Computational Study of Hydrogen Bonding in CH$_3$CN•••H-X (X=OH, F, Cl, NH$_2$) Complexes

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Highlights

- Hydrogen bonding in CH$_3$CN•••HX (X= F, Cl, OH, NH$_2$) has been observed.
- Molecular Electrostatic Potential analysis is done to identify electron rich and electron deficient regions.
- Strong correlation between energy and stretching frequency is observed.
- The hydrogen bonding parameters are more for HF donor and low for NH$_3$ donor.

Abstract

In this work first principles study of acetonitrile complexes (acetonitrile•••H-X, X=F, Cl, NH$_2$, OH) has been carried out using electrostatic potential analysis, ab initio (MP2/6-311++g(2d, 2p), B3LYP/6-311++g(2d, 2p) and AIM theoretical calculations and these calculations confirm the hydrogen bonding interaction for these complexes. The geometrical parameters, binding energy and (3, -1) bond critical points confirm that HF donor is found to form strong hydrogen bond and NH$_3$ donor is found to form weaker hydrogen bond for these complexes.

Introduction

The name hydrogen bond implies the participation of hydrogen atom generally in intermolecular interactions. It was first proposed in the literature in 1920 [1] and its name, hydrogen bond, was introduced in 1928 [2, 3]. A hydrogen bonding interaction is considered an important phenomenon that has been reported regularly and a lot of research on it has been performed. This type of interaction can generally be depicted as D-H• • •A, where D is the donor atom and A is the hydrogen bond acceptor [4-9].

There have been several computational studies that describe the geometries and energetic properties of the hydrogen bonds taking diverse donors and acceptors [10-13]. In this work, we report a computational study of acetonitrile molecule with four different lone pair donors. They are hydrofluoric acid, hydrochloric acid, water and ammonia.

So far there are few reports regarding computational studies of acetonitrile complex [14-21]. In almost all studies acetonitrile-water complexes have been reported. One of the previous works on the acetonitrile complex is by Doo-Sik Ahn and Sungyul Lee. They have two works on this system [14, 15]. They examined CH$_3$CN•••(H$_2$O)$_n$ clusters (n=1-4 for first work and n= 4, 8 for second work) and found two isomers. They reported that the acetonitrile molecule could interact with water in two ways. The first type of interaction is linear (interaction of OH and lone pair electrons of N atom) and the second type is perpendicular interaction of OH and CN. The former was named a σ-type hydrogen bond and the latter was called a π-type hydrogen bond. Mainly, relative energy and vibrational frequency of C≡N stretching mode were reported in their study.

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Another computational work on acetonitrile complex is by Eugene S. Kryachko and Minh Tho Nguyen [16]. They studied acetonitrile complex with phenol. Like previous works [14, 15], they also concentrated on C≡N stretching mode in both σ type (OH and CN linear interaction) and π (OH and CN perpendicular interaction) hydrogen bonds.

The effect of hydrogen-bonded interactions of one of the astromolecules, the aminoacetonitrile (H_2NCH_2CN) with HCN, and Glycine system was reported recently. Authors of this work investigated the structural and spectroscopic properties of these systems [22].

The above works motivate us to study further on this system. However, we limited only σ-type (CN linear interaction) H-bonding. In work reported here, we first analyzed the Molecular Electrostatic Potential Surface of the acetonitrile molecule. This analysis is used to identify the sites for hydrogen bond formation. We then analyzed geometrical parameters of the complex followed by binding energy, change in stretching vibrational mode of donors and then we analyze electron density and Laplacian of electron density using Atoms in Molecules AIM theory.

Computational Methods

All the calculations performed in this work have been carried out using the Gaussian03 suits of the program [18] at Møller-Plesset second-order perturbation (MP2) [23-25] theory and B3LYP (DFT) [26-28] of theory with 6-311++g(2d,2p) basis set. We have also carried out frequency calculations for all the geometrical structures to know whether they are true minima or not. The counterpoise method of Boys and Bernandi has been employed for BSSE correction [27]. The AIM calculations were performed with the AIMALL software package [28] using Gaussian wave functions.

In order to find the regions of high or low electron density distributions molecular electrostatic potential surface of the acetonitrile molecule has been mapped. For this Gauss View and Multiwfn software have been used [29, 30].

Results and Discussion

Acetonitrile molecule and its electrostatic potential

We began our work with the analysis of electrostatic potentials of acetonitrile molecule. This technique has been used by many authors to identify electron rich and electron-deficient regions [31-33]. Surface map of electrostatic potentials at 0.001 a.u. electron density isosurfaces have been shown in Figure 1. To know how far these positions of potentials from the atoms of the acetonitrile molecule the X, Y and Z coordinates of atoms of the acetonitrile molecule was given in Table 2.

There have been several locations in which this molecule can form a complex (see electrostatic potential map). In this work, we have identified a low electron density region and studied a hydrogen-bonded complex taking four different donors. Along the axis of the CN moiety low electron density region was observed and due to this hydrogen (H) atom of hydrogen bond donors (HX) automatically moves towards the nitrogen atom of acetonitrile (CH_3CN) to make a hydrogen bond (X-H●●●Y-Z) (Figure 1 and Figure 2). In this way, the equilibrium state of the CH_3CN●●●HX complex was obtained.
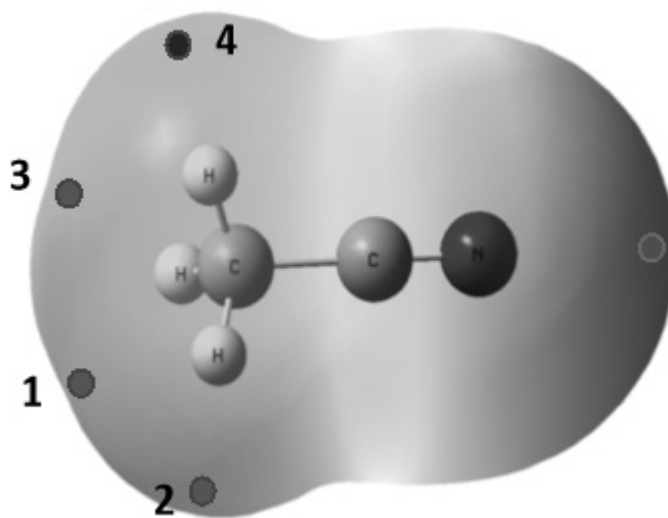

Fig 1: Molecular Electrostatic Potential Surface Map of acetonitrile molecule.

Table 1: *Surface minima, surface maxima in kcal/mol and their X, Y, and Z coordinates in Å*

Surface minima				
Position	Potential Energy	X	Y	Z
1	-38.62	3.333	0.016	0.014
Surface maxima				
Position	Potential Energy	X	Y	Z
1	24.41	-3.025	0.014	0.008
2	28.08	-2.247	-1.708	-1.321
3	28.08	-2.225	-0.236	2.158
4	28.08	-2.202	1.994	0.888

Table 2: *Atoms of acetonitrile molecule and their X, Y, Z coordinates in Å*

Atoms	X	Y	Z
C	-1.176	0.001	-0.001
H	-1.556	-0.141	1.009
H	-1.550	0.804	-0.632
H	-1.547	0.949	-0.385
C	0.281	-0.002	0.004
N	1.431	0.001	-0.002

Geometrical Features, Frequency Shifts, and Interaction Energy for acetonitrile· · · H-X complexes

　　To characterize non-covalent interactions geometrical features, frequency shifts, and interaction energies of the complex were used in many studies [11-13, 34]. We have also used these parameters to characterize hydrogen bonding in this study. Geometries of the acetonitrile•••H-X complex have been optimized at the MP2 and DFT (B3LYP) level of theories with 6-311++g (2d, 2p) basis set. The optimized structures at MP2 level of theory are depicted in Figure 1. There will be similar type of structures at the B3LYP level of theory. All the harmonic vibrational frequencies of optimized structures are found to be positive. This confirms that the optimized structures are true minima.
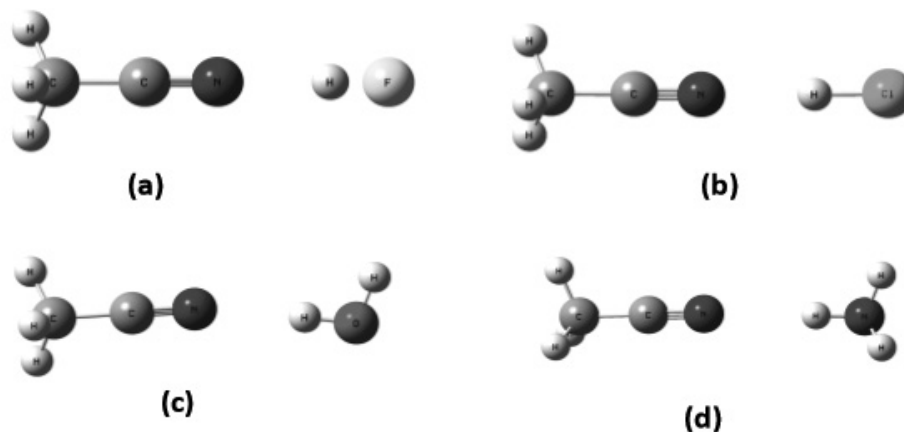

Fig. 2 *Optimized geometry of CH_3CN•••HX complex (X=F, Cl, OH, NH2) in MP2 level of theories with 6-311++G (2d, 2p) basis sets.*

(a) CH_3CN•••HF, (b) CH_3CN•••HCl, (c) CH_3CN•••HOH, (d) CH_3CN•••HNH_2.

Table 1 shows the geometric features ($R_{N\cdots H}$ and ΔR_{H-X}) bond distance in Å, $\angle N\bullet\bullet H-X$ in degree, BSSE corrected binding energy in kcal/mol, change in frequency shift of X-H stretching modes ($\Delta\nu$) in cm^{-1} for acetonitrile$\bullet\bullet\bullet$HX complex where, N is acceptor atom of CH_3CN molecule and X-H is hydrogen bond donors using 6-311++G(2d, 2p) basis set.

Table 3: *Geometric features $R_{Y\cdots H}$ (hydrogen bond distance), $\Delta R_{X\cdots H}$ (change in bond length of donors) in Å, N...H-X in degree, BSSE corrected binding energy (BE) in kcal/mol, change in frequency shift of X-H stretching modes ($\Delta\nu$) in cm^{-1} for acetonitrile$\bullet\bullet\bullet$HX complex where, Y is acceptor atom and X-H is hydrogen bond donor molecules using 6-311++G(2d, 2p) basis set.*

Complex	Level of Theory	$R_{N\cdots H}$	ΔR_{X-H}	$\angle N\bullet\bullet H-X$	BE	$\Delta\nu$
$CH_3CN\bullet\bullet\bullet HF$	MP2	1.807	0.015	179.77	-8.33	-347.0
	B3LYP	1.773	0.019	179.91	-9.72	-415.1
$CH_3CN\bullet\bullet\bullet HCl$	MP2	1.983	0.017	179.38	-5.49	-228.2
	B3LYP	1.980	0.019	179.16	-6.44	-247.8
$CH_3CN\bullet\bullet\bullet HOH$	MP2	2.060 2.142*	0.006	177.8	-4.47 -3.80*	-75.9
	B3LYP	2.076	0.007	179.3	-4.11	-83.8
$CH_3CN\bullet\bullet\bullet HNH_2$	MP2	2.331	0.003	175.1	-2.23	-19.2
	B3LYP	2.398	0.002	174.8	-1.83	-13.6

* The results of Ahn and Lee [14]

As mentioned already, we have studied four HX molecules (X=F, Cl, OH and NH_2) with CH_3CN. The Y$\bullet\bullet\bullet$H (Y is Nitrogen atom of CH_3CN) is hydrogen bond distance ($R_{N\cdots H}$). These values in the MP2 and DFT(B3LYP) level of theory using a basis set 6-311++G(2d, 2p) are given in the third column of Table 3. The fourth Column of Table 3 displays the change in bond length of donors. Column five, column six and column seven of this Table represent respectively the angle made by the donor group with the acceptor atom, BSSE corrected binding energy and change in frequency of the donor group after complex formation.

For HF molecule, the $R_{N\cdots H}$ distance is found to be 1.806 Å in MP2 level and 1.773 Å in B3LYP level of theory. The nitrogen atom of the CH_3CN molecule is highly electronegative and accepts the hydrogen atom of H-F molecules to form hydrogen bonding. The H-F molecule is called hydrogen bond donor molecules. We have also calculated the change in bond distance of hydrogen bond donor ΔR_{H-F} and found to be 0.015 Å in MP2 level and 0.019 Å in B3LYP level, which is positive and shows F-H bond elongation during hydrogen bond formation. We have also analyzed the $\angle N\bullet\bullet H-F$ and found to be 179.77^0 in MP2 level and 179.91^0 in B3LYP level.

We have calculated the BSSE (basis set superposition error) corrected binding energy and found that the binding energies for this complex calculated by the B3LYP level of theory are higher than that calculated by the MP2 level of theory. These values are found to be -8.33 kcal/mol in MP2 level and -9.72 kcal/mol in B3LYP level. From our calculation, we obtain frequency shifts of X-H stretching modes are negative in both MP2 and B3LYP level of theories, which indicate the proper hydrogen bonding that is red-shift with X-H bond lengthening.

A similar type of calculations has been performed for the $CH_3CN\bullet\bullet\bullet HCl$ complex. However, the parameters are found to be lower than those found in the $CH_3CN\bullet\bullet\bullet HF$ complex (second row of Table 3). For this complex, the hydrogen bond distances are found to be 1.983 Å in MP2 level and 1.980 Å in B3LYP level of theories respectively. The Y$\bullet\bullet\bullet$H(Y= N atom of CH_3CN) bond distance ($R_{Y\cdots H}$) in the MP2 and DFT (B3LYP) level of theories using a basis set 6-311++G(2d, 2p) for HCl donor has been studied as well. This $R_{Y\cdots H}$ distance is found to be 1. 983 Å and 1.980 Å in MP2 and B3LYP levels of theories respectively. We have also calculated the change in bond distance ΔR_{Cl-H} and found to be 0.017 Å in MP2 level and 0.019 Å in B3LYP level, which is positive and shows X-H bond elongation, which is one of the criteria of hydrogen bond formation. These values are lower than that of the $CH_3CN\bullet\bullet\bullet H-F$ complex. We have also analyzed the $\angle N\bullet\bullet\bullet H-Cl$ and found to be 179.38^0 in MP2 level and 179.16^0 in

B3LYP level. We have calculated the BSSE corrected binding energy for this complex and found to be -5.49 kcal/mol in MP2 level and -6.44 kcal/mol in B3LYP level. From our calculation, we obtain frequency shifts of Cl-H stretching modes are negative in both MP2 and B3LYP level.

The third donor molecule that has been taken in this work is water. The parameters are even found to be lower when compared with $CH_3CN\cdots HF$ and $CH_3CN\cdots HCl$ complexes. For comparison, the results of Ahn and Lee [14] are also given in the third row of Table 3. The N•••H distance in this case, is 2.060 Å in MP2 level of theory. The same value in the B3LYP level of theory is 2.076 Å. The O-H elongation after bond formation for this complex are 0.006 Å and 0.007 Å in MP2 and B3LYP level of theory respectively. The $\angle N\cdots H\text{-}O$ are 177.8^0 and 179.3^0 respectively. The BSSE corrected binding energy for this complex is -4.47 kcal/mol (MP2 level) and -4.11(B3LYP level) kcal/mol. Like the other above two complexes, the change in vibrational frequencies after complex formation is observed for this complex as well. These values are -75.9 cm^{-1} in MP2 level and -83.8 cm^{-1} in B3LYP level respectively.

NH_3 molecule is the fourth donor that we have chosen in this work. The $R_{N\cdots H}$ distance has found to be 2.331Å in MP2 level and 2.398Å in B3LYP level of theory. We have also calculated the change in bond distance between $\Delta R_{X\cdots H}$ [X= NH_2] and found to be 0.003 Å in MP2 level and 0.002 Å in B3LYP level, which is positive and shows X-H bond elongation. We have also analyzed the $\angle N\cdots H\text{-}N$ and found to be 175.1^0 in MP2 level and 174.8^0 in B3LYP level, which shows hydrogen bonding with acetonitrile. We have calculated the BSSE corrected binding energy and found to be -2.83 kcal/mol in MP2 and -1.83 kcal/mol in B3LYP level which are within the range of hydrogen bond energy given by IUPAC technical report [10]. From our calculation, we obtain frequency shifts of X-H stretching modes are negative in both MP2 and B3LYP level, which indicate the proper hydrogen bonding that is red-shift with X-H bond lengthening. These values are respectively 19.2 and 13.6 respectively. It has been observed that the hydrogen bond parameters for NH_3 donor are low in comparison to other three donors studied in this work.

AIM Theoretical Analysis

Quantum theory of Atoms in Molecules (QTAIM or AIM) has been used to analyze hydrogen bonding in many systems. We have also used AIM theory to analyze hydrogen bonding for this complex. The molecular structure of the acetonitrile•••HX complex is shown in Figure 4. In this complex, hydrogen bond critical points (HBCP) is found at the bond paths of hydrogen bonding (H•••N, N is acceptor atom) and the bond critical point (BCP) are found in all bond they are bonded each other.
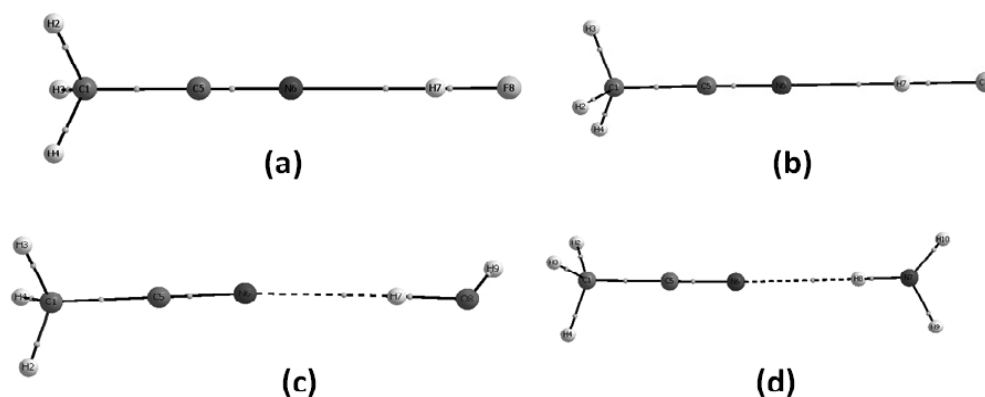

Fig 3: Molecular graph of CH₃CN•••HX complexes (X=F, Cl, OH, NH₂)

Table 4 presents electron density values $\rho(r)$ and Laplacian of electron density values $\nabla^2\rho(r)$ at the HBCPs between interacting atoms of all the complexes. The characteristic of closed-shell interaction is that the $\nabla^2\rho(r)$ values should be positive and these values were found to be positive in all $CH_3CN\cdots HX$ complexes. Furthermore, Table 4 shows that electron density and Laplacian of electron density values at the BCPs are within the range prescribed for hydrogen bonds [32].

Table 4: *Topological analysis (electron density (ρ(r)) and the Laplacian of electron density (∇²ρ(r)) values at the intermolecular BCP for acetonitrile•••HD complex in atomic units (a.u) in MP2 and B3LYP level of theory using 6-311++G(2d, 2p) basis set.*

Complex	Level of Theory	ρ(r)	∇²ρ(r)
CH₃CN•••HF	MP2	0.0342	0.1109
	B3LYP	0.0382	0.0980
CH₃CN•••HCl	MP2	0.0310	0.1006
	B3LYP	0.0253	0.0748
CH₃CN•••HOH	MP2	0.0196	0.0696
	B3LYP	0.0190	0.0671
CH₃CN•••HNH₂	MP2	0.0114	0.0413
	B3LYP	0.0100	0.0344

Like other hydrogen bond parameters, electron density values ρ(r) and Laplacian of electron density values ∇²ρ(r), at the intermolecular BCPs for CH₃CN•••HX complex are found to be high for HF donor and low for NH₃ donor.

Comparison of our works with other acceptors

Comparison with other type of hydrogen bonding is made taking different acceptors and donors and the results are given in Table 5. For this, different works were taken [11, 13, 33]. All the results presented in Table 5 are from MP2(full)/6-311g++(d,p) level of theory. The hydrogen bond parameters such as hydrogen bond distance, binding energy, change in bond length of the donor, change in frequency of the stretching mode, electron density and laplacian of the electron density of the complexes given in Table 5 and the hydrogen bond parameters for CH₃CN•••HX (Table 3 and Table 5) reveal that CH₃CN•••HOH and CH₃CN•••HNH₂ are weak hydrogen bond in comparison to the hydrogen bonding interactions shown in Table 5. Although CH₃CN•••HF and CH₃CN•••HCl hydrogen bonding interactions (Table 3) seems somehow stronger if binding energies of these interactions are compared with the hydrogen bonding interactions shown in Table 5, these interactions look weak comparison to H₂O•••HF and H₂O•••HCl interactions when the change in bond length of donors (X), the change in frequency shift of X-H stretching modes, electron density and Laplacian of electron density are compared.

Table 5: *Geometric features $R_{Y...H}$ (hydrogen bond distance), $\Delta R_{X...H}$ (change in bond length of donors) in Å, ∠Y...H-X in degree, binding energy (BE) in kcal/mol, change in frequency shift of X-H stretching modes (Δν) in cm⁻¹, electron density (ρ(r)) and the Laplacian of electron density (∇²ρ(r)) values at the intermolecular BCP in atomic units (a.u) for different hydrogen-bonded complex where, Y is acceptor atom and X-H is hydrogen bond donor molecules.*

Complex	$R_{Y...H}$	ΔR_{X-H}	∠Y•••H-X	BE	Δν	ρ(r)	∇²ρ(r)
H₂O•••HF Ref. [11]	1.694	0.018	178,0	-9.4	415	0.0436	0.1048
H₂O•••HCl Ref. [13]	1.810	0.020	178.7	-5.4	171	0.0351	0.0957
H₃N•••HOH Ref. [13]	1.950	0.010	171.0	-6.33	238	0.0187	0.0573
HF...HF Ref. [33]	1.873	0.005	171.1	-2.03	238	0.0119	0.0548

Conclusions

We have studied acetonitrile molecule using electrostatic potential analysis and its complexes with HF, HCl, and NH₃ molecules using ab initio (MP2/6-311++g(2d, 2p), B3LYP/6-311++g(2d, 2p) and AIM theoretical calculations. From electrostatic potential

calculations, the negative value of electrostatic potential was found on the nitrogen atom of acetonitrile molecules. HF, HCl molecules show the strong hydrogen bonding with acetonitrile molecules while NH_3 molecules shows weak hydrogen bonding with acetonitrile molecule. This hydrogen bond is similar to other hydrogen bonds.

Acknowledgements

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