of ILs.

## Computational Methods

An Intel Core™ i5-3470 desktop computer (3.20 GHz and 8.0 GB memory) and the Gaussian 09W (version 9.6) software package [13] were used to perform *ab initio* calculation. The optimum geometries of the IL-CO<sub>2</sub> compound complexes were found using DFT (B3LYP/6-31+G(d,p)) along with dispersion correction [14]. Specifically, the standard Grimme dispersion implemented in Gaussian was used. Once the optimized geometry was obtained, the interaction energy between IL and CO<sub>2</sub> was determined by assessing the complex energy; then cancelling the energy of each molecule, for IL and CO<sub>2</sub>, anion in IL and CO<sub>2</sub>, or cation in IL and CO<sub>2</sub>. This interaction energy was corrected for basis set superposition error (BSSE) using the counterpoise correction method [15]. The interaction energies are herein reported with and without the BSSE corrections. Second-order interaction energy, E<sup>(2)</sup>, in different conformer was analyzed by the natural bond orbital (NBO) method [11].

## Results and Discussion

### Optimum geometries and interaction energy

The geometries were optimized at B3LYP/6-31+G(d,p) with gd2 correction level from different initial guesses. The vibrational frequency analysis for each structure was carried out to obtain no imaginary frequencies to ensure a genuine minimum energy optimum structure. After successfully obtained the optimized structure, we calculated the interaction energy using equation (1).

$$\Delta E = E_{cluster} - \sum E_i \quad (1)$$

where  $\Delta E$  is the interaction energy,  $E_{cluster}$  is the energy of the cluster, and  $E_i$  is the energy of pure substance in an optimized geometry. The interaction energy was corrected by BSSE and is shown in Table 1.

In the absence of CO<sub>2</sub>, the optimized configurations of four ILs were presented in Figure 1. There are three hydrogen bonds, C2-H...[X], C5-H...[X], and C13-H...[X], in [EMIM][X], where X is a halogen atom. The bond length between acidic proton and halogen atom was increased as X was varied from F, Cl, to Br, as expected. For example, the bond lengths of C2-H...X were (2.026, 2.668, and 2.847) Å as X was varied from F, Cl, to Br, respectively (Table 2a). We utilized

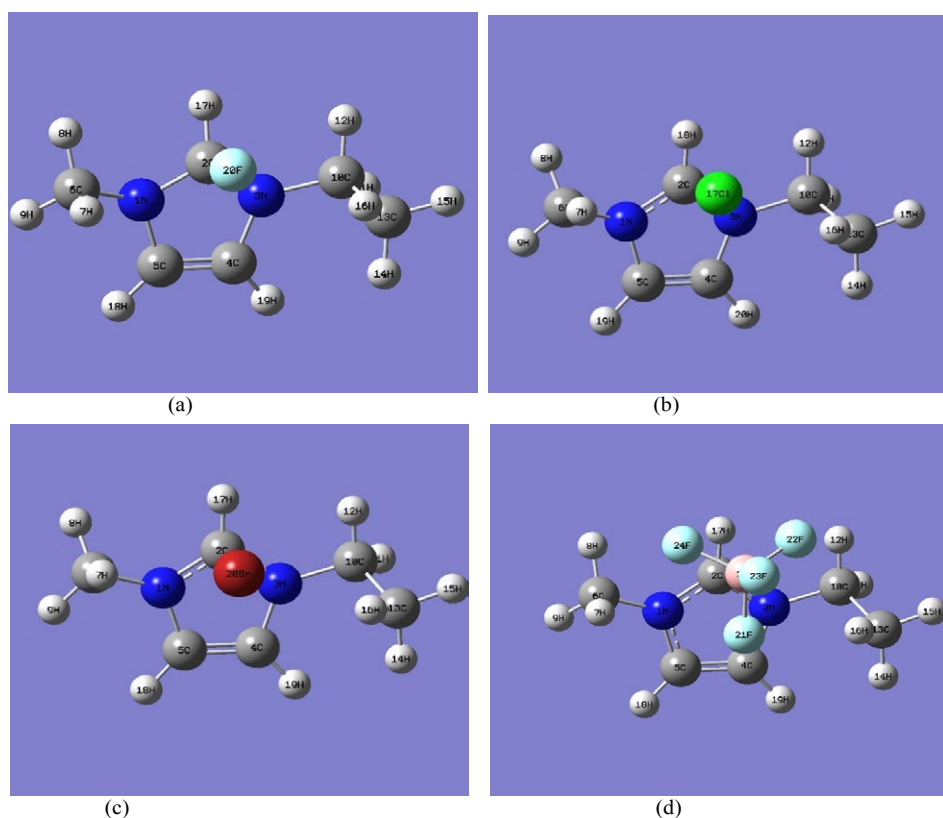
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**Table 1:** Interaction energies (kcal/mol) of different conformers at B3LYP/6-31+G\*\* with gd2 correction.

| Conformers | $\Delta E^a$ | $\Delta E_{corr}^b$ |
|------------|--------------|---------------------|
| A          | -117.9       | -115.8              |
| B          | -93.0        | -92.7               |
| C          | -97.0        | -89.5               |
| D          | -91.5        | -90.7               |
| E1         | -4.8         | -4.4                |
| E2         | -4.5         | -4.1                |
| E3         | -3.2         | -2.7                |
| E4         | -3.9         | -3.4                |
| F1         | -7.4         | -6.2                |
| F2         | -5.3         | -4.8                |
| F3         | -8.0         | -6.8                |
| F4         | -6.2         | -5.6                |
| G1         | -7.3         | -6.6                |
| G2         | -2.6         | -2.3                |
| G3         | -6.8         | -6.1                |
| G4         | -6.5         | -6.1                |
| H1         | -9.8         | -6.1                |
| H2         | -2.5         | -2.1                |
| H3         | -8.5         | -5.4                |
| H4         | -8.6         | -5.5                |
| I1         | -7.4         | -6.8                |
| I2         | -2.7         | -2.3                |
| I3         | -6.3         | -5.6                |
| I4         | -6.4         | -5.8                |

**Note:** a: interaction energy; b: BSSE corrected interaction energy.



**Figure 1:** The optimized configurations of [EMIM][X] calculated at the B3LYP/6-31+G (d,p) with gd2 correction level in the absence of CO<sub>2</sub>. (a) X=F, (b) X=Cl, (c) X=Br and (d) X=BF<sub>4</sub>.

a yardstick of 3.0 Å bond distance to determine hydrogen bond interaction, as Issaoui et al. described [16]. Given the higher number of hydrogen bonds formed between hydrogens in imidazolium and halogens allowed [EMIM][X] to form optimized geometries. If X was replaced by BF<sub>4</sub>, an optimized conformer of which the fluorine made as many as seven hydrogen bonds, the result was more stable geometry than with conformers containing a lesser number of hydrogen bonds. The bond length ranged from 2.371 Å for C2-H...F24 to 3.029 Å for C6-H...F21.

As can be seen in Figure 2, four optimized configurations of [EMIM]...CO<sub>2</sub> were found. Interestingly, the hydrogen bonds between oxygen in CO<sub>2</sub> and hydrogen in the ethyl substitutes in the imidazolium cation play a role in achieving the optimized structure. While the bond lengths of C2-H...O and C10-H...O were 2.367 and 2.557 Å, respectively, in the E1 conformer; those of C2-H...O and C10-H...O were 2.399 and 2.592 Å, respectively, in the E2 conformer. In contrast, in both E3 and E4 conformers, no hydrogen bonds were formed, with the result that the latter

Table 2a: Bond distance calculated in the absence of CO<sub>2</sub>.

| Conformer   | Cation-only | A     | B     | C     | D     |
|-------------|-------------|-------|-------|-------|-------|
| N1-C2       | 1.338       | 1.396 | 1.340 | 1.342 |       |
| C2-N3       | 1.339       | 1.400 | 1.343 | 1.344 |       |
| N3-C4       | 1.382       | 1.409 | 1.386 | 1.386 |       |
| C4-C5       | 1.366       | 1.348 | 1.361 | 1.361 |       |
| N3-C6       | 1.381       | 1.452 | 1.461 | 1.461 |       |
| N1-C7       | 1.481       | 1.456 | 1.470 | 1.470 |       |
| C7-C8       | 1.527       | 1.534 | 1.529 | 1.53  |       |
| C2-H...X    |             | 2.026 | 2.668 | 2.847 |       |
| C6-H...X    |             | 2.708 | 2.746 | 2.815 |       |
| C13-H...X   |             | 2.443 | 2.723 | 2.808 |       |
| C2-H...F24  |             |       |       |       | 2.371 |
| C2-H...F22  |             |       |       |       | 2.348 |
| C6-H...F21  |             |       |       |       | 3.029 |
| C6-H...F24  |             |       |       |       | 2.459 |
| C10-H...F22 |             |       |       |       | 2.450 |
| C13-H...F22 |             |       |       |       | 2.482 |
| C13-H...F21 |             |       |       |       | 2.491 |

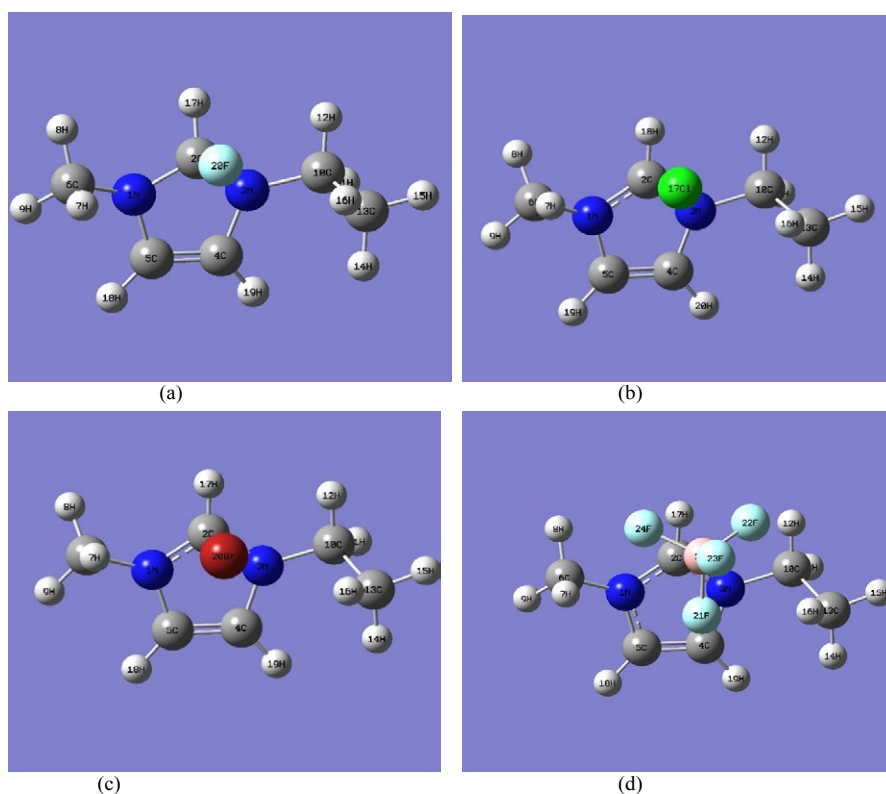


Figure 2: The optimized configurations of [EMIM]...CO<sub>2</sub> calculated at the B3LYP/6-31+G (d,p) with gd2 correction level. (a) E1, (b) E2, (c) E3 and (d) E4.

two conformers yielded much lower interaction energy than for E1 and E2.

In the case of the [EMIM][F]...CO<sub>2</sub> complex, the F1 conformer was found to have higher interaction energy than other conformers, as shown in Figure 3 and Table 2b. The bond angles of CO<sub>2</sub> were (140.1, 175.9, 138.7, and 176.7)° for each conformer (F1, F2, F3, and F4, respectively). There was a higher degree of bending for CO<sub>2</sub>, and stronger interaction energy in the conformer containing F as an anion in the [EMIM] cation-based IL. One possible reason for the higher degree of bending of the CO<sub>2</sub> molecule may be the repulsion of the oxygen in CO<sub>2</sub> by fluorine, which affected the number of hydrogen bonds formed not only between hydrogen and oxygen in CO<sub>2</sub>, but also between hydrogen and fluorine in [EMIM][F]. While there were three hydrogen bonds in F3 (C2-H...O, C10-H...O, and C13-H...O), there were five in F1 (C2-H...O, C5-H...O, C13-H...O, C2-H...F, and C10-H...F). Given the difference in the number of hydrogen bonds formed in both F1 and F3 conformers, higher number of hydrogen bonds resulted in much higher interaction energy.

In the cases of chlorine and bromide (Figure 4), G1 and H1 conformers were much higher interaction energy conformers than were the other conformers. The reason for this result might be that these G1 and H1 conformers allowed a larger number of hydrogen bonds than did the other conformers. Specifically, G1 had as many as five hydrogen bonds, which is far more than with other conformers. Similar results were obtained for the H1 conformers.

When BF<sub>4</sub> served as an anion in the IL, the interaction between the IL and CO<sub>2</sub> seemed interesting. The angles of CO<sub>2</sub> in I1, I3, and I4 conformers were (176.8, 176.9, and 176.8)°, respectively, however, that in the I2 conformer was 179.8°; so the angle in CO<sub>2</sub> somehow

illuminates the role of the interaction between fluorine and CO<sub>2</sub> (Figure 5). The distance between fluorine and CO<sub>2</sub> was too far to make Lewis base and Lewis acid interaction in the I2 conformer. The dihedral angle between the plane of the imidazolium ring (C2-H), and the B-F group in all four conformers, was nearly 180°. Therefore the geometry of CO<sub>2</sub> plays a critical role in determining the optimized structure in [EMIM][BF<sub>4</sub>]...CO<sub>2</sub> conformers (Figure 6). One possible reason for the I1 conformer having higher interaction energy would be that the Lewis acid (CO<sub>2</sub>) and Lewis base (BF<sub>4</sub>) interaction seems to be such an important factor. As Bell et al. claimed [10] the role of CO<sub>2</sub> depended strongly on the presence of other molecules.

### Natural Bond Orbital (NBO) analysis

An NBO analysis was carried out to prove the existence of interaction between the Lewis base of filled lone pairs (LP) and Lewis acid of the unfilled anti-bond ( $\sigma^*$ ). The magnitude of the second-order interaction energy,  $E^{(2)}$ , was determined using NBO 6.0 [17] and is reported in Table 3. The intermolecular O-H...X hydrogen bonds are formed by the orbital overlap between the LP(O) and  $\sigma^*(O-H)$ .

For [EMIM][F]...CO<sub>2</sub>, the energies of the hyper conjugate interactions for LP2(O22)  $\rightarrow$   $\sigma^*(C2-H17)$  and LP1(O22)  $\rightarrow$   $\sigma^*(C2-H17)$  were (2.77 and 2.20) kcal/mol, respectively, in the F1 conformer. These values in the F1 conformer were much higher than those in other conformers, which is in good agreement with the optimum geometry and bond length discussed in Section 5.1.

When the fluorine anion was replaced by chlorine, the values of  $E^{(2)}$  in the G conformers seemed inconsistent. Although the lowest interaction energy containing conformer, G2, had a lower  $E^{(2)}$  value than the other conformers, the highest interaction energy

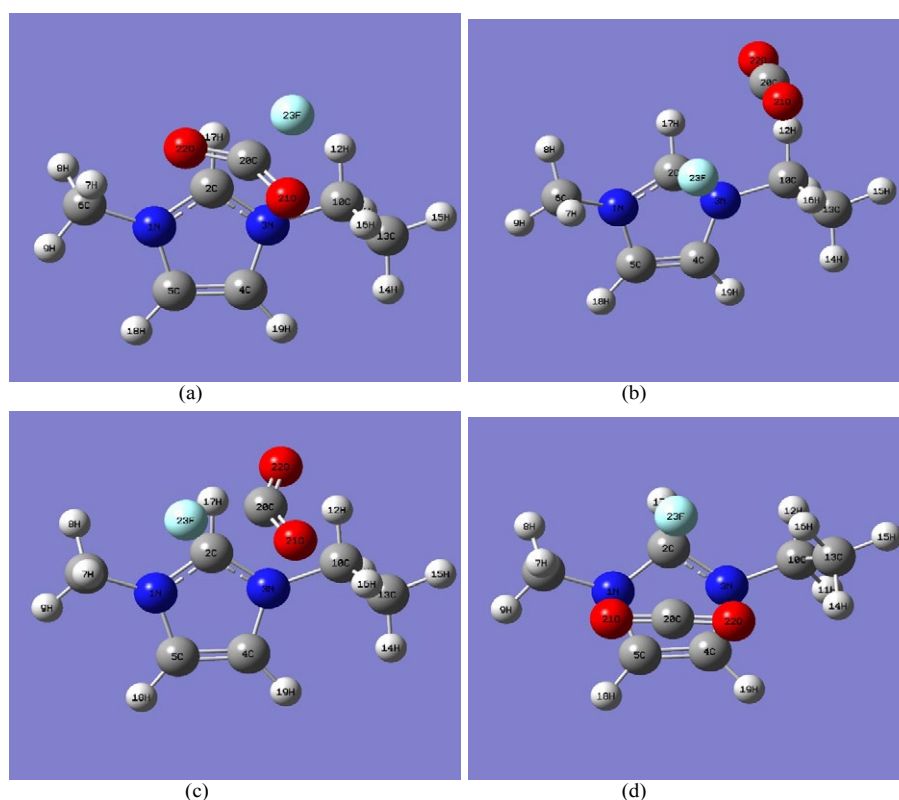


Figure 3: The optimized configurations of [EMIM][F]...CO<sub>2</sub> calculated at the B3LYP/6-31+G (d,p) with gd2 correction level. (a) F1, (b) F2, (c) F3 and (d) F4.

Table 2b: Bond distance and angle calculated in the presence of CO<sub>2</sub>.

| Conformer                   | F1    | F2    | F3    | F4    | G1    | G2    | G3    | G4    | H1    | H2    | H3    | H4    | I1    | I2    | I3    | I4    |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CO <sub>2</sub> (angle)     | 140.1 | 175.9 | 138.7 | 176.7 | 174.2 | 179.9 | 174.5 | 174.7 | 173.8 | 179.4 | 174.4 | 174.5 | 176.8 | 179.8 | 176.9 | 176.8 |
| C2-H...B-F*                 |       |       |       |       |       |       |       |       |       |       |       |       | 177.6 | 177.2 | 179.3 | 179.8 |
| X...C (in CO <sub>2</sub> ) | 1.558 | 2.619 | 1.535 | 2.767 | 3.116 |       | 3.132 | 3.149 | 3.212 | 6.826 | 3.234 | 3.220 |       |       |       |       |
| C2-H...O                    | 2.446 | 2.559 | 2.100 |       | 2.315 |       | 4.625 | 4.624 | 2.256 | 5.887 | 4.796 | 4.804 | 2.191 |       |       |       |
| C10-H...O                   |       | 4.123 | 2.410 |       | 2.505 | 4.050 | 5.044 | 5.985 | 2.737 | 2.785 | 3.251 | 6.314 | 3.576 |       |       |       |
| C13-H...O                   | 2.346 | 3.08  | 2.414 | 2.753 | 3.682 | 3.587 | 3.025 | 4.282 | 4.169 | 2.693 | 3.251 | 4.335 |       |       |       |       |
| C5-H...O                    | 2.245 |       |       |       |       |       |       |       | 2.805 |       |       |       | 3.440 |       |       |       |
| C2-H...X                    | 2.190 |       |       |       | 2.713 |       |       |       | 2.944 |       |       |       | 2.428 |       |       |       |
| C10-H...X                   | 2.356 |       |       |       | 2.732 |       |       |       | 2.788 |       |       |       | 2.471 |       |       |       |
| B...N1                      |       |       |       |       |       |       |       |       |       |       |       |       | 3.537 | 3.604 | 3.697 | 3.51  |
| B...N3                      |       |       |       |       |       |       |       |       |       |       |       |       | 3.532 | 3.576 | 3.72  | 3.549 |
| F1...H19                    |       |       |       |       |       |       |       |       |       |       |       |       | 2.471 | 2.503 | 2.406 | 2.432 |
| F1...C2                     |       |       |       |       |       |       |       |       |       |       |       |       | 2.868 | 2.857 | 2.92  | 2.843 |
| F2...H16                    |       |       |       |       |       |       |       |       |       |       |       |       | 2.473 | 2.456 | 2.298 | 2.84  |
| F2...C2                     |       |       |       |       |       |       |       |       |       |       |       |       | 2.889 | 2.876 | 2.919 | 2.844 |
| F...C(CO <sub>2</sub> )     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       | 2.715 |
| O2...H14                    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       | 2.921 |
| O2...H16                    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       | 2.457 |

Note: \*: dihedral angle

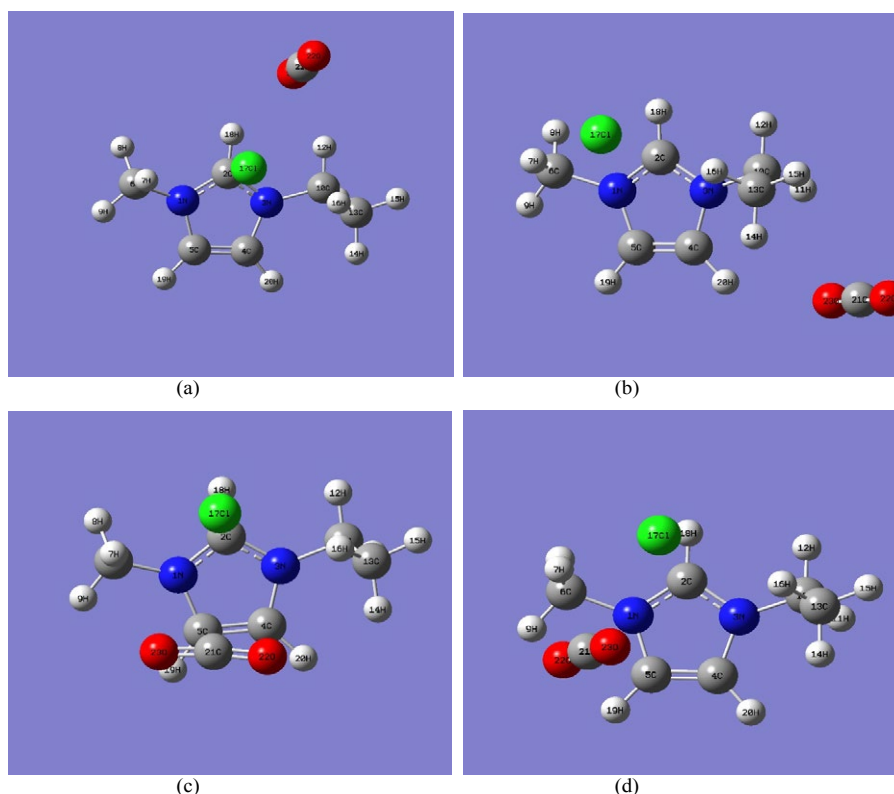


Figure 4: The optimized configurations of [EMIM][Cl]...CO<sub>2</sub> calculated at the B3LYP/6-31+G(d,p) with gd2 correction level. (a) G1, (b) G2, (c) G3 and (d) G4.

conformer, G1, did not have highest E<sup>(2)</sup> value. While E<sup>(2)</sup> values in the G1 conformer for LP2(O23) →σ\*(C2-H18) and LP1(O23) →σ\*(C2-H18) were (1.73 and 1.62) kcal/mol, respectively, those in the G3 conformer for LP2(Cl17) →σ\*(C13-H16) and LP3(Cl17) →σ\*(C13-H16) were (2.12 and 1.25) kcal/mol, respectively. The E<sup>(2)</sup> values in the G4 conformer for LP3(Cl17) →σ\*(C13-H16) and LP2(Cl17) →σ\*(C13-H16) were (2.08 and 1.34) kcal/mol, respectively.

This result illuminates the effect of chlorine as a Lewis base to interact with acidic hydrogen, on intermolecular hydrogen bonding.

While the H1 conformer contains not only C-H...O intermolecular hydrogen bonds but also C-H...Br intermolecular interactions, other H conformers do C-H...Br interactions only. For example, there were LP2(O22) →σ\*(C2-H17) and LP1(O22) →σ\*(C2-H17), as well as LP3(Br23) →σ\*(C13-H16) and LP1(Br23)

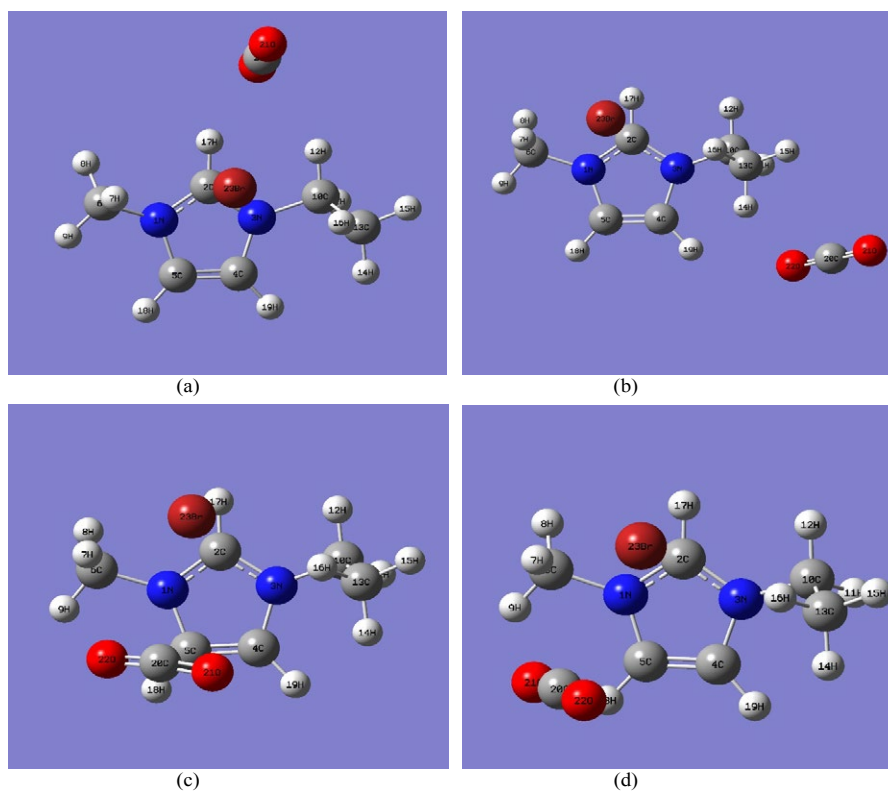


Figure 5: The optimized configurations of [EMIM][Br]...CO<sub>2</sub> calculated at the B3LYP/6-31+G(d,p) with gd2 correction level. (a) H1, (b) H2, (c) H3 and (d) H4.

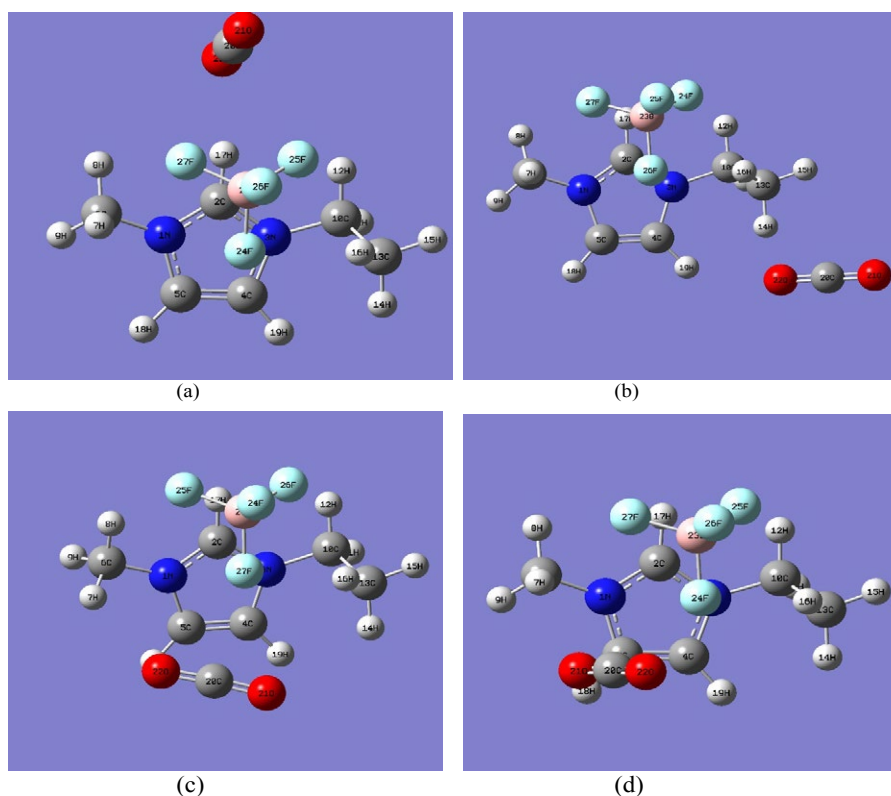


Figure 6: The optimized configurations of [EMIM][BF<sub>4</sub>]...CO<sub>2</sub> calculated at the B3LYP/6-31+G(d,p) with gd2 correction level. (a) I1, (b) I2, (c) I3 and (d) I4.

→σ\*(C13-H16) interactions in H1 the conformer. However, other H conformers (except the H1 conformer) contain LP(Br23) →σ\*(C-H), resulting in lower interaction energy, as discussed in Section 5.1.

The case for BF<sub>4</sub> as an anion in [EMIM][BF<sub>4</sub>]...CO<sub>2</sub> seems to exhibit a trend similar to that in the previous case. In other words, as long as E<sup>(2)</sup> is much higher in certain conformer (e.g. I1) higher binding energy is expected. Specifically, the E<sup>(2)</sup> values in I1 for LP2(O22) →σ\*(C2-H17) and LP1(O22) →σ\*(C2-H17) were (3.75 and 3.04) kcal/mol, respectively; much higher than those in other conformers. Thus there is a significant correlation between the interaction energy of [EMIM][Anion]...CO<sub>2</sub> and the energy of hyper conjugate interactions. The higher degree of interaction between a Lewis base in lone pairs (in particular, oxygen in CO<sub>2</sub>) and Lewis acid in imidazolium cation means a much higher interaction energy in imidazolium-based IL and CO<sub>2</sub>; so long as the anions are F, Cl, Br, or BF<sub>4</sub>.

### Vibrational spectrum

Wulf et al. [18] used infrared spectroscopy for the study of hydrogen bonding, and it is now considered a powerful tool to theoretically calculate the shift (Δν) of the C-H stretching frequency. Regarding the interaction energy of [EMIM][X] in the absence of CO<sub>2</sub>, the interaction energy shows a linear relationship with regard to the shift of the C2-H stretching frequency. Specifically, the interaction energy of [EMIM][F] and ν were determined to be as high as -115.8

kcal/mol and 169 cm<sup>-1</sup>, respectively. In the case of [EMIM][Br] (Figure 5), the interaction energy and Δν were -89.5 kcal/mol and 37 cm<sup>-1</sup>, respectively (Table 4). This result signals that vibrational shifts in the C-H stretching frequency in the imidazolium cation might be related to the hydrogen bonding. The shift of C-H stretching frequency changed dramatically from 3124 cm<sup>-1</sup> for [EMIM][F] to 3296 cm<sup>-1</sup> in the presence of CO<sub>2</sub>. This huge shift to a higher wavenumber suggests enhanced interaction between IL and CO<sub>2</sub>. This result echoes that the one that the presence of fluorine tended to enhance the solubility of the catalyst in CO<sub>2</sub> [19].

### Conclusion

The interaction energies of 1-ethyl-3-methylimidazolium cation based ILs was determined using the DFT method by varying the anions among F, Cl, Br, and BF<sub>4</sub>. In order to investigate the effect of CO<sub>2</sub> on interaction between cation and anion, the interaction energy of the ILs was calculated with and without CO<sub>2</sub>. In the case of [EMIM] based ILs, the stable conformers depended strongly on the number of hydrogen bonds formed between the anion that served as a Lewis base, and the acidic proton in the cation. The formation of hydrogen bonds in the presence of CO<sub>2</sub> considerably impacted the stability of IL...CO<sub>2</sub> cluster. The NBO results also suggested that there was a certain degree of hydrogen bonding between the oxygen in CO<sub>2</sub> and the acidic proton in the imidazolium cation. The shift of vibrational wavenumber in C-H stretching frequency in the imidazolium cation,

Table 3: Second-order interaction energy, E(2), in different conformer.

| Conformers | Donor (i)   | Acceptor (j)     | E <sup>(2)</sup> |
|------------|-------------|------------------|------------------|
| A          | LP (1) N1   | BD*(1) C2 - F20  | 31.44            |
|            | LP (1) N3   | BD*(1) C2 - F20  | 34.43            |
| B          | LP (1) N1   | BD*(2) C2 - N3   | 75.83            |
|            | LP (1) N1   | BD*(2) C4 - C5   | 31.47            |
| C          | LP (1) N1   | BD*(2) C2 - N3   | 75.15            |
|            | LP (1) N1   | BD*(2) C4 - C5   | 31.11            |
| D          | LP (1) N1   | BD*(2) C2 - N3   | 79.58            |
|            | LP (1) N1   | BD*(2) C4 - C5   | 31.47            |
| F1         | LP (2) O22  | BD*(1) C2- H17   | 2.77             |
|            | LP (1) O22  | BD*(1) C2- H17   | 2.20             |
| G1         | LP (1) O 23 | BD*(1) C2- H18   | 1.62             |
|            | LP (2) O 23 | BD*(1) C2- H18   | 1.73             |
| G3         | LP (3)Cl17  | BD*(1) C13 - H16 | 1.25             |
|            | LP (2)Cl17  | BD*(1) C13 - H16 | 2.12             |
| G4         | LP (2)Cl17  | BD*(1) C13 - H16 | 1.34             |
|            | LP (3)Cl17  | BD*(1) C13 - H16 | 2.08             |
| H1         | LP (1) O 22 | BD*(1) C2- H17   | 2.22             |
|            | LP (2) O 22 | BD*(1) C2- H17   | 1.89             |
|            | LP (1)Br23  | BD*(1) C13- H16  | 3.62             |
|            | LP (3)Br23  | BD*(1) C13- H16  | 3.78             |
| I1         | LP (2) O 22 | BD*(1) C2- H17   | 3.75             |
|            | LP (1) O 22 | BD*(1) C2- H17   | 3.04             |

Table 4: Calculated vibrational frequencies and their assignment in different conformers.

| Conformer                        | E                    | A    | B      | C       | D       | F1                   | G1     | H1      | I1      |                      |
|----------------------------------|----------------------|------|--------|---------|---------|----------------------|--------|---------|---------|----------------------|
| Compound                         | BMIM BF <sub>4</sub> | EMIM | EMIM F | EMIM Cl | EMIM Br | EMIM BF <sub>4</sub> | EMIM F | EMIM Cl | EMIM Br | EMIM BF <sub>4</sub> |
| ν <sub>SS</sub> -CH <sub>3</sub> | 2888                 | 3056 | 3010   | 3024    | 3015    | 3056                 | 3043   | 3044    | 3015    | 3057                 |
| ν <sub>FR</sub> -CH <sub>3</sub> | 2960                 | 3153 | 3089   | 3122    | 3114    | 3158                 | 3141   | 3142    | 3117    | 3156                 |
| ν <sub>AS</sub> -CH <sub>3</sub> | 2974                 | 3168 | 3115   | 3149    | 3149    | 3172                 | 3159   | 3166    | 3150    | 3172                 |
| ν(C2-H)                          | 3122                 | 3293 | 3124   | 3335    | 3330    | 3320                 | 3296   | 3357    | 3324    | 3304                 |
| ν(C4,5-H)                        | 3162                 | 3286 | 3271   | 3307    | 3290    | 3290                 | 3291   | 3309    | 3291    | 3292                 |

had some relation to the degree of intermolecular hydrogen bonding in imidazolium based ILs.

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