



Interaction of Dibromomethylimidazolium Ion with Trihalomethanesulfonates (CX₃SO₃⁻, Where X = F, Cl, Br and H): A Model for Organic Ionic Liquids

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The imidazolium ion is a typical species that is used for providing the cation part in the organic ionic liquid. The DFT calculations on the interaction between dibromomethylimidazolium cation and trihalomethane sulfonates, CX₃SO₃⁻ where X = F, Cl, Br and H, have been performed. The intermolecular interactions which usually control the properties of these organic liquids were investigated based on DFT calculations. It was found that intramolecular interaction is most favored when X is equal to H. These interactions in the complex units were found to depend on the electrostatic force between the positively charged Br-atoms in the dibromomethylimidazolium and the free O2-atom in the CX₃SO₃⁻ ion. The overlap between the HOMO of the CX₃SO₃⁻ as electron-rich Lewis base and the empty LUMO of the dibromomethylimidazolium cation indicates that these interactions are orbitally controlled.

Keywords: Organic ionic liquid, DFT, Imidazolium cation, DFT-MEP.

INTRODUCTION

The organic ionic liquids became of highly interest due to their use as functional, low vapor pressure and reaction beneficial solvents¹⁻⁴. The physicochemical properties and functionalities of organic ionic liquids can be easily tuned by chemical modification of their functional groups⁵. Of these organic ionic liquids, the halogen substitutions on the imidazolium cation, a typical cation of ionic liquids, provide highly dense⁶ and hydrophobic⁷ ionic liquids. The antibonding orbitals of organic halide groups act as electron acceptor sites, the halide group associated with an electron-poor carbon interacts linearly with a Lewis base. Therefore, earlier studies focused on a halide group acting as a highly directional Lewis acidic group⁸⁻¹⁵. This intermolecular interaction is generally called halogen bonding (XB). Changing the structure of the Lewis acid or Lewis base control the strength of this interaction which will lead to a new generation of ionic liquids¹⁶, which give an important information on the correlation between interionic interaction strengths and physical properties of the ionic liquids¹⁷. Theoretical calculations on these organic salts provide valuable information on these interionic interactions and could help in the design and synthesis of more sophisticated organic ionic liquids. In the present work, we studied theoretically the interaction of dibromomethylimidazolium ion with trihalomethanesulfonates (CX₃SO₃⁻ where X = F, Cl, Br and H).

COMPUTATIONAL METHODS

All calculations for the monomers as well as their corresponding complexes were calculated using Gaussian-03 software¹⁸ on Pentium IV processor personal computer. The calculations were performed using the B3LYP/6-311G level. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. Gauss view¹⁹ has been used to draw the structures of the optimized geometries.

RESULTS AND DISCUSSION

Energies and thermodynamics of the reaction: Thermodynamics and interaction energies (ΔE) of the formation reactions of complexes **1-4** are calculated using DFT/B3LYP method at 6-311G(d,p) basis set. The results are shown in Table-1. The negative value of ΔE indicates the higher stability of the complexes relative to the reactant molecules. Also, the formation reaction is spontaneous as indicated from the negative value of ΔG . The interaction is most favored when X = H indicating that, the electron attracting groups (X = F, Cl or Br) decreases the interaction between the monomer molecules. The rate constant (K) for the complex formation reaction is

calculated using the equation $K = e^{\frac{-\Delta G}{RT}}$ where the gas

TABLE-1
 CALCULATED ΔE , ΔG , ΔS AND ΔH VALUES OF THE STUDIED COMPLEXES

	1 (X = F)	2 (X = Cl)	3 (X = Br)	4 (X = H)
ΔE^a	-87.621	-84.958	-85.082	-96.725
ΔG^a	-77.730	-74.472	-74.670	-85.149
ΔS^b	-0.031	-0.033	-0.033	-0.039
ΔH^a	-87.011	-84.388	-84.489	-96.736
K	4.094×10^{56}	1.733×10^{54}	2.417×10^{54}	1.035×10^{61}
μ (Debye)	13.519	13.615	13.393	9.965

^aCal/mol and ^bCal/mol-Kelvin

constant (R) is 2×10^{-3} Kcal/mol, the temperature (T) is 298.15 K and the quantity ΔG is taken from Table-1. For these reactions the entropy change (ΔS) is nearly neglected or at least very small. The calculated ΔS and the rate constant values are provided in Table-1.

Geometry description: The optimized geometry of the studied complexes and their monomers are calculated using the B3LYP/6-311G (d,p) method. As noted from Table-2 and Fig. 1, most of the bond distances and bond angles are unchanged. Only S_1-O_2 , S_1-O_4 and S_1-C_8 bond distances and $O_3-S_1-O_4$ bond angle have changed very slightly. The predicted H-bonding intermolecular distances for the studied complexes are given in Table-3. These results indicate the presence of H-bonding interaction between the O-atoms and the neighboring H-atoms. The O---H9 intramolecular H-bonding distances are shorter and hence stronger than the others. The results are in good agreement with the known fact that, the C-H9 bond has high acidic character as it lies between two strong electronegative N-atoms. It is found that, the H-bonding interactions in case of complexes **1**, **2** and **3**, where X = F, Cl or Br, are much weaker than that in complex **4** (X = H). It is noted that, the orientation of the $CH_3SO_3^-$ group is not the same as that for complexes **1**, **2** and **3**. Significantly, the orientation of the free O2-atom of **1** not allows the linear aggregation of the complex molecular units. Therefore, complex **1** is the least suitable structure for obtaining ionic liquid. In contrast, complexes **2-4** have free O-atom oriented to the outside which gives the possibility of good linear molecular packing (Fig. 1).

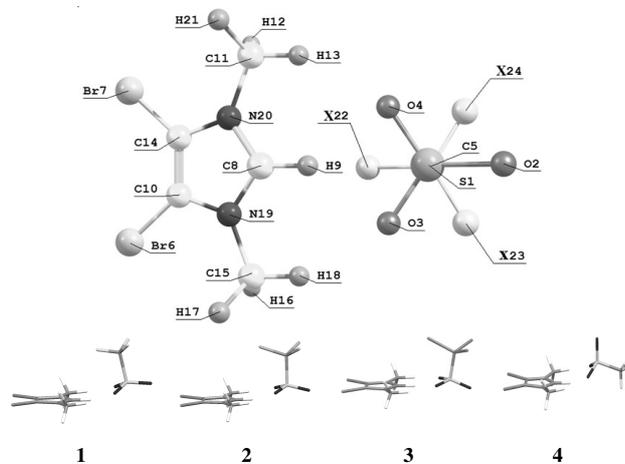


Fig. 1. Atom numbering scheme and the optimized geometry of the ionic liquid model complexes that consist of dibromomethylimidazolium ion and trihalomethanesulfonates ($CX_3SO_3^-$ where X = F, Cl, Br and H for complexes **1**, **2**, **3** and **4**, respectively). (Note the change of the orientation of the O2-atom in complex **4**)

 TABLE-2
 CALCULATED GEOMETRIC PARAMETERS (BOND DISTANCES AND ANGLES) OF THE COMPLEXES 1-4

Parameter	1	2	3	4
R(1-2)	1.456	1.456	1.457	1.470
R(1-3)	1.488	1.486	1.486	1.504
R(1-4)	1.489	1.485	1.487	1.502
R(1-8)	1.874	1.925	1.918	1.806
R(5-8)	1.337	1.815	1.957	1.089
R(6-8)	1.337	1.784	1.957	1.089
R(7-8)	1.356	1.784	1.989	1.089
R(9-13)	1.863	1.863	1.863	1.864
R(10-17)	1.863	1.863	1.863	1.864
R(11-12)	1.082	1.082	1.083	1.085
R(11-22)	1.335	1.335	1.334	1.335
R(11-23)	1.335	1.335	1.334	1.335
R(13-17)	1.368	1.368	1.369	1.368
R(13-22)	1.387	1.387	1.387	1.387
R(14-15)	1.089	1.089	1.089	1.090
R(14-16)	1.090	1.090	1.09	1.092
R(14-23)	1.472	1.472	1.472	1.472
R(14-24)	1.090	1.090	1.09	1.089
R(17-23)	1.387	1.387	1.387	1.387
R(18-19)	1.089	1.089	1.089	1.090
R(18-20)	1.090	1.090	1.09	1.089
R(18-21)	1.090	1.090	1.09	1.092
R(18-22)	1.472	1.472	1.472	1.472
A(2-1-3)	116.7	116.6	116.4	114.3
A(2-1-4)	116.7	116.6	116.4	114.5
A(2-1-8)	105.6	104.6	104.6	107.2
A(3-1-4)	111.3	111.4	111.2	109.7
A(3-1-8)	102.0	102.6	103.0	105.1
A(4-1-8)	102.0	102.6	103.0	105.2
A(1-8-5)	111.6	108.9	109.6	108.1
A(1-8-6)	111.5	109.6	109.6	108.5
A(1-8-7)	109.6	109.6	109.2	108.1
A(5-8-6)	108.6	109.2	110.3	110.7
A(5-8-7)	107.7	109.2	109.1	110.5
A(6-8-7)	107.7	110.3	109.1	110.7
A(9-13-17)	129.7	129.7	129.7	129.7
A(9-13-22)	123.3	123.3	123.3	123.4
A(10-17-13)	129.7	129.7	129.7	129.6
A(10-17-23)	123.3	123.3	123.3	123.4
A(12-11-22)	125.4	125.2	125.4	124.9
A(12-11-23)	125.2	125.4	125.2	125.7
A(22-11-23)	109.4	109.4	109.4	109.3
A(11-22-13)	108.3	108.3	108.3	108.4
A(11-22-18)	123.6	123.6	123.6	123.3
A(11-23-14)	123.6	123.7	123.5	123.4
A(11-23-17)	108.4	108.3	108.3	108.4
A(17-13-22)	107.0	107.0	107.0	107.0
A(13-17-23)	107.0	107.0	107.0	107.0
A(13-22-18)	128.0	128.0	128.1	128.3
A(15-14-16)	110.1	110.0	110.3	111.6

A(15-14-23)	109.1	109.1	109.2	109.6
A(15-14-24)	110.0	110.0	110.0	110.0
A(16-14-23)	107.0	107.1	107.0	106.7
A(16-14-24)	111.1	111.1	110.8	110.0
A(23-14-24)	109.6	109.5	109.5	108.9
A(14-23-17)	128.0	128.0	128.1	128.2
A(19-18-20)	110.0	110.0	110.0	110.0
A(19-18-21)	110.1	110.0	110.3	111.5
A(19-18-22)	109.0	109.1	109.2	109.7
A(20-18-21)	111.1	111.0	110.8	110.0
A(20-18-22)	109.6	109.6	109.5	108.9
A(21-18-22)	107.0	107.1	107.0	106.7

TABLE-3
CALCULATED H-BONDING INTERMOLECULAR
DISTANCES OF THE COMPLEXES 1-4

	1	2	3	4
O ₃ ...H ₉	2.0903	2.0764	2.0772	2.0285
O ₂ ...H ₉	2.0706	2.0967	2.0586	2.0931
O ₄ ...H ₁₃	2.2006	2.2113	2.2228	2.1222
O ₃ ...H ₁₈	2.1923	2.2198	2.2122	2.1495

Natural atomic charges: The natural atomic charges (NAC) are calculated using B3LYP/6-11G(d,p) method. The natural atomic charges values for the most important atomic sites are given in Table-4. It is known that, the interaction between the Br-atoms of the dibromomethylimidazolium ion as Lewis acid and the O-atoms of the CX₃SO₃⁻ ion as Lewis base is responsible for the formation of highly directional organic ionic liquid. One of the factors that affect such interactions is the electrostatic attraction force between these two units. The calculations showed that, the Br-atoms of the Lewis acid has positive charge while the O-atoms in the CX₃SO₃⁻ ion have negative charge densities. From this point of view, it is concluded that the interaction between these molecular units is controlled by electrostatic attraction force.

TABLE-4
CALCULATED NATURAL ATOMIC CHARGES
OF THE STUDIED COMPLEXES

Atom	1	2	3	4
O2	-0.9109	-0.9062	-0.9066	-0.9626
O3	-1.0173	-1.0098	-1.0090	-1.0540
O4	-1.0178	-1.0093	-1.0094	-1.0526
Br6	0.1689	0.1697	0.1689	0.1625
Br7	0.1689	0.1697	0.1688	0.1626

Molecular electrostatic potential (MEP): Molecular electrostatic potential (MEP) is a useful quantity to illustrate the charge distributions of molecules. It is also used to visualize variably charged regions of a molecule. Since the charge distributions can give information about how the molecules interact with another molecule, therefore molecular electrostatic potential is widely used as a reactivity map for determining sites of intermolecular interaction and associations²⁰⁻²³. To predict these reactive sites, the molecular electrostatic potential at the B3LYP/6-311G(d,p) optimized geometry was calculated. Molecular electrostatic potential decreases in the order blue, green, yellow, orange, red in the colour coded orbitals. The negative (red) regions of the molecular electrostatic potential are related to the electrophilic reactivity and the positive (blue) regions are related to the nucleophilic reactivity. The molecular

electrostatic potential map shows that the region of the maximum negative electrostatic potential is located around O2 with molecular electrostatic potential values around -0.0792, -0.0773, -0.0779 and -0.0846 a.u. for complexes 1, 2, 3 and 4, respectively. On the other hand, the most positive regions are localized on Br-atoms having values of + 0.0547, +0.0550, +0.0551 and +0.0486 a.u. for complexes 1, 2, 3 and 4, respectively. These results confirm the importance of the electrostatic interactions forces between the Br-sites of one complex unit and the O2-atom of the other unit.

Frontier molecular orbitals (FMOs): Frontier molecular orbitals (FMOs) *i.e.* the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown in Fig. 2. The HOMO and LUMO are very popular quantum chemical parameters. They determine the molecular reactivity of the molecule. The HOMO has high orbital population at O2-atom which means that this site is considered as electron rich Lewis base site. In contrast, the LUMO high orbital populations are located at the Br-atoms which have an empty antibonding orbital electron acceptor sites making them a suggested electron acceptor Lewis acid. The interaction between the molecular units in the ionic liquid structure is orbitally controlled by the linear overlap between the antibonding orbitals of the organic halide groups as empty electron acceptor sites (Br-atoms) and the filled bonding molecular orbital of the Lewis base (O2-atom). This intermolecular interaction is generally called halogen bonding.

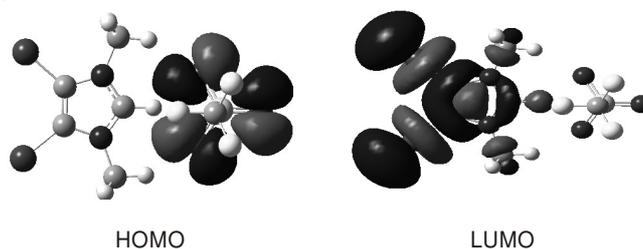


Fig. 2. Ground state isodensity surface plots of the frontier molecular orbitals of the studied model ionic liquid complexes (dibromomethylimidazolium cation and trihalomethanesulfonates anion)

Conclusion

Four complexes of imidazoliumcation with CX₃SO₃⁻ ions (X = F, Cl, Br and H) have been calculated using DFT/B3LYP method. The results were used as a model for organic ionic liquid. The results of the quantum chemical calculations were used to predict the possible factors that affect the interaction between the complex units. Electrostatic, HOMO-LUMO and dipole-dipole interactions are among the main factors that control these interactions.

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