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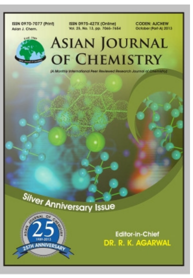

Theoretical Study of the Structure of 2,6-Dibromopyridinium Halide Salts

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Theoretically, the role played by the halogen…halide interactions (C-Br…X^-) and hydrogen bonding interaction (N-H…X^-) in the crystal structure of 2,6-dibromopyridinium halide (2,6-DBP)X (X = Cl^-, Br^-) has been studied. The computational results are compared with previous experimental results for analogous compounds. There is a clear presence of (C-Br…X^-) interactions and (N-H..X^-) interactions in (2,6-DBP)X with almost linear (C-Br…X^-) interactions angles (178.55°) and (N-H…X^-) interactions angles (*ca.* 179.92°) and the results are then compared to experimental results for analogous compounds. This study shows that the (C-Br…X^-) interactions have comparable strength with the corresponding strong NH…X^- hydrogen bonds in (2,6-DBP)X. This is different from a previous result in which the (C-Br…X^-) interactions are stronger than hydrogen bonding interactions in (2,5-DBP)X (X=Cl, Br and I). The study has proven the existence of N(π)…..X^- (X = Cl, Br and I) interaction. The existence of nitrogen (π) … halide ion interaction [N(π)….X^-] is investigated. Calculations has been performed for the following compounds: (2,6DBP)Br, (2,6-DBP)Cl, (2,5-DBP)Br and (2,5-DBP)Cl. Calculations of energy changes that occur when the halide ion site changes above the nitrogen atom in the pyridinium bromide salt have been conducted. The position of the bromine anion was varied in three dimension forming an imaginary cubic shape above a nitrogen atom. The studied ranges of the coordinates are as follows: x= -2 to 2 Å, y = -2 to 2 Å and z = 1.5-4.5 Å. In the pyridinium bromide salt, the minimum energy for the N(π)…Br^- interaction is located at a distance of 3.5-3.7 Å from the nitrogen atom to the halide anion and at an angle of *ca.* 25° between the N…Br^- line and the normal to the plane of the pyridinium cation. These values are in good agreement to previously studied systems of similar nature.

Key Words: Halogen halide interactions, Hydrogen bonding interactions, 2,6-Dibromopyridinium, Computational chemistry, Gaussian.

INTRODUCTION

Crystal engineering deals with the forces that hold atoms within the crystalline lattice. The physical properties (*e.g.*, nonlinear optical behaviour and magnetic and electrical properties) of solid-state materials depend not only on the molecular structure of the building units but also on the arrangement of these structural units inside the crystal lattice[1]. Therefore, crystal engineering of molecular materials has become a subject of interest to chemists involved in the design and properties of solid materials. Scientist are moving from structure design to property design[2]. The prediction of the crystal structure of molecules is the ultimate goal of experimentalists.

Intermolecular interactions have been the subject of many previous studies. Some dealt with the arrangement of the structural units within the crystal lattice[3]. Other studies investigated the intermolecular forces such as the strong classical hydrogen bonding or the weak π-π stacking[4].

Many studies highlighted the role of hydrogen bonding in dictating structures of solid materials. Studies have been carried out to show the importance of halogen interactions with other electronegative species[3].

Halogen bonding (XB) has some ionic character (non-covalent) and somehow analogous to hydrogen bonding (HB). In the latter, a hydrogen atom is shared between an atom, group or molecule that "donates" and another that "accepts" it. In halogen bonding, it is a halogen atom, X, that is shared between a donor D and an acceptor A. Thus the two types of interaction can be represented as DH…A for the HB and DX…A for the XB. X can be chlorine, bromine or iodine, but not, fluorine. The angle D-X-A is close to 180º in most compounds[5].

Hydrogens are known to bear partial positive charges and therefore interact attractively with electronegative atoms. However, halogens bear partial negative charges and are expected to behave differently in the XB compared to HB. A reasonable explanation for this phenomenon arise from the term "σ-hole" originally referred to the electron-deficient outer lobe of a half-filled p (or nearly p) orbital involved in forming a covalent bond. Sufficient electron deficiency causes a region of positive electrostatic potential which can interact attractively (noncovalently) with negative sites on other molecules (σ-hole bonding). The σ-hole bonding has been observed, experimentally and computationally, for many covalently-bonded atoms[6] of groups V-VII.

The literature contains examples of different types of halogen bonds. Karpfen[7] studied the complexes between dihalogens XY and Lewis bases nucleophiles (Nu), XY…Nu. Jagarlapudi *et al.*[8] investigated complexes between carbon-halogen atoms and nucleophiles (Nu), C-Y…. Nu. Halogen….. halogen contacts have already been used to design new materials. Matsumuto *et al.*[9] used chlorine···chlorine interactions to prepare highly stereoregular polymers.

The halogen bond between a halide ion and a halogen atom attached to positively charge species is of high importance in determining the structure of crystalline materials in comparison to the other types of halogen bonds[10]. This interaction is characterized by the linear C-Y….X angles[11].

Logothetis *et al.*[12] found that C-Br···I^- interactions play a crucial role in influencing the structure of N-methyl-3,5-dibromopyridinium iodide. A recent study carried out by Awwadi *et al.*[10] have shown the role that the linear arylbromine-halide ion interactions, in conjunction with traditional hydrogen bonding interactions, play in the development of the crystal structures of the 2,5-dibromopyridinium halide salts, (2,5-DBP)X and the 3,5-dibromopyridinium halide salts, (35DBP)X (X = Cl, Br, I).

Yamamoto *et al.*[1] used these interactions to develop organic-based conducting materials and showed that the interaction was fundamental to the conducting property and the internal architecture of the lattice. Farina *et al.*[13] separated a racemic mixture of 1,2-dibromohexafluoropropane by crystallizing it with trialkylammonium hydrobromides using the bromine-bromide interaction forces.

Previous studies showed, by *ab initio* calculations and crystal structures measurements, that many factors influence the strength of the halogen…..halide contacts including the type of halogen atom, type of the halide ion, hybridization of atoms and type of substituents in the aromatic system.

Awwadi *et al.*[4] defined the nitrogen-halide ion interaction represented by N(π)…X^-, as the interaction between the nitrogen atom and the halide ion that is located above the plane of the pyridinium cation.

This interaction is well seen in many X-ray results for various pyridinium salts in the literature. For example the nitrogen-halide interactions are found in $(nCP)_2CuX_4\cdot mH_2O$ (nCP+ = n-chloropyridinium; n = 2, 3 and 4; X = Cl^- and Br^- ; m = 0 except for $(3CP)_2CuBr_4\cdot H_2O$][4]. The presence of these interactions was also observed in the simple n-halopyridinium halide (nYP)X salts (Y= Cl, Br and I ; X = Cl, Br and I)[14].

Because of the importance of the N(π)….X^- interaction in the development of three-dimensional shape of the crystal building, theoretical calculations are carried out to investigate the existence of this type of interactions.

One motivation to carry out this study is the significant importance of the charge assisted halogen-halide interactions on supramolecular synthesis. It necessitates a thorough investigation of the role that these interactions play on the crystal structure of new compounds which in turn will be reflected on supramolecular syntheses.

A second motivation is to determine the relative strength of the halogen….halide interactions (C-Br…X^-; X = Cl, Br) by DFT calculations for the 2,6-dibromopyridinium bromide (2,6-DBP)Br and 2,6-dibromopyridinium chloride (2,6-DBP)Cl and compare them with the relative strength of the halogen···halide interactions in the already studied analogous compound 2,5- dibromopyridinium bromide (2,5-DBP)Br and 2,5- dibromopyridinium chloride (2,5-DBP)Cl.

The relative strength of hydrogen bonding interactions (N-H…X^-; X = Cl, Br) by DFT calculations for the (2,6-DBP)Br and the (2,6-DBP)Cl and comparing them with the relative strength of the hydrogen bonding in the (2,5-DBP)Br and the (2,5-DBP)Cl is investigated.

The role of the halogen …. hailde interactions (C-Br…X^- ; X = Cl , Br) and hydrogen bonding interactions (N-H…X^-; X = Cl, Br) in the crystal structure of the (2,6-DBP)Br (2,6-DBP)Cl is discussed.

Finally, theoretical calculations are carried out to investigate the existence of N(π)…..X^- interaction in halopyridinium halide.

COMPUTATIONAL METHOD

Gaussian 03 was used for geometry optimization[15]. DFT calculations were carried out for the optimization of the salts. The cc-pVQZ basis set is a linear combination of two basis functions of different sizes for the valence orbitals. These types of functions allow the orbital to change its size. Halogen···halide interactions are based on deformation of electronic charge on the halogen atom. Therefore, diffuse function is added to the halogen atom and halide anion. Diffuse functions allow the orbital to occupy a larger size in space and hence, reduce the constraints on electron motion[16].

The structures of the salts were optimized using two different starting geometries. In the first the angle C-Br……X is set to 180º (Fig. 1(A)) while in the second the angle N-H…..X is set to 180º (Fig. 1(B)). The N-H distance in the second geometry (B) was constrained to the distance obtained by optimizing the geometry of the 2bromopyridinium cation (1.02 Å).

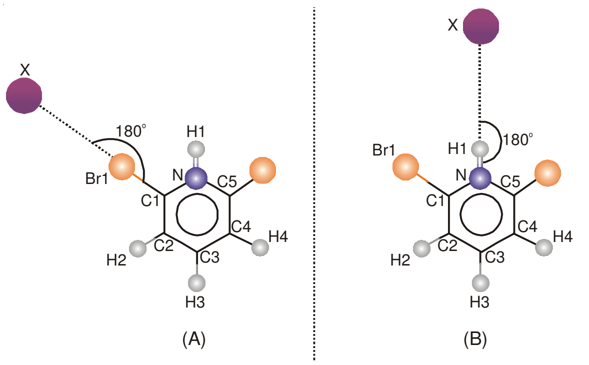

Fig. 1. Starting geometries of the modeled compounds; 2,6-dibromopyridinium halide salts (2,6-DBP)X (X = Cl, Br)

For the potential energy of pyridinium bromide salt, geometry optimization and total electronic energy were computed with DFT calculation using B3LYP/cc-pVQZ basis set. STATISTICA program version 7.0 (2004) was used in the analysis and plotting of the potential energy diagram.

Method: All calculations started by finding the optimal structures and the best calculational method and basis sets. The relative strength of the (2,6-DBP)Br and the (2,6-DBP)Cl molecules was investigated using ab initio calculations. The results comprising of the distances of (Br….X^-; X = Br, Cl) and (N-H….X^-; X = Br, Cl) and the angles of (C-Br….X^-; X = Br, Cl) and (N-Br….X^-; X = Br, Cl) were compared to previously studied similar systems.

To ensure the reliability of our calculations, we started with the reported system of 2-bromopyridinium bromide (2BP)Br and the 2-bromopyridinium chloride (2BP)Cl[10]. Both molecules are illustrated in Fig. 2. The optimization was carried out using DFT/B3LYP/cc-pVQZ method. The results were then compared.

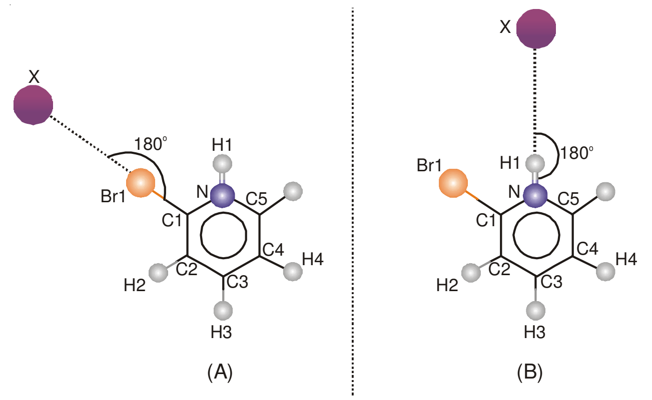

Fig. 2. Starting geometries of the modeled compounds, (2BP)X (X = Cl, Br)

TABLE-1
ANGLES OF (C-Br…X^-) AND (N-H…X^-)
FOR (2DBP)Br AND (2DBP)Cl

Compound	Angle value			
	N-H…X^-		C-Br…X^-	
	Previous work[10]	This work	Previous work[10]	This work
(2DBP)Br	158.10°	158.22°	177.96°	177.91°
(2DBP)Cl	–[(a)]	–[(a)]	178.0°	178.10°

[a]No convergence to an energy minimum.

Table-1 summarizes the results and compare them to the previous study of Awwadi *et al.*[10] for the (2DBP)X system. We notice the similarities in the computed angle values of Halogen … halide interactions (C-Br…X^-) and hydrogen bonding interactions (N-H…..X^-) in both studies. Our method of calculation is therefore deemed accurate and trustable.

All possible combinations of dibromopyridinium halide salts (n,n'-DBP)X (n = 2,3; n'= 4,5,6; X = Cl, Br) were tested for their stability using DFT/B3LYP/cc-pVQZ. Table-2 shows the results of the minimum energy of the parent molecule as well as the reactants and products used to make the dibromopyridinium halide salts. Among the tested molecules, the results clearly show that only two dibromopyridinium halide salts are the most stable. The first set of molecules (2,5-DBP)X (X = Cl,Br) was recently studied by Awwadi *et al.* [10]. In this study, we will theoretically investigate the second set of molecules (2,6-DBP)X (X = Cl, Br).

The introduction of two Br atoms at the 2- and 6- positions increases the basicity of the ring. This may oppose the inductive effect a halogen has on the ring since a halogen has significantly higher electronegativity. However, the electron withdrawing through the sigma bonds resonates that effect by shielding the effective nuclear charge with its lone pair electrons. This in turn increases the flow of electrons into the aromatic ring *via* the π-conjugation and increases the basicity of the N atom. The protonated 2,6-dibromopyridine is expected to create some important centers of interaction with the bromide anions, *e.g.*, N-H….Br, C-H….Br and possibly some other interaction like aryl-aryl stacking.

The influence of these interactions on the crystal structures of (2,6-DBP) X (X = Cl, Br) using pure theoretical calculations will be carried out.

The relative strengths of bromine….halide interactions (Br….X^-) and hydrogen bonding interactions (H…X^-) in (2,6-DBP)X (X = Cl, Br) are by examining the Br….X^- distances and H…X^- distances. The shorter the distances, the stronger the interactions. Another parameter for the relative strength of these interactions is examining the C-Br…..X^- and N-H…..X^- angles. The more linear the angles, the stroner the interaction. To ensure the ability of theoretical calculations alone in the prediction of the relative strength of the interactions, calcula-

TABLE-2
RESULTS OF THE MINIMUM ENERGY OF THE PARENT MOLECULE AS WELL AS THE
REACTANTS AND PRODUCTS FOR MAKING THE DIBROMOPYRIDINIUM HALIDE SALTS

Compound	Initial Energy of reactants		Average final energy of product (Hatree)	ΔE (Hatree)	ΔE (kJ/mol)
	Energy of DBP (Hatree)	Energy of HX (Hatree)			
–	–	(HBr)	Energy of (n,n 'DBP) Br	–	–
2,6-DBP	5395.40869573	2574.75835455	7970.14145965	-0.02559063	-67.18819906
2,5-DBP	5395.40620953		7970.13418454	-0.03037954	-79.76148227
2,4-DBP	539540698150		7970.16079104	-0.00454501	-11.93292376
2,3-DBP	5395.40221526		7970.15573743	-0.00483238	-12.68741369
3,4-DBP	5395.40047603		7970.15924984	-0.00041926	1.10076713
3,5-DBP	5395.40367941		7970.15992563	-0.00210833	-5.53542042
–	(HCl)	Energy of (n,n 'DBP) Cl	–	–	–
2,6-DBP	5395.40869573	460.82216434	5856.19878610	-0.03207397	-84.21022136
2,5-DBP	5395.40620953		5856.19067165	-0.03770222	-98.98716987
2,4-DBP	539540698150		5856.21975357	-0.00939227	-24.65940489
2,3-DBP	5395.40221526		5856.21473500	-0.00964460	-25.32189730
3,4-DBP	5395.40047603		5856.21830847	-0.00433190	-11.37340345
3,5DBP	5395.40367941		5856.21892209	-0.00692166	-18.17281833

tions were performed for the structures of the two compounds: (2,5-DBP)Br and (2,5-DBP)Cl. Comparison of our theoretical findings to experimental results will serve as a powerful measure of the goodness of the technique.

The three structures that can have a bromine-bromide interactions (C-Br1….Br), (C-Br2….Br) and hydrogen bonding interaction (N-H…..Br) of (2,5-DBP)Br are shown in Fig. 3. The optimization of these structures was carried out.

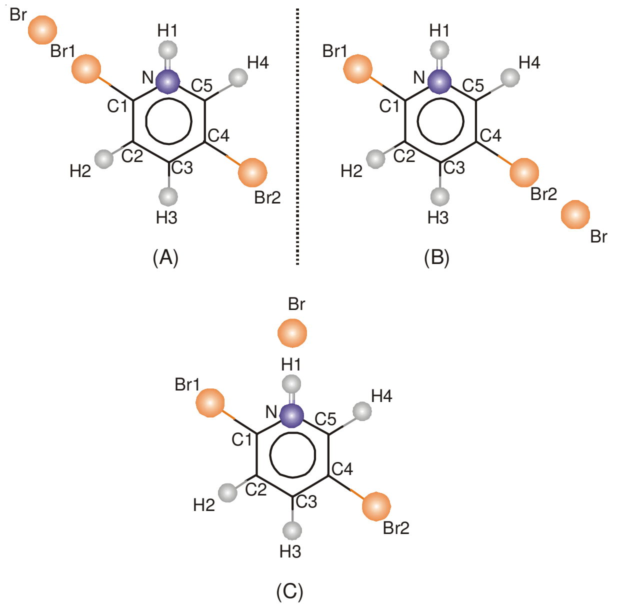

Fig. 3. Three structures that can show a halogen-halide interactions and hydrogen. Bonding interaction of (2,5-DBP) Br (schemes A , B and C)

The optimization of the three structures that show a chlorine-chloride interactions (C-Br1….Cl), (C-Br2….Cl) and hydrogen bonding interaction (N-H…..Cl) of (2,5-DBP)Cl (Fig. 4) is also carried out. Table-3 shows the results of optimization interms of interaction angles and distances for the (2,5-DBP)X (X = Br and Cl) molecules using DFT/cc-pVQZ method for schemes A ,B and C above.

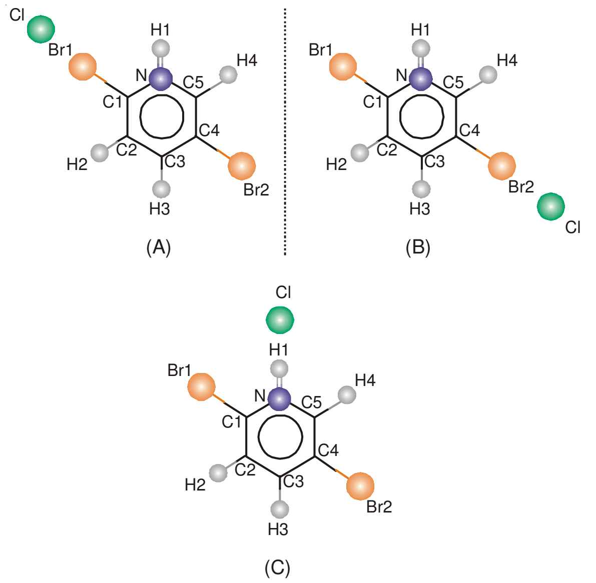

Fig. 4. Three structures show a halogen-halide interactions and hydrogen bonding interaction of (2,5-DBP)Cl (schemes A , B and C)

TABLE-3
DFT CALCULATIONS OF INTERACTIONS ANGLES AND DISTANCES FOR THE (2,5-DBP)X X = Br AND Cl) MOLECULES USING cc-pVQZ FORMULA FOR SCHEMES A, B AND C

Interaction angle or distances (Å)	Compounds	
	(2,5-DBP)Br	(2,5-DBP)Cl
N-H1…X	159.72°	160.66°
C1-Br1…X	179.64°	177.95°
C2-Br2…X	178.11°	179.76°
H1…X	1.9702	1.7967
Br1…X	2.6768	2.5273
Br2…X	2.7201	2.5650

The results for the two studied compounds are then compared to experimental values as summarized in Table-4. We notice a large difference in Br…X^- and H….X^- between theoretical and experimental data in the distances. The average percent error is around 18.5 %. Therefore, theoretical calculations are not reliable in explaining the distances in the studied molecules. Hence, there is more into the investigating of the strength of bromine…halide interactions and hydrogen bonding interactions.

TABLE-4
THEORETICAL AND EXPERIMENTAL DATA OF BROMINE…HALIDE INTERACTIONS LENGTHS, HYDROGEN BONDING INTERACTIONS LENGTHS OF (2,5-DBP)X (X = Cl, Br) AND THE CORRESPONDING PERCENT ERRORS

Interaction distance	Value (Å)		
	Theoretical	Experimental	Error (%)
H1…Br	1.9702	2.2940	14.1
Br1…Br	2.6768	3.2580	17.8
Br2…Br	2.7201	3.4420	21.0
H1…Cl	1.7967	2.1220	15.3
Br1…Cl	2.5273	3.1200	19.0
Br2… Cl	2.5650	3.3510	23.5

We note that the calculated Br….X^- and H…X^- distances are always shorter than the experimental values. This trend has been noticed in previous studies. Awwadi *et al.*[10] interpreted this phenomenon as a competition between of halogen…halide interactions and hydrogen bonding interactions within the crystal lattice[14].

The case with angles is very much different from that with the distance . There is a clear similarity in the theoretical values of the C-Br…X^- and N-H….X^- bond angles and experimental data. The average percent error is around 3.0 % as shown in Table-5. This agreement shows that theoretical calculations are reliable in investigating of the relative strength of bromine…halide interactions and hydrogen bonding interactions in terms of spatial configuration (angles).

To study the spatial interaction of bromine atom over the pyridinium molecule, a potential energy diagram for the interaction of a nitrogen atom in pyridinium with a Br-anion above it is constructed. The pyridinium bromide salt is chosen where a simple pyridinium cation and a bromine as the anion. The search for a minimum energy where the bromine anion is positioned above the pyridinium cation by placing a bromine anion at various positions starting from the position (x = 0 Å, y = 0 Å, z = 3 Å) taking the nitrogen atom position in the pyridinium cation as the origin (0, 0, 0) as shown in Fig. 5.

TABLE-5
THEORETICAL AND EXPERIMENTAL DATA OF BROMINE…HALIDE INTERACTION ANGLES, HYDROGEN BONDING INTERACTION ANGLES OF (2,5-DBP)X (X = Cl, Br) AND THE CORRESPONDING PERCENT ERRORS

Interaction distance	Value (Å)		
	Theoretical	Experimental	Error (%)
N-H1…Br	159.72°	163.39°	2.2
C1-Br1…Br	178.11°	179.32°	0.7
C2-Br2…Br	179.64°	168.68°	6.5
N-H1…Cl	160.66°	160.05°	0.4
C1-Br1…Cl	177.95°	179.79°	1.0
C2-Br2…Cl	179.76°	167.54°	7.3

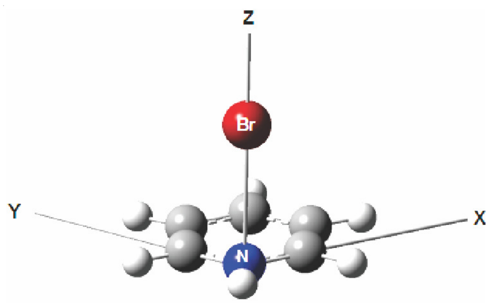

Fig. 5. Starting structural orientation of the interaction between bromine anion and pyridinium cation. Nitrogen atom is located at the origin (0, 0, 0) and the bromide is located at (0, 0, 3) as a starting position

The position of the bromide was varied in three dimensions forming a cubic shape above the nitrogen atom. The studied ranges of the bromide coordinates were as follows: x = -2 to 2, y = -2 to 2 and z = 1.5 to 4.5.

RESULTS AND DISCUSSION

To analyze the bromine…halide interaction and hydrogen bonding interaction in the (2,6-DPB)X (X = Cl,Br), the optimi-zation was carried out by investigating the linearity of angles of the interactions. The two optimized structures showing a halogen-halide interaction (C-Br1….Br) and hydrogen bonding interaction (N-H…..Br) of (2,6-DBP)Br are shown in Fig. 6.

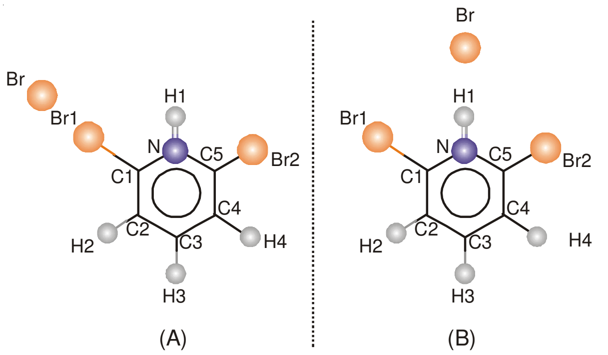

Fig. 6. Two structures showing halogen...bromide interaction (A) and hydrogen bonding interactions (B) in the (2,6DBP)Br

The calculated results of this optimization for the two schemes (A, B) can be shown in interaction angles of both halogen-halide interaction and hydrogen bonding interactions. In scheme A, the C1-Br1… Br angle was found to be 178.57° while in scheme B the N-H1…. Br was found to be 179.93°.

In the case of the structures with chloride ion interactions of (C-Br1….Cl) and hydrogen bonding interaction (N-H…..Cl) of (2,6-DBP)Cl shown in Fig. 7. The results of the optimization for **Scheme-A**, the angle of inteaction was found to be 178.54° (C1-Br1…….Cl) while it was 179.91° (N-H1…Cl) in **Scheme-B**.

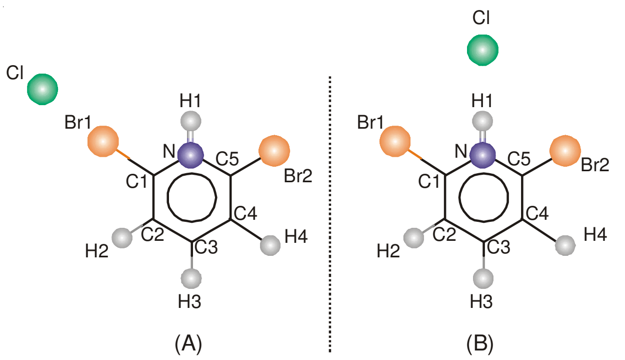

Fig. 7. Two structures showing halogen-chloride interactions (A) and hydrogen bonding interactions (B) in (2,6-DBP)Cl

We notice good linearity in the angular values of the C-Br…X^- in the (2,6-DBP)Br and the (2,6-DBP)Cl (178.57 and 178.54°). This linearity suggests high relative strength of C-Br…..X^- interactions that is usually reflected on the crystal geometry of these compounds. It is noticed that both halides gave similar angular values.

In the same manner, by analyzing the angular values of the N-H…X^- in the (2,6-DBP)Br and the (2,6-DBP)Cl, we find them to be 179.93 and 179.91°, respectively. This linearity means that the relative strength of N-H…X^- interactions are large and effective in terms of crystal geometry.

A comparison of the angles of N-H…X^- calculated for the (2,6-DBP)X with the experimental and theoretical results of (2,5-DBP)X is given in Table-6. There is no noticeable difference between the angles (179.93 and 179.91°). The angles for the (2,6DBP)X molecules show higher linearity compared to the (2,5-DBP)X values. Since the bromine substituents are farther apart in the (2,6-DBP)X than in the (2,5DBP)X, this difference in the (N-H…X^-) angles can be attributed to the bulkiness of the halogen atom.

TABLE-6
HYDROGEN BOND ANGLES (N-H…X^-) OF (2,5-DBP)X (X = Cl, Br) AND (2,6-DBP) X (X = Cl, Br)

Compound	N-H…X^- angle	
	Experimental	Theoretical
(2,5-DBP)Br	163.39° (a)	159.72° (a)
(2,5-DBP)Cl	160.05° (a)	160.66° (a)
(2,6-DBP)Br	–	179.93°
(2,6-DBP)Cl	–	179.91°

The computed values of angles of the C-Br…X^- and the N-H…X^- in (2,6-DBP)X are nearly equal. This indicates that the C-Br…X^- interactions have comparable strength to the corresponding strong N-H…X^- hydrogen bonds.

The results imply that the halogens hydrogen bonding play an comparable role in determining the crystal structure of these compounds. However, the C-Br…X^- interactions show more linearity than the N-H…X⁻ hydrogen bonds in (2,5-DBP)X implying that the strength of C-Br…X⁻ interactions are stronger than that of NH…X⁻ hydrogen bonds. This indicates that the C-Br…X⁻ interactions play a more important role in determining the crystal structure of (2,5-DBP)X compounds.

Our results agree well with experimental results of a recent study carried out by Al-Far *et al.*[17] using the 2,6-dibromopyridinium tetrabromidometallates: $(C_5H_4Br_2N)_2[MBr_4]\cdot 2H_2O$ (M = Cu (II), Cd (II) and Hg (II)). When we compare the angles in the previous study for C-Br….Br with those from the C-Br….X for the compound (2,6DBP)X, we see many similarities and serves as a motive to conduct an experimental X-ray crystal structure determination.

If we consider the hydrogen bonding and compare the angles of N-H….O in the previous study (174-177°) with the angles of N-H….X for the compound (2,6-DBP)X in our study (179.9°), we find very good resemblance proving the presence of hydrogen bonding and hence its importance on the crystal structure.

The molecular electrostatic potential of (2,6-DBP)X (X = Br or Cl) has been determined. Calculations show that a positive electrostatic potential gap is located along the σ bond axis and a negative electrostatic potential ring in the π region of the atom in chlorine and bromine.

For the 2,6-dibromopyridinium bromide (2,6-DBP)Br, a positive potential develops on the outermost portion of the bromine surface around its intersection with the C-Br axis as shown in Fig. 8. This positive electrostatic potential region, which is centered on the C-X axis, can interact with a negative site of another molecule (*e.g.* Br^-) to form halogen-halide bond within the crystal structure (lattice).

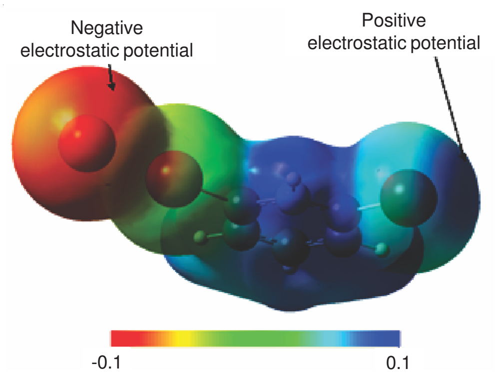

Fig. 8. Molecular electrostatic potential of the of (2,6-DBP)Br surface (Hartrees)

To study the interaction between the different molecules, we performed a detailed study of the optimum position of the atom with respect to the adjacent molecule. The spatial position of the bromine atom of one molecule was varied relative to the pyridine ring of the other molecules. The minimum energy was calculated and a contour study analysis showed the best structural orientation. The results are displayed in polar coordinates (distance and angle) in Fig. 9.

It is clear that the minimum energy for the N(π)…Br⁻ interaction lies at distance from the nitrogen atom to the bromine anion = 3.5-3.7 Å and at an angle between the N…Br⁻ line and the normal to the plane of the pyridinium cation of around 25°. Results for similar systems studied previously[4] showed N(π)…Br⁻ angles of 25.48° in some cases in agreement with our calculations.

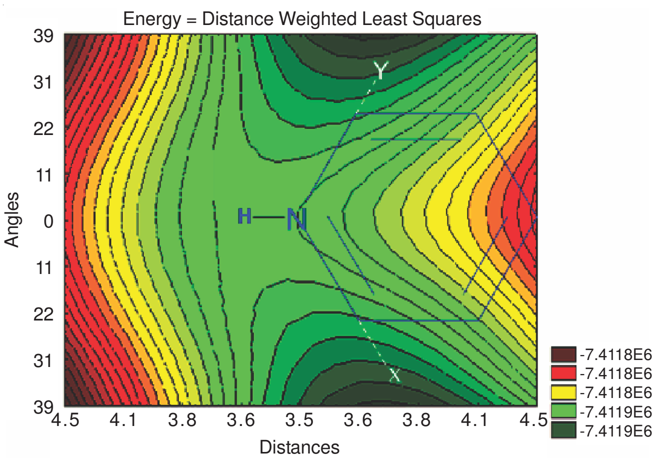

Fig. 9. Potential energy diagram for the interaction of a nitrogen atom in the pyridinium ion with a Br ion above it

Conclusion

The theoretical study of the 2,6-dibromopyridinium halide salts (2,6-DBP)X has shown that the halogen…halide interactions and hydrogen bonding are characterized by linear CBr…X⁻ and NH…X⁻ geometries, respectively. The C-Br…X⁻ interactions have comparable strength to the corresponding strong N-H…X⁻ hydrogen bonds in (2,6-DBP)X. However, in the 2,5-dibromopyridinium halide salts (2,5-DBP)X, the CBr…X⁻ interactions are stronger than that of N-H…X⁻ hydrogen bonds.

Combined to other studies of similar compounds, the important role played by each of the halogen…halide interactions and hydrogen bonding interactions in determining crystal structure of halopyridinium halide salts is demonstrated. This study has proven, theoretically, the existence of N(π)…X⁻ interaction in halopyridinium halide salts and this is in good agreement with experimental data for a similar system.

The results of this work provide a strong motivation for the experimental preparation of the 2,6-dibromopyridinium halide salts and determining their X-ray structures with our findings. This in turn will shed light on the importance of the halogen …halide interactions and hydrogen bonding interactions in the crystal structure of 2,6-dibromopyridinium halide as we predict.

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