Computational Study of CO_2 Capture by 1-Ethyl-methylimidazolium bis(trifluoro methylsulfonyl)imide, [EMI][TFSI] and 1-Ethyl-methylimidazolium tetrafluoroborate [EMI][BF_4]

Rawiporn Meechoo[1], Piyarat Nimmanpipug[1*]

[1]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

Abstract

Interactions of [EMI][TFSI] and [EMI][BF_4] with CO_2 were studied using DFT calculations at the B3LYP/6-311G+(2d,p) level. The anions of [TFSI] and [BF_4] exhibit symmetric structures with evenly distributed charges. CO_2 captures were observed with structural changes, including a slight increase in C=O bond length and a decrease in the OCO angle. The interaction with [BF_4] was stronger, as indicated by a greater reduction in boron (B) charge upon CO_2 binding, which was further supported by infrared (IR) analysis showing a larger redshift in C=O stretching frequencies for [BF_4] compared to [TFSI].

Introduction

Global warming, caused by increased CO_2 emissions, has led to climate change. CO_2 capture methods, including using ionic liquids (ILs) like [EMI][TFSI] and [EMI][BF_4], are effective for reducing CO_2 levels. These ILs are stable, have low melting points, and are highly efficient in absorbing CO_2.

Objectives

- To study the molecular geometry of [EMI][TFSI] and [EMI][BF_4] and calculate their binding energy using DFT at the B3LYP/6-311G+(2d,p)
- To analyze and compare the CO_2 capture efficiency of [EMI][TFSI] and [EMI][BF_4] using computational chemistry

Methods

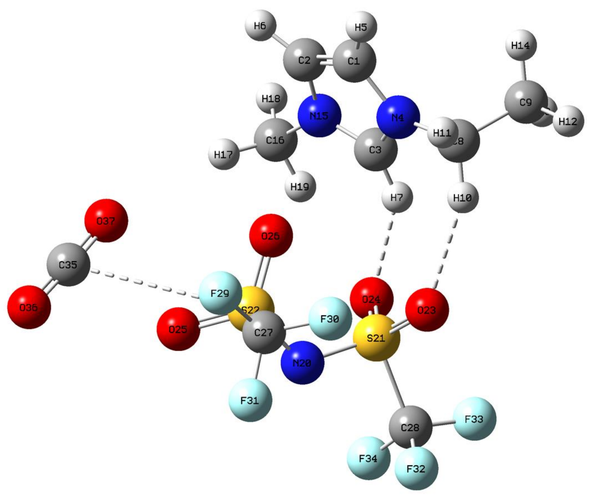
Optimization Structure: The structures of $[EMI]^+$, [EMI][TFSI], and [EMI][BF_4] were optimized using DFT at the B3LYP/6-311G+G(2d,p) level.

CO_2 Interaction: The CO_2 interaction with [EMI][TFSI] and [EMI][BF_4] was studied by optimizing their configurations with CO_2.

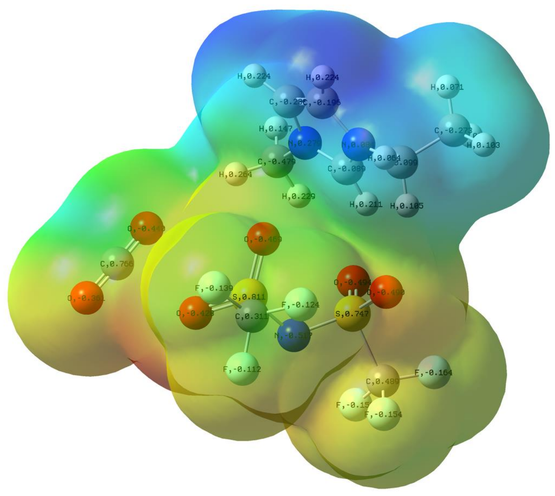
Energy Calculations: Binding energies (E_{bind}) were calculated.

Charge and Spectral Analysis: Electrostatic potential (ESP) charge analysis and IR spectral analysis were used to study the interactions and bonding changes.

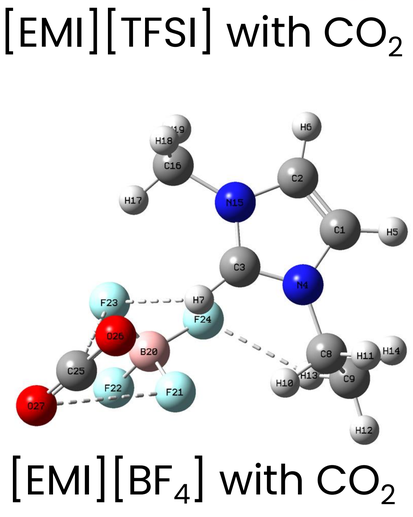
Results: Stable Structures of CO_2 with [EMI][TFSI], and [EMI][BF_4]



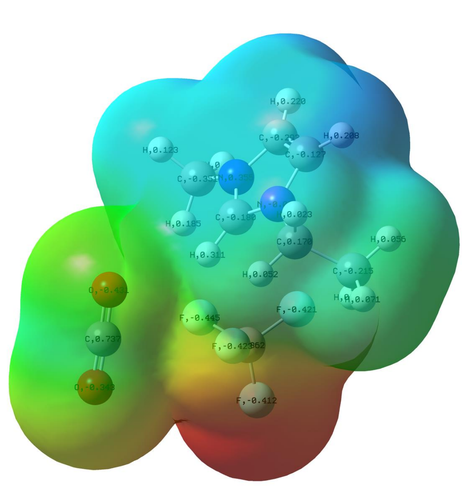
[EMI][TFSI] with CO_2



ESP charge & ESP Map



[EMI][BF_4] with CO_2



Binding Energy

Compound/Complex	Total Energy (Hartree)	Binding Energy (kJ/mol)
CO_2	-188.6506	-
[EMI][BF_4]	-769.4734	-
[EMI][TFSI]	-2172.4610	-
[EMI(BF_4)(CO_2)]	-958.1293	-13.91
[EMI(TFSI)(CO_2)]	-2361.1157	-10.57

IR spectrum Analysis

Structure	Frequency of C=O (cm^{-1})		Change (cm^{-1})	IR Intensity (Before ⟶ After)
	Before CO_2 Capture	After CO_2 capture		
[EMI][BF_4]	1595.36	1598.10	+2.74	47.60 ⟶ 44.59
[EMI][BF_4]	1603.69	1604.56	+0.87	15.87 ⟶ 22.55
[EMI][TFSI]	1597.48	1598.87	+1.39	N/A

Conclusion

$[EMI]^+$ has a stable quasi-planar structure with balanced charge distribution. CO_2 binding affects bond lengths and angles, with stronger interactions observed in [EMI][BF_4] than [EMI][TFSI], enhancing CO_2 capture efficiency.

References

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- Bazargani Z. Sabzi F. (2016). **Thermodynamic modeling of CO_2 absorption in 1-butyl-3-methylimidazolium-based ionic liquids.** Journal of Molecular Liquids, 223, 235-242.