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Articles and Statements

Natural Bond Order Analysis of HCN→HNC Isomerization Mechanism in the Interstellar Clouds Conditions: DFT Investigation

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Abstract

The optimum geometries and quadratic force constants of HCN, HNC, intermediates (INT1 and INT2) and the transition state connecting them (CHN) have been determined at the DFT (density functional theory) level of theory. Energy differences were evaluated using the DFT method in conjunction with 6-311++g(d,p) basis set. The most reliable structure obtained for the transition state has bond distances of 1.184, 1.193 and 1.391 Å for r_{CN} , r_{CH} and r_{NH} , respectively. Including a correction for zero-point vibrational energies, the transition state activation energy is predicted to be 44.6 kcal/mol. So the transition state of isomerization pathway is highly energetic and subsequently cannot occur efficiently in the gas phase.

Keywords: isomerization, DFT, HCN, Zero point energy, Gas phase.

1. Introduction

HCN and HNC molecules are of great interest in astronomy. They have been observed in many galactic and extragalactic objects, ranging from circumstellar masers through interstellar clouds to planetary atmospheres. The role of hydrogen cyanide (HCN) in the prebiotic formation of primitive nucleobases and amino acids has been studied for decades (Oro, 1961; Kliss et al., 1962; Chakrabarti et al., 2000; Glaser et al., 2007; Roy et al., 2007; Ferris et al., 1984; Rehder, 2010; Ghosh et al., 1980; Smith et al., 2001; Kikuchi et al., 2000; Hughes, 2009; Benallou, 2016; Benallou, 2017; Benallou, 2017). The interconversion of hydrocyanic and hydroisocyanic acids (HCN and HNC, respectively) is arguably one of the simplest isomerization processes in all of the chemistry. The former isomer is more stable thermodynamically, and presents the dominant form found on Earth. However, the isomeric ratio in deep space is not under thermodynamic control, and the abundance of the less stable form (HNC) is comparable to that of HCN (and in fact exceeds that of HCN along certain lines of sight). The HCN/HNC interconversion has been extensively studied both experimentally and theoretically.

The purpose of this study to a new and accurate estimate the HCN/HNC isomerization process as it proceeds via a straightforward proton transfer mechanism. Given the simplicity of the system, the mechanism of the HCN→HNC isomerization is so rarely studied by the new method in which having used the electronic correlation in their calculation. In our work, we will try to investigate the different pathway of the isomerization

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mechanism of compound HCN in the interstellar clouds conditions in order to study the probability of prebiotic formation in earth conditions.

2. Computational methods

The geometry of the complexes has been optimized with B3LYP/6-311++G** (Becke, 1993; Lee et al., 1988; Hariharan et al., 1973) computational methods. All the calculations were performed with the GAUSSIAN G09 program package (Frisch et al., 2009). The electronic structures are analyzed at the stationary point by using the NBO (natural bond orbital) method (Benallou et al., 2015; Benallou et al., 2016; Glendering et al., 1998). The minima or transition state nature of the complexes has been established based on the sign of the harmonic vibrational frequencies calculated at the B3LYP/6-311++G** level using the geometries obtained at the corresponding computational levels. The interaction energy of the complexes has been calculated as the difference between the total energy of the complexes and those of the isolated monomers.

3. Results and discussion

3.1. HCN, CHN and HNC isomers formation mechanism

The DFT optimized structures, of CHN, HCN and HNC are presented in Figure 1. Analyst's structures of HCN to HNC isomerization of DFT method give a reliable comprehension of the mechanism reaction, the reaction of HCN isomerization has three stationary points in which two intermediates and a transition state characterized by a single imaginary frequency as we noted in figure 1. However, we noticed that the equilibrium distance between atoms of HCN is about 1.066Å for H-C and 1.149Å for C-N in good agreement with experimental values (1.065 and 1.153Å) (Herzberg, 1966) as well for intermediate CHN (INT1) the proton did a rotation about the CN bond of an angle to 80.241° in such that the distance of this bond is changed to 1.156Å, so the H proton will move from carbon to nitrogen atom correspond to an extension to the C-N bond to 1.181Å. TS or CHN will be determined by the negative vibration frequency of Hessian matrix, in which the imaginary frequency to be -1127,3259cm⁻¹, thus their geometry illustrate that the proton is positioned closer to C atom than that nitrogen N in such the H-C distance is 1.193Å (against 1.392Å of H-N), as long as the CN bond has been increased slightly to 1.184Å, this latter bond is unsaturated and still triple form (C≡N), HCN and HNC angles are very acute, especially from HNC in which has a value of 54° degree, the geometry of the intermediate 2 (CHN2) show that the final shift from the proton (H) of the carbon to nitrogen atom is at this monomers because the distance between H and N becomes very short to be 1.079Å, at this INT2 the C-N distance becomes longer to be 1.202Å in which mean that this bond becomes feeble. In the HNC isomer, the HN bond becomes stronger than that HC of the HCN isomer such as its distance will be 1.000Å (against 1.066Å from HC) and the CN distance becomes longer than that of the starting HCN isomer (1.149Å to 1.169Å) and are very similar to experimental results r(NH)=0.986 and r(CN)=1.173Å (Harmony et al., 1979), so HNC isomer is less stable than HCN isomer. Subsequently, these results strongly indicate that DFT calculations are in consistency with the experimental results.

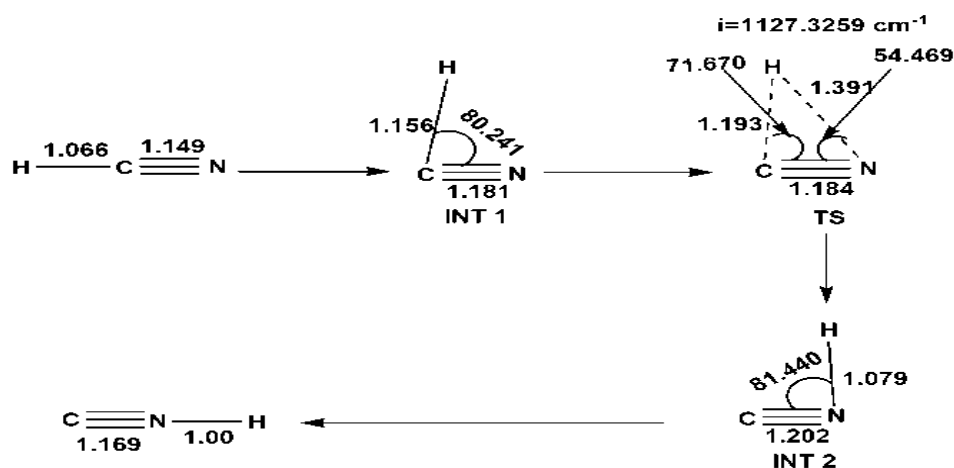


Fig. 1. Isomerization pathway calculated on the DFT method in the 6-311++(d,p) basis set, angles are given in degree and distances in Å

After the location of the maximum point (transition state), hence we can know whether that the latter (TS) connect the two minima HCN and HNC isomers by IRC (Intrinsic reaction coordinate) calculation of the transition state at several points of the isomerization process as shown in [Figure 2](#).

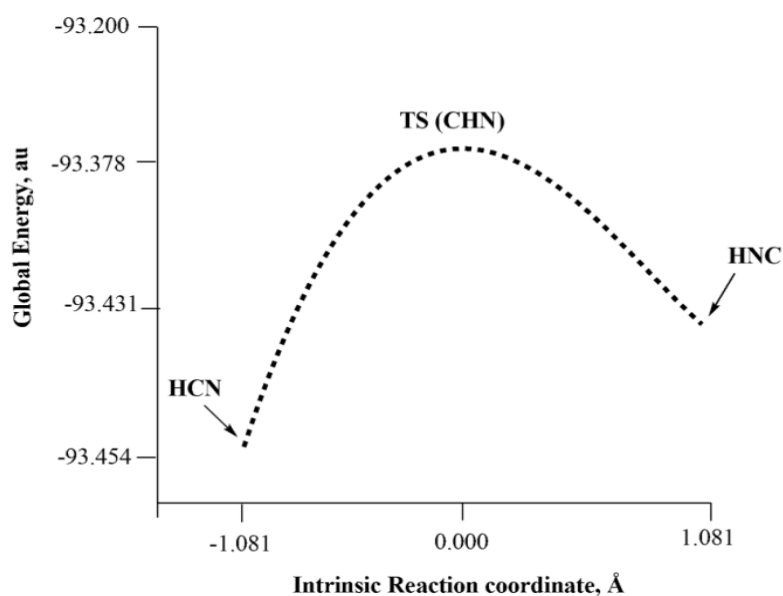


Fig. 2. Intrinsic reaction coordinates of HCN/HNC isomerization

The analysis of Figure 2 confirms that this transition state is totally verified the isomerization process such as that mechanism passes principally by three stationary points, two minima (HCN and HNC) and a maximum (CHN; TS).

In order to evaluate the progress of the HCN→HNC isomerization and H–C, C–N and H–N bond orders, we calculated the Wiberg index (Wiberg, 1968) by using the NBO (natural bond order) analysis, the found results are displayed in [Table 1](#).

Table 1. Wiberg index of H–C, C–N and N–H bonds calculated to the HCN, HNC and the connecting transition state (CHN)

Species	H-C	C-N	N-H
HCN	0.9363	2.9907	0.0181
CHN	0.5822	2.5856	0.3191
HNC	0.0310	2.4746	0.7841

Bond orders calculated using the Wiberg index are helped us to note that the C–H bond goes through a cycle of destruction or breaking process such as the bond orders become very small when going from HCN to HNC of 0.9363 to 0.0310 as well the N–H bond is strengthened and becomes very short in such the bond order was increased from 0.0181 (HCN) to 0.7841 (HNC) that meaning NH is finally formed, while C–N bond order is slightly reduced to be 2.9907 to 2.4746 in which this bond has been extended but does not break. Therefore, this result gives a reliable conclusion of isomerization process in which HCN will be transformed theoretically to HNC isomer in the gas phase.

3.2. Energy difference between HCN and HNC and then the energy difference between HCN and CHN isomers

The global energies of the HCN, HNC and CHN stationary points, obtained with the DFT electron-correlation method at 6-311++(d,p) basis sets, are portrayed in [Table 2](#).

Table 2. Global energy (E) in (au) of HCN, INT1, CHN (TS), INT2 and HNC species calculated on DFT method at 298K

HCN	INT1	CHN	INT2	HNC
-93.454	-93.380	-93.378	-93.395	-93.431

au: atomic units

The global energies calculated on the DFT method demonstrate that HCN is the most energetic species and the transition state (TS) has a less energy compared with other species such as we have found for HCN, -93.4545au and for TS, -93.3780au, therefore the HCN isomer is more stable to that of HNC in which HNC-HCN energy difference is noticeably positive, 14.432kcal/mol. Consequently, this isomerization process is energetically endothermic and thus the HCN→HNC process ongoing from stable to unstable state, therefore HNC isomer can be dissociated easily in the presence of another chemical compound.

In order to determinate the vibrational energy related to the HCN, CHN and HNC species at 0°C we have calculated the zero point energy (ZPE) of these species, the results are depicted in [Table 3](#).

Table 3. Zero point energy (ZPE) of HCN, CHN and HNC species

	HCN	CHN	HNC
ZPE(kcal/mol)	10.265	6.658	9.861

We have seen that the ZPE energy of HCN, CHN, and HNC species at 0°C has been known an increase toward the stability of these species, such as the transition state (CHN) that has the lowest energy of ZPE to be 6.658 kcal/mol in which less stable compared to the other isomers. Equally, HNC isomer that is less stable than HCN has an average value of ZPE to be 9.861 kcal/mol. Therefore, the greatest value of ZPE energy is belonging to the most stable isomer in such HCN of 10.265 kcal/mol. Thus, ZPE identification of each species we help us to calculate the thermodynamic energy at 298K, the results are given in [Figure 3](#). The zero point energy has been included carefully to these energies.

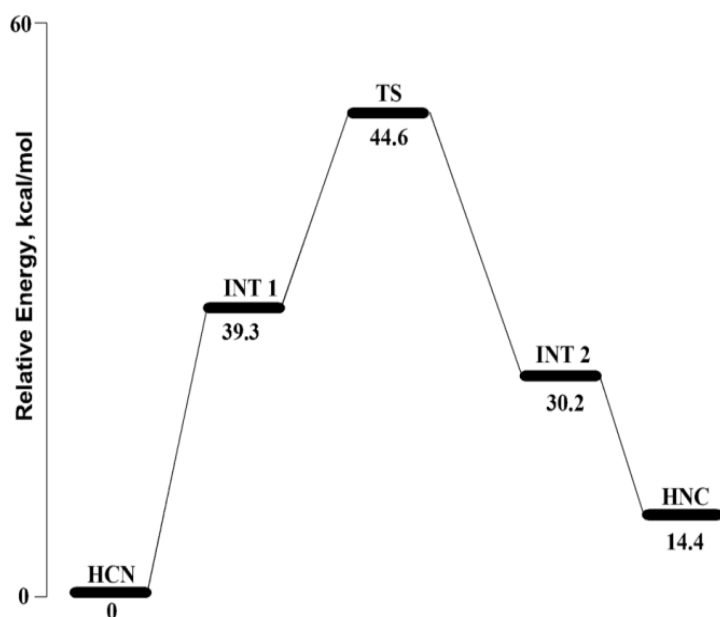


Fig. 3. Profile energetic in kcal/mol, of the HCN→HNC isomerization process

The mentioned results in [Figure 3](#) show that the relative energy (E), calculated using the DFT method is sufficiently positive and greater than 0 kcal/mol. Therefore, this isomerization process is endothermic. However, HCN isomerization ongoing through the barrier energy of 44.6 kcal/mol to likely takes place. In addition, the isomerization process passes through two intermediates, in which the first intermediate 1 (39.3 kcal/mol) is essential for HCN shifts to the CHN (TS) and the second intermediate 2 (30.2 kcal/mol) is necessary for CHN take place to the final HNC compound (14.4 kcal/mol) in agreement with the calculation of energies barrier of the intermediate 1 and 2 in which the activation energy are $E_a(\text{INT}2) < E_a(\text{INT}1) < E_a(\text{TS})$.

So the isomerization pathway is done as follows: HCN→INT2 (proton rotation around of the carbon)→CHN (the proton moves between the carbon and nitrogen atoms)→INT2 (proton shifts from carbon to the nitrogen atom)→ HNC.

In order to identifying the charge transfer between H, C, and N atoms in the studied isomers, we will be calculated the Mulliken charge, the results are given in [Table 4](#).

Table 4. Atomic charge of Mulliken (e) calculated by DFT method

Atoms	HCN	CHN	HNC
H	0.175522	0.214231	0.278070
C	0.063687	-0.182765	-0.157088
N	-0.239209	-0.031466	-0.120983

In [Table 4](#), we have remarked that the H proton has a perceptible positive charge in the beginning of the reaction will acquire an electrophilic character because has lost many important charge along the isomerization process to become more electrophilic; 0.175522e from HCN to 0.278070e of HNC. However, the carbon atom that has previously positive charge in HCN to be 0.063687e which took a negative charge at CHN and HNC isomers, -0.182765e and -0.157088e, respectively. Subsequently, the carbon atom has accepted more electronic charge from nitrogen and hydrogen atoms in which take more nucleophilic character (HC bond breaking) as well the nitrogen atom was negative charge in HCN isomer will lose many considerable charges during the isomerization process as in CHN and HNC isomers (charge transferred principally to the carbon atom).

4. Conclusion

The HCN and HNC isomers and the transition state connecting them (CHN) have been studied using DFT method theory. The optimum geometries and harmonic frequencies of the HCN, HNC and CHN stationary points have been determined at the 6-311++(d,p) basis set level. The isomerization process involved two intermediates in which INT1 and INT2 and a transition state connecting the HCN to HNC. The energy difference (ΔE) between HCN and HNC and the energy difference (E_a) between HCN and CHN have been evaluated. The best estimates for ΔE and E_a obtained in this work are 14.4 kcal/mol and 44.6 kcal/mol respectively. The results of this study show that the isomerization process is thermodynamically endothermic and needing more energy from external source to likely takes place in the gas phase of interstellar clouds.

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