



Quantum Mechanical Ab Initio Calculations on 1:1 Dimer Involving Hydrogen Bonds

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ABSTRACT

Conformational studies of Hydrogen Cyanide (HCN) with Hydrogen Chloride (HCl) molecule involving Hydrogen bonds of 1:1 dimer were studied using quantum Ab Initio calculations. The calculations were carried out at RHF/6-31G(d,p), MP2/6-31G(d,p) and DFT/6-31G(d,p)B3LYP5 using Firefly ver. 8.11. Cyanide complexes involving Nitrogen atom is found to be stable than involving Chlorine atoms when the hydrogen bonds are formed. In addition to the optimized geometrical calculations, frequency calculations were also done. Dipole moment, Hydrogen bond length and hydrogen bond energy or interaction energy were also reported.

Key Words: Conformational study, HCN–HCl, Ab-initio, Hydrogen bonded dimer

INTRODUCTION

The increasing amount of gas phase information from the spectroscopists as well as the increasingly sophisticated methodology employed by the Ab-initio quantum experts, the interest in weakly bonded complexes, particularly hydrogen bonded complexes continues [1]. In the investigation of weakly bound complexes formed from two molecules, the much needed information regarding the relative positions, orientations and the extent of any electric charge redistribution that accompanies the formation of complex, as well as, the nature and strength of the weak binding have been focused. In addition, there has been considerable interest in the use of binary molecular complexes as precursors for the study of chemical reactions under oriented conditions [2, 3]. The theoretical study of Hydrogen bond (HB) was initiated by Alfred Werner in 1903. He proposed that an Ammonium Salt has a configuration in which a proton lies between the Ammonia molecule and the ion linking the two. He symbolized the interaction as (H₃N...H) X.

HB energies are expressed in the units of kcal mol⁻¹ and their values range from 3 to 7 kcal mol⁻¹[4].

In this paper, we are reporting the conformational analysis of HCN with HCl along with monomers. Here the dimer had

been tried for the 1:1 structures.

Method of Calculation

All the calculations have been performed using ab-initio program package[5, 6]. Two isomers of HCN with HCl are tried. Which is carried out at RHF/6-31G(d,p), MP2/6-31G(d,p) and DFT/6-31G(d,p)B3LYP5 using Firefly 8.11 version [5, 6]. The Interaction energy or the hydrogen bonding energy is calculated by the procedure[7].

$$\Delta E = \Delta T - \Delta M$$

where, ΔT is total energy of the complex, ΔM is the sum of the total energy of the monomers and ΔE is the interaction or HB energy expressed in kcal mol⁻¹. Calculations were carried out at the R&D center of the department of Physics, RRCE, Bangalore.

RESULTS AND DISCUSSION

Structure of hydrogen cyanide, hydrogen chloride and the hydrogen bonded 1:1 complexes involving HCN with HCl is shown in Figure 1. Calculated total energies, interaction energy or HB energy, dipole moment, bond lengths including HB length and the frequency analysis are depicted in Tables 1-5.

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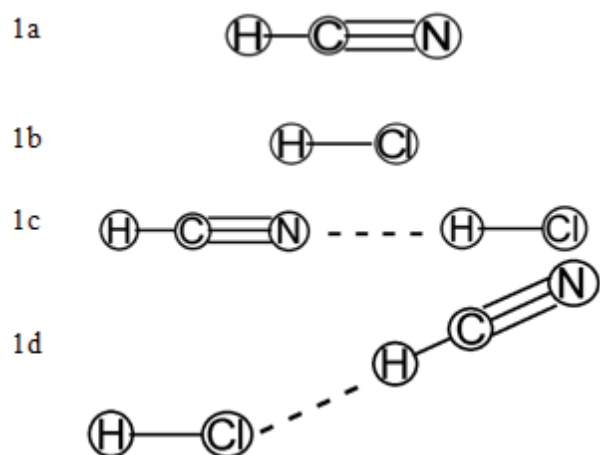


Figure 1: a) Structure of HCN, b) structure of HCl, c) structure of HCN...HCl dimer and d) structure of HCN...HCl dimer.

Table 1: Total energy in atomic units.

Structure	TOTAL ENERGY (atomic units)		
	RHF/ 6-31G(d,p)	MP2/ 6-31G(d,p)	DFT/ 6-31G(d,p) B3LYP5
HCN	-92.877138	-93.16617	-93.37287
HCl	-460.06621	-460.20544	-460.73182
HCN...HCl	-552.95014	-553.38037	-554.11318
HCl...HCN	-552.94535	-553.37475	-554.10721

Table 2: Interaction energy in kcal mol⁻¹.

Structure	INTERACTION ENERGY (k cal mol ⁻¹)		
	RHF/ 6-31G(d,p)	MP2/ 6-31G(d,p)	DFT/ 6-31G(d,p) B3LYP5
HCN			
HCl			
HCN...HCl	4.26	5.49	5.32
HCl...HCN	1.24	1.97	1.58

Table 3: Dipole moment in debye

Structure	DIPOLE MOMENT (Debye)			
	RHF/ 6-31G(d,p)	MP2/ 6-31G(d,p)	DFT/ 6-31G(d,p) B3LYP5	EXPT.
HCN	3.20	2.90	2.89	2.98 ^a
HCl	1.47	1.43	1.43	1.08 ^a
HCN...HCl	5.50	5.30	5.51	
HCl...HCN	3.86	3.83	3.84	

^areference 8

Table 4: Bond length of conformers in angstrom units.

Structure	Bonding atoms	RHF/ 6-31G(d,p)	MP2/ 6-31G(d,p)	DFT/ 6-31G(d,p) B3LYP5
HCN...HCl	H-C	1.0597	1.0655	1.0701
	C≡N	1.1315	1.1756	1.1548
	N...H	2.2201	2.0972	2.0397
	H-Cl	1.2718	1.2785	1.2991
	Hydrogen bond	3.4919 (3.405 ^b)	3.3757 (3.405 ^b)	3.3388 (3.405 ^b)
HCl...HCN	HCl	1.2663	1.2704	1.2874
	Cl...H	2.9611	2.6781	2.7260
	H-C	1.0602	1.0665	1.0720
	C≡N	1.1330	1.1779	1.1576
	Hydrogen bond	4.0213	3.7446	3.7980

^breference 9,10

Table 5: Dimeric frequency results, frequencies in cm⁻¹

Structure	RHF/ 6-31G(d,p)	MP2/ 6-31G(d,p)	DFT/ 6-31G(d,p) B3LYP5	Mode of description
HCN...HCl	3647.2	3549.5	3491.8	CH stretch
	3130.9 (2888c)	3024.5 (2888c)	2794.3 (2888c)	ClH stretch
	2444.8	2061.2	2235.7	CN stretch
	893.4	728.0	771.6	CH bend
	893.4	727.8	771.3	CH bend
	367.8	416.7	417.5	NHCl bend
	367.4	416.2	412.2	NHCl bend
	110.1	125.1	127.8	H-Bond stretch
	59.8	60.5	56.3	stretch
	59.8	60.0	51.0	CN rock HCN rock
HCl...HCN	3638.3	3525.4	3449.5	CH stretch
	3173.5	3130.0	2954.7	ClH stretch
	2433.3	2042.7	2213.0	CN stretch
	905.3	806.2	810.2	CHCl bend
	901.4	802.8	806.9	CHCl bend
	187.2	213.3	197.5	ClHwagg weak HB
	60.7	94.0	84.2	HCN rock
	57.2	87.3	74.5	HCN rock
	39.9	77.3	66.5	ClHwagg+ HCN rock

^creference 10,11

Total energy of the dimer favors the nitrogen atom bound HB structure as a stable one than the Chlorine atom bound HB 1:1 dimer. The interaction energy or the HB energy also favors the same trend. Calculated dipole moment of monomers was compared with the experimental values [8] and is found to be in good agreement. For the 1:1 dimer it needs the experimental support from the gas phase spectroscopy experts. The HB length of the conformer with nitrogen atom

is 3.4919 Å at RHF/6-31G(d,p), 3.3757 Å at MP2/6-31G(d,p) and 3.3388 Å at DFT/6-31G(d,p)B3LYP5, which is in very good agreement with the experimental value of 3.405 Å [9, 10]. For the second conformer involving Chlorine atom the HB length is reported in the table, which needs the experimental proof. So far no experimental work is reported for this conformer.

Calculated frequencies are analyzed and tabulated. Absence of negative frequencies indicates the validity of the stable 1:1 binary complexes of HCN with HCl involving HB bonds. The experimentally observed [10,11] stretching frequency of 2888 cm⁻¹ for the ClH stretching mode is in good agreement with 3130.9 cm⁻¹ at RHF/6-31G(d,p), 3024.5 cm⁻¹ at MP2/6-31G(d,p) and 2794.3 cm⁻¹ at DFT/6-31G(d,p)B3LYP5.

From the above results it is clear that if we go for higher method of quantum mechanical calculations the accuracy seems to be closer for monomers and dimer with few atoms [12-15].

CONCLUSION

Ab-initio Calculations at all the three levels of RHF/6-31G(d,p), MP2/6-31G(d,p) and DFT/6-31G(d,p)B3LYP5 supports the linear hydrogen bonded structure in which the Nitrogen atom involved is found to be more stable than the non-linear hydrogen bonded structure in which the Chlorine atom is involved. This may be due to the strong bonding nature of Nitrogen atom. This study emphasizes the need for gas phase spectroscopy at its best to support the theoretical calculations for the dimer.

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