

Understanding the temperature and pressure role of HCN→HNC isomerization as well as vibrational and rotational energies of these species

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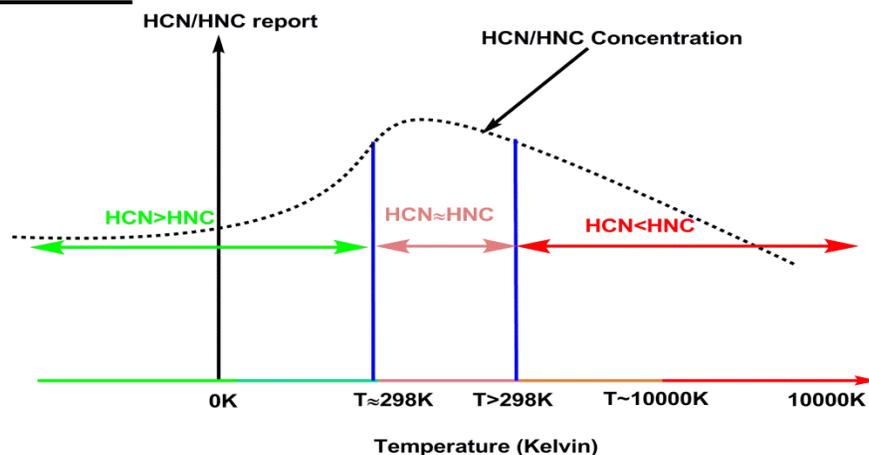
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• **Novelty and Highlights:**

- HCN is more stable than HNC at the temperature less than 298K.
- HNC is more stable than HCN at the temperature more than 298K.
- HCN/HNC isomerisation is dependent strictly on the temperature.
- Pressure does not have any role of HCN/HNC isomerisation.
- Isomerization process increases with temperature elevation

• **Graphical Abstract:**



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Abstract: The optimum geometries of HCN, HNC and the transition state connecting them (CHN) have been determined at the DFT (density functional theory) levels of theory. Energy differences of different temperature and pressure were evaluated using the DFT method in conjunction with 6-311++g(d,p) basis sets. The most appropriate temperature of HCN/HNC isomerization is more than 298K, thus in this temperature, the activation energies have been diminished and HCN becomes less stable compared to HNC isomer, therefore the pressure effect on the isomerization process is negligible. Equally vibrational and rotational energies are proportional augmented with respect to the temperature.

Key words: Isomerization, HCN, Vibrational and rotational energies, Transition state, DFT.

Introduction

The role of hydrogen cyanide (HCN) in the prebiotic formation of primitive nucleobases and amino acids has been studied for decades [1–11]. Thus 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 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 overwhelmingly 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 work is to understand the likely effect of temperature and pressure on the HCN to HNC isomerization process as well their vibration and rotation energies in order to look at what points of temperature and pressure HCN will become unstable to that of HNC and that their isomerization to HNC becomes more

accessible and less energetically, in this work we have used the most reliable method of conceptual DFT (density functional theory).

The geometry of the complexes has been optimised with B3LYP/6-311++G** [12-14] computational method available in the Gaussian 09 [15]. The electronic structures are analysed at the stationary point by using the NBO (natural bond orbital) method [16-18]. The minimum 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** levels using the geometries obtained at the corresponding computational levels. The location of a transition state is followed by an IRC calculation [19,20] to determine pathway reaction and connect the TS to the minima (HCN and HNC).

Results and Discussions

The structure of HCN, CHN and HNC isomers The DFT optimised structures, of CHN, HCN and HNC are presented in figure 1. Analysts structures of HCN to HNC isomerization give a reliable comprehension of mechanism reaction and a good assessment of thermodynamic quantities, HCN isomerization through by three stationary points, two intermediates and a

transition state, the latter is characterized by a single imaginary frequency as we noted in figure 1 ($i= -1127.3259\text{cm}^{-1}$) and is confirmed by IRC calculation as is represented in figure 2 of different point step.

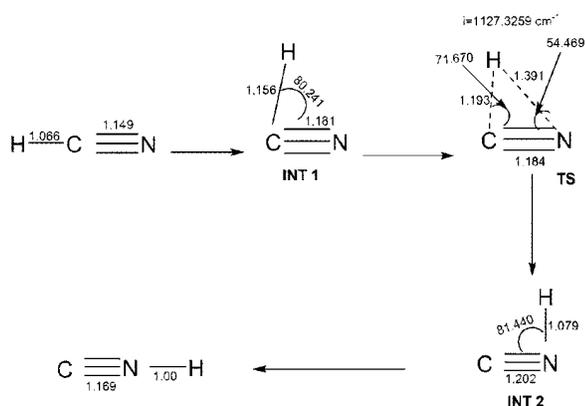


Figure 1 Isomerization process calculated on the DFT method at the 6-311++(d,p) basis set.

After the location of the maximum point (transition state) in the potential energy surface, we can know 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.

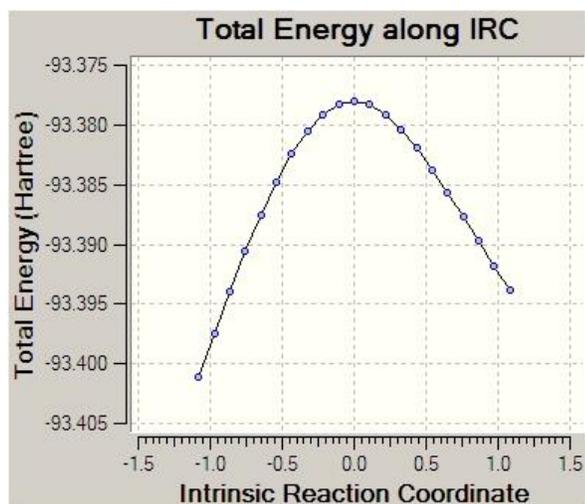


Figure 2 Intrinsic reaction coordinates of HCN→HNC isomerization.

The analysis of figure 2 we at leads to confirm that this transition state is totally verified the isomerization process such as the isomerization at crossed by three stationary points, two minima (HCN and HNC) and a

maximum (CHN; TS), to know that the HCN isomer and more stable than HNC in accordance with the results found previously in the literature as in Figure 2. In this end, after having regard to these results we will attempt to know the temperature in which the HCN to HNC isomerization process becomes more accessible and very fast or the temperature in which HCN becomes less stable than that HNC.

Appropriate temperature of HCN→HNC isomerization

In order to identify the proper temperature on the progress of the HCN to HNC isomerization process, we tried to determine the thermodynamic quantities corresponding to the optimized geometries of both isomers as well the relative electronic energy ΔE , enthalpies of reaction ΔH , free enthalpies of reaction ΔG and activation energies E_a , the variations of these quantities in function of the temperature (10K to 10000K) are determined and grouped in table 1.

Table 1. Relative energies ΔE , enthalpies of reaction ΔH , free enthalpies of reaction ΔG and activation energies E_a of HCN to HNC isomerisation with respect to the temperature.

Temperatures (Kelvin)	ΔE^*	ΔH^*	ΔG^*	E_a^*
10	13.998	13.998	13.998	44.385
100	13.998	13.999	14.000	44.475
150	13.998	14.018	13.997	44.521
223	13.998	14.083	13.975	44.565
298	13.998	14.164	13.926	44.560
353	13.998	14.220	13.877	44.524
373	13.998	14.239	13.857	44.506
433	13.998	14.291	13.791	44.435
1000	13.998	14.535	12.985	43.343
2000	13.998	14.569	11.407	40.961
2100	13.998	14.566	11.250	40.704
2300	13.998	14.560	10.934	40.181
2500	13.998	14.553	10.618	39.649
2525	13.998	14.553	10.579	39.583
2550	13.998	14.552	10.540	39.515
2600	13.998	14.550	10.462	39.381
2700	13.998	14.547	10.304	39.110
2800	13.998	14.544	10.147	38.838
3000	13.998	14.537	9.833	38.289
3500	13.998	14.523	9.050	36.897
4000	13.998	14.512	8.269	35.483
5000	13.998	14.492	6.711	32.612
10000	13.998	14.449	-1.048	17.938

*: Kcal/mol.

The results noted in table 1 are represented in Figure 3. The results reported in table 1 and figure 3 shows that the thermodynamic quantities of HCN to HNC isomerization has happened through several stages following the elevation of the temperature, such as the

calculation of thermodynamic quantities at different temperatures of 10 °K to 10000 °K.

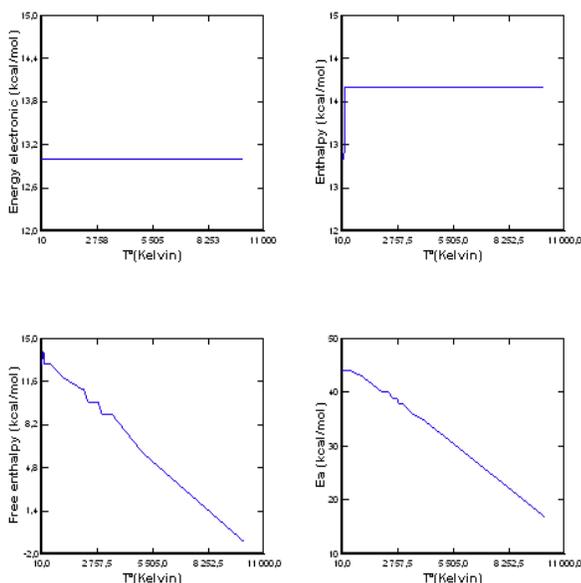


Figure 3. Graphic representation of thermodynamics quantities variations with respect to the temperature.

In order to identify the potential energy surface (PES) at these temperatures in sequence to put in evidence the effect of temperature to improvement of the isomerization process, the study made by the calculation of relative electronic energy ΔE , enthalpies of reaction ΔH , free enthalpies of reaction ΔG and activation energies E_a revealed that the thermodynamic quantities of the isomerization process pursue the following paths in function on the temperature such as ΔE , this quantity has remained stable despite increasing of temperatures that are taken into account from 10K to 10,000 °K. Effectively, the electronic energy does not depend on the temperature. ΔH , this quantity ($\Delta H > 0$, endothermic process) knows a steady increase with the elevation of the temperature (from 10K to 2000 °K). However in more than 2000 °K we noticed that this energy decreased with increasing the temperature (2100 °K to 10000 °K), this mean that this isomerization at higher temperature becomes less energetically, so it is important to note that in the high temperature ($T > 2000K$) the energy required to be provided to the isomerization process will decrease such as: (in $T = 10$ °K ($\Delta H = 13.998$ kcal/mol), in $T = 2000$ °K ($\Delta H = 14.569$ kcal/mol), in $T = 2100$ °K ($\Delta H = 14.566$ kcal/mol) and in $T = 10000$ °K ($\Delta H=14.449$ kcal/mol).

- ΔG : This quantity is higher than 0, that is to say that this isomerization process is not spontaneous and that the latter require more temperature to be activated, seen the values found in function of the temperature from 10K to 10000K we noted that: of 10 °K to 100 °K: ΔG knows a slight increase of 13.998 kcal/mol to 14.000 kcal/mol, so the degree of non-spontaneity is also increased. Of 150 °K to 5000 °K: ΔG knows a successive decrease at the temperature 150 °K, so the free enthalpy of the isomerization is regularly reducing with the elevation of the temperature, subsequently, ΔG tends towards 0kcal/mol to more than 5000K and that will be a balance between HCN and HNC species. More than 5000 °K to 10,000 °K, the isomerization passing through a nonspontaneous state ($\Delta G > 0$ at the temperature less than 10,000 °K) to a spontaneous state ($\Delta G < 0$ to the high temperature close than 10,000 °K). Thereby the HCN isomer at the temperature under 1000K is more stable than HNC, as well it needing more energy to have isomerization at HNC isomer, in the case while the temperature is close to 10,000 °K and more, HCN isomer becomes unstable and subsequently, will be isomerized spontaneously to HNC ($\Delta G < 0$). Consequently, free enthalpy of this isomerization takes a maximum value to 100 °K followed by a successive decrease until will become negative close to 10,000 °K. E_a , this quantity has taken two different steps during the thermolysis process; the first step takes place between the temperature of 10K and 298 °K (25 °C) in which the activation energy increased to a maximum value of 44.560 kcal/mol at temperature 298 °K. Thus, the HCN isomer is energetically more stable than HNC at room temperature, in this case, HCN/HNC isomerization is endothermic. At high temperature than that of 298 °K, the circumstance will have changed because the activation energy begins regularly to reduce in function of the elevation of temperature (298 °K to 10,000 °K) such as the activation energy E_a has been decreased, this may explain that HCN becomes a little bit unstable at the high temperatures in contradiction with the HNC isomer. Subsequently, HCN/HNC isomerization process becomes more accessible in temperature further than 298 °K in accordance with the results of the free energy. Therefore, the appropriate temperature in the isomerization process is located at 298 °K and more.

The appropriate pressure of HCN→HNC isomerization
Determining the proper temperature of isomerization or rather beginning instability of HCN and beginning stability of HNC isomer, at this point we want to make

out the possible effect of the pressure in the process of isomerization. For this purpose, we will calculate the various thermodynamic quantities corresponding to the optimised geometries of both isomers at pressure atmospheric of 1.0, 2.0, 4.0 and 10 of ambient temperature (298 °K) and of an arbitrary temperature of 2,525 °K. The results are presented in table 2.

Table 2. Relative electronic energies ΔE , enthalpies of reaction ΔH , free enthalpies of reaction ΔG and activation energies E_a of HCN to HNC isomerization with respect to the temperature (2,525 °K and 298 °K) and pressure 1.0, 2.0, 4.0, 10 atm.

T (K°)	P (atm)	ΔE^*	ΔH^*	ΔG^*	E_a^*
252	2.0	13.99	14.55	10.58	39.58
	4.0	13.99	14.55	10.58	39.58
	10.0	13.99	14.55	10.58	39.58
	1.0	13.99	14.16	13.92	44.56
298	2.0	13.99	14.16	13.92	44.56
	4.0	13.99	14.16	13.92	44.56
	10.0	13.99	14.16	13.92	44.56

*: kcal/mol.

The results mentioned in table 2 shows that the pressure has no influence on the thermodynamic quantities concerning the HCN/HNC isomerization process, such as even that atmospheric pressure increased at 1.0, 2.0, 4.0 and 10 atm with respect to the temperatures of 298 °K and 2,525 °K, these quantities stay unchanged with increasing of pressure. Thereby, according to this result, the only factor predominant and influencing the isomerization of HCN to HNC is the temperature.

In order to highlight the effect of temperature on the vibrational and rotational energy of HCN and HNC isomers at different temperatures from 10 °K to 10,000 °K, we are calculated those energies at a different temperature, the results are given in table 3.

Following to results noted in table 3 and in figures 4, 5 and 6, we can say that the vibration and rotation energies are proportional to increase of the temperature; these energies have been increased with elevation of the temperature. In addition the most relevant results that the rotational energy is equal of both HCN and HNC isomers, although for vibrational energy there are two situations are distinguished, one to less than 433 °K in which the vibration energy of HCN isomer is greater by report of HNC isomer, thus for the second situation to more than 433 °K we can observe an inverse than that of

the first situation because the vibration energy of HCN isomer is small by report of HNC isomer.

Table 3. Vibrational and rotational energies ($E_v + E_r$) of HCN and HNC isomers with respect to the temperatures.

Temperatures (K)	HCN		HNC	
	E_{vib}^*	E_{rot}^*	E_{vib}^*	E_{rot}^*
10	10.265	0.020	9.861	0.020
100	10.265	0.199	9.863	0.199
150	10.268	0.298	9.884	0.298
223	10.297	0.443	9.977	0.443
273	10.344	0.543	10.079	0.543
298	10.377	0.592	10.139	0.592
353	10.469	0.702	10.287	0.702
373	10.508	0.742	10.345	0.742
433	10.533	0.861	10.643	0.861
1000	12.792	1.987	12.925	1.987
2000	18.752	3.970	18.919	3.974
2300	20.807	4.571	20.964	4.571
2550	22.569	5.067	22.719	5.067
2600	22.926	5.167	23.074	5.167
2700	23.644	5.365	23.789	5.365
2800	24.367	5.564	24.508	5.564
3000	25.826	5.962	25.961	5.962
3500	29.533	6.956	29.654	6.956
4000	33.301	7.949	33.410	7.949
5000	40.957	9.936	41.047	9.936
10000	80.101	19.872	80.148	19.872

These results are represented in figures 4, 5 and 6 respectively.

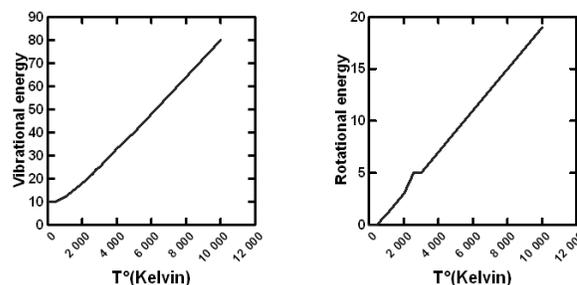


Figure 4 Vibrational and rotational energies of HCN isomer with respect to the temperature.

Subsequently, vibrational energy is proportional to stabilities of these isomers, it's great when these isomers are more stable and vice versa, this confirms the results found during the calculation of thermodynamic

quantities which stipulates that HCN becomes less stable in the increase of the temperature at contradictorily of HNC isomer which will stabilize gradually to this increase.

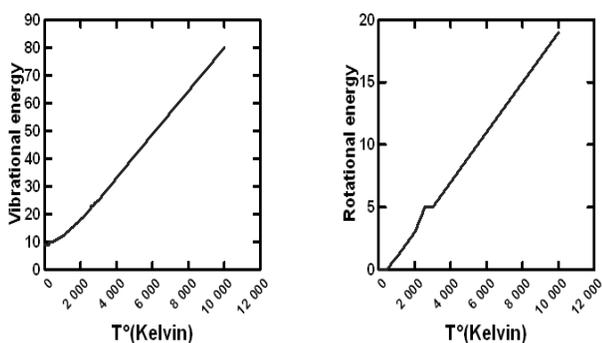


Figure 5. Vibrational and rotational energies of HNC isomer with respect to the temperature

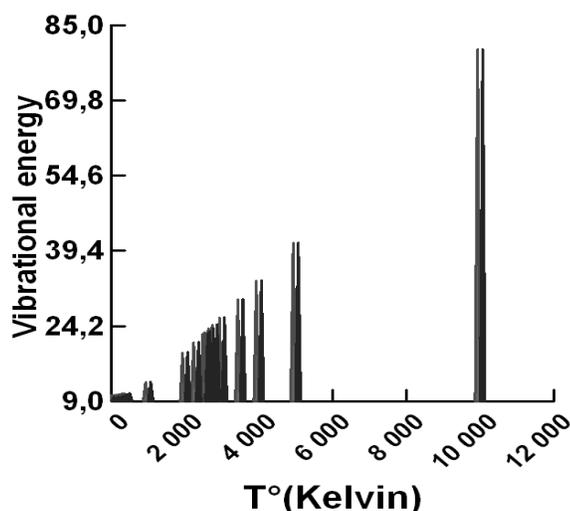


Figure 6 Vibrational energy (E_v) of HCN and HNC isomers with respect to the temperature.

In order to confirm that the temperature is a lone factor of vibrational and rotational energies we are going to keep the temperature constant at 298 °K and we will calculate these energies to several values of pressure ranging from 1.0 to 10atm, found results are given in table 4.

As it is mentioned in table 4, vibration and rotation energetic are unchanged despite the elevation of atmospheric pressure (1.0, 2.0, 4.0 and 10) applied to these HCN and HNC isomers. Of this fact, the temperature is exclusively the lone factor influencing these quantities from this study.

Table 4. Vibrational and rotational energies (E_V+ER) of HCN and HNC isomers in various pressures.

Pressures	HCN		HNC	
	E_{Vib}^*	E_{Rot}^*	E_{Vib}^*	E_{Rot}^*
1.0 atm	10.377	0.592	10.139	0.592
2.0 atm	10.377	0.592	10.139	0.592
4.0 atm	10.377	0.592	10.139	0.592
10.0 atm	10.377	0.592	10.139	0.592

* kcal/mol

Conclusion

Proper temperature and pressure of HCN/HNC isomerization have been identified using DFT method theory. The optimum geometries of the HCN, HNC and CHN species and the thermodynamical quantities have been determined at the 6-311++(d,p) basis sets. The results of this study show that the isomerization process is thermodynamically endothermic and needing more energy for barrier activation. In addition, the isomerization process of HCN to HNC is favourable energetically at the temperature more than 298 °K such as at this temperature and more the activation energy E^a will be reduced. Subsequently, HCN at high temperature is less stable than HNC so the isomerization step is easy to do. Otherwise, the pressure not has any role of HCN to HNC isomerization. Equally, vibrational and rotational energies of HCN and HNC species are dependent strictly on the temperature as well those energies will be increased in function at the elevation of temperature.

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