



Spectroscopic Parameters of HTiCN/HTiNC: New Titanium Compounds of Astrochemical Interest

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Abstract

A theoretical study of the [C, Ti, H, N] isomers, which are species of possible interstellar interest, has been carried out. We have employed different *ab initio* and density functional theory methodologies. Eleven isomers on the singlet, triplet, and quintet potential energy surfaces (PES) are characterized. The three most stable isomers of this system are obtained on the $^3A''$ PES from the interaction of the titanium atom of TiH with the cyano radical, CN, giving the open chains hydrotitanium cyanide/isocyanide (HTiCN/HTiNC) and the cyclic arrangement HTi-CN. For the most stable isomers we apply a composite approach that considers the extrapolation to the complete basis set limit, relativistic, and core-valence electron correlation corrections at the coupled-cluster level, including single and double excitations and a perturbative treatment of triple excitations (CCSD(T)). The lowest-lying isomer, HTiNC, is predicted to lie about $3.67 \text{ kcal mol}^{-1}$ and $3.86 \text{ kcal mol}^{-1}$ below HTiCN and the cyclic structure HTi-CN, respectively. The isomerization processes between these isomers shows that the cyclic structure could easily isomerize into HTiNC (the energy barrier is estimated to be only $0.48 \text{ kcal mol}^{-1}$). We report harmonic and anharmonic frequencies, infrared intensities, and rotational constants that could help in their experimental characterization.

Key words: astrochemistry – ISM: general – ISM: molecules – molecular data

1. Introduction

Several metals and metal-containing molecules have been characterized among the components of the interstellar medium. The presence of neutral metals and ions in the gas phase of the circumstellar envelope of the C-rich star IRC +10216 (Mauron & Huggins 2010) could help to explain the metal chemistry. In 1987 metal halides NaCl, AlCl, KCl, and AlF were the first molecules containing metals detected in this source by Cernicharo & Guélin (1987). Next, the metal cyanide/isocyanide compounds MgNC (Guélin et al. 1993; Kawaguchi et al. 1993), NaCN (Turner et al. 1994), MgCN (Ziurys et al. 1995), SiCN (Guélin et al. 2000), AlNC (Ziurys et al. 2002), SiNC (Guélin et al. 2004), KCN (Pulliam et al. 2010), and FeCN (Zack et al. 2011) were characterized. In 2013, the related molecule hydromagnesium isocyanide, HMgNC, was also identified in the laboratory and in the C-rich star IRC+10216 (Cabezas et al. 2013). Additionally, in oxygen-rich circumstellar envelopes, the metal oxygen molecules FeO (Walmsley et al. 2002), AlO (Tenenbaum & Ziurys 2009), AlOH (Tenenbaum & Ziurys 2010), TiO, and TiO₂ (Kamiński et al. 2013) were detected. Therefore, cyanides/isocyanides are the most common metal-containing molecules detected so far in carbon-rich circumstellar shells, especially in IRC+10216. Although early models of photospheric and inner shell chemistry (Tsuji 1973) predicted the existence of some metal-bearing molecules such as metal halides and oxides, the observation of metal cyanide/isocyanide compounds was not expected. Thus, the chemistry of metal-containing molecules in space is not yet well-understood (Pulliam et al. 2010).

Related to metal cyanide/isocyanide compounds are hydro-metal cyanide/isocyanide compounds of which there is little information nowadays that is either theoretical or experimental. As we have pointed out, only HMgNC was detected in space

(Cabezas et al. 2013). The rotational spectrum of both isomers of hydrides of silicon, HSiCN/HSiNC, was characterized in the laboratory (Sanz et al. 2002), and an *ab initio* calculation predicts that both isomers are close in energy, and the isocyano isomer, HSiNC, is located only $3.2 \text{ kcal mol}^{-1}$ above the HSiCN isomer at the BLYP/6-311G** level (Maier et al. 1998). The structure of hydride of zinc cyanide, HZnCN, was characterized using Fourier transform microwave spectroscopy (Sun et al. 2009), according to a theoretical study that predicts that HZnCN is the lowest-lying isomer and the isocyanide counterpart, HZnNC, is located $5.13 \text{ kcal mol}^{-1}$ above HZnCN at the CCSD(T)/aug-cc-pVQZ level (Redondo et al. 2015). A high-level theoretical study that includes corrections at the CCSD(T)/aug-cc-pVQZ level for complete basis set (CBS), core-valence (CV) correlation energy, and relativistic effects, predicts HFeCN and HFeNC ($0.5 \text{ kcal mol}^{-1}$ below HFeCN), in their $^6\Delta$ states, as the most stable structures for the system [C, Fe, H, N] (Redondo et al. 2016).

Other metal cyanide compounds could be present in C-rich circumstellar gas and could provide important information on the regions where the different species formed as well as their formation mechanism. Theoretical estimation of spectroscopic parameters for these compounds could help in their experimental characterization in the laboratory and/or in space. Given the relevance of metal cyanide compounds, here we will focus on the hydrotitanium cyanide/isocyanide.

Among transition metals, titanium has a relatively large cosmic abundance; it is quite similar to chlorine, for instance (Urey 1952). Titanium is one of the metals detected in the circumstellar envelope of IRC+10216 (Mauron & Huggins 2010). In addition to TiO and TiO₂ detected molecules, TiC should form in regions of enhanced density in asymptotic giant branch carbon stars (Bernatowicz et al. 2005). Nevertheless, theoretical spectroscopic constants have been reported for TiH₂, which is proposed as a plausible interstellar molecule

(Sharma et al. 2017). With regards to cyanide derivatives of titanium, a theoretical study (Rayón et al. 2007) predicted for cyanide and isocyanide of titanium a $^4\Phi$ ground state, and TiNC is located $2.53 \text{ kcal mol}^{-1}$ below TiCN at the CCSD(T)/6-311+G(3df) level. The interconversion barrier $\text{TiNC} \rightarrow \text{TiCN}$ is estimated to be around $8.07 \text{ kcal mol}^{-1}$ at the CCSD(T)/6-311+G(3df). Therefore, both isomers could be present in the interstellar medium.

In the present work, we carry out a theoretical study of the system [C, Ti, H, N]. We start locating the minima on the singlet, triplet, and quintet potential energy surfaces (PES) to later focus on the study of the most stable isomers. It is noteworthy that these compounds present various isomeric forms and some of them could be present in the interstellar medium; for example, both MgNC and MgCN have been characterized in space (Guélin et al. 1993; Kawaguchi et al. 1993; Ziurys et al. 1995). From a computational point of view, the characterization of the ground state for transition metal compounds is a relatively difficult task because they usually have many states of different multiplicity with similar energy. High-level theoretical calculations, in particular coupled-cluster (CC) theory with additive corrections, have been proven to correctly describe these compounds (DeYonker 2015). To the best of our knowledge neither theoretical nor experimental studies have been devoted to hydrotitanium cyanide/isocyanide.

2. Computational Methods

The geometries of the possible [C, Ti, H, N] isomers were optimized as a first approach at the density functional theory (DFT) level, employing the B3LYP hybrid exchange correlation functional (Becke 1986, 1988a, 1988b; Lee et al. 1988) in conjunction with the Dunning’s aug-cc-pVTZ (correlation-consistent polarized valence triple-zeta, including diffuse functions) basis set (Dunning 1989; Woon & Dunning 1993). These types of systems present a large number of states that are close in energy; thus, to establish the lowest-lying one for each multiplicity, a stability test has been performed. On each optimized geometry, harmonic vibrational frequencies were calculated. This allows estimation of the zero-point vibrational energy correction (ZPE), as well as confirmation of the nature of the stationary points located on the PES, either a true minimum (all vibrational frequencies real) or a transition state (one of the frequencies, and just one, imaginary).

For the most stable isomers characterized at the B3LYP level, we apply the B2PLYP double hybrid exchange correlation functional (Grimme 2006), and different ab initio methods, namely, a second-order Møller–Plesset (MP2; Møller & Plesset 1934), a coupled-cluster with single and double excitations (CCSD), and a CCSD(T) that also includes a perturbative treatment of triple excitations (Raghavachari et al. 1989). The Dunning’s aug-cc-pVTZ (correlation-consistent polarized valence triple-zeta including diffuse functions) basis set (Dunning 1989; Woon & Dunning 1993) was used for optimization. Single-point energy calculations were also performed at the CCSD(T) level by employing the aug-cc-pVQZ basis set (Dunning 1989; Woon & Dunning 1993), which has a quadruple-zeta character and includes both diffuse and polarization functions.

To analyze the viability of single-reference results we estimated the T1 diagnostic in the CCSD(T) calculations (Lee & Taylor 1989). Jiang et al. (2012) suggested that a T1 value

less than 0.05 is necessary to obtain reliable energetics and spectroscopic properties in 3d transition metal compounds using single-reference-based methods.

Additional calculations, at the same level employed in the previous study of hydro-iron cyanide/isocyanide (Redondo et al. 2016), were performed for the most stable isomers in order to provide a more reliable description. We estimated geometrical parameters and energies including additive corrections to those calculated at the CCSD(T)/aug-cc-pVQZ level through a composite procedure (Heckert et al. 2005, 2006). The effect of CV correlation was accounted for by including 3s3p orbitals for Ti and 1s orbitals for C and N at the CCSD level (denoted as CCSD-rw) in conjunction with the weighted CV basis set aug-cc-pwCVTZ (Peterson & Dunning 2002; Balabanov & Peterson 2005). We have not included 1s2s2p orbitals in the calculations because in a previous study for FeCN/FeNC systems (DeYonker 2015) they were shown to have a negligible effect. To take into account relativistic effects, Douglas–Kroll-type calculations (Hess 1985, 1986; Jansen & Hess 1989) at the CCSD level, in conjunction with the basis set aug-cc-pVTZ-DK (denoted as CCSD-DK/aug-cc-pVTZ-DK), were performed.

The composite bond distances are calculated by the expression

$$r(\text{composite}) = r(\text{CBS}) + \Delta r(\text{CV}) + \Delta r(\text{DK}),$$

where $r(\text{CBS})$ corresponds to the CBS limit evaluated through the n^{-3} extrapolation formula Helgaker et al. (1997) applied to the case $n = 3, 4$ (T, Q), employing the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ optimized parameters. The corrections $\Delta r(\text{CV})$ and $\Delta r(\text{DK})$ account for the CV electron correlation and relativistic effects, respectively, and they are evaluated as:

$$\begin{aligned} \Delta r(\text{CV}) &= r(\text{CCSD-rw/aug-cc-pwCVTZ}) \\ &\quad - r(\text{CCSD/aug-cc-pVTZ}) \\ \Delta r(\text{DK}) &= r(\text{CCSD-DK/aug-cc-pVTZ-DK}) \\ &\quad - r(\text{CCSD/aug-cc-pVTZ}). \end{aligned}$$

Composite energies using the same approach were estimated from the CBS limit-extrapolated energy corrected by the CV electron correlation, relativistic effects, and ZPV energy (calculated at the CCSD/aug-cc-pVTZ level):

$$E(\text{composite}) = E(\text{CBS}) + \Delta E(\text{CV}) + \Delta E(\text{DK}) + \text{ZPV}.$$

Harmonic vibrational frequencies were computed on the optimized geometries at the CCSD-rw/aug-cc-pVTZ level using analytic second derivatives of the energy. To help with the possible experimental detection of these conformers by infrared (IR) spectroscopy, we also computed anharmonic vibrational frequencies. We found convergence problems in the calculation of anharmonic contributions at the CCSD/aug-cc-pVTZ level, thus a hybrid model suggested by Barone et al. (2014) is employed. In this hybrid approach, the anharmonic corrections were calculated at the B2PLYP/aug-cc-pVTZ level of theory within a second-order perturbation treatment (VPT2) (Barone 2005) based on a full cubic force field (CFF) and semi-diagonal quartic force constants. Vibration–rotation interaction constants were also evaluated from the CFF calculations, allowing for the correction of rotational constants, including vibrational effects.

Table 1

Relative Energies in kcal mol⁻¹ for the [C, Ti, H, N] Isomers Calculated at Different Levels of Theory in Conjunction with the Aug-cc-pVTZ Basis Set

Isomer	State	B3LYP	B2PLYP	MP2 = full	CCSD ^a	CCSD (T) ^{a,b}
HTiCN	¹ A'	35.40				
	³ A''	4.62	6.52	6.94	4.01	3.65
	⁵ Φ	69.46				
HTiNC	¹ A'	29.67				
	³ A''	0.00	0.00	0.00	0.00	0.00
	⁵ Φ	66.34				
HTi-CN	³ A	5.51	5.89	1.84	2.14	2.24
HN(Ti)N	¹ A'	28.99				
	³ A''	11.08	29.45	18.96	24.72	19.95
	⁵ A'	29.52				
HN(Ti)C	¹ A'	52.80				
	³ A''	35.42	46.29	51.69	44.39	42.46
	⁵ A'	42.57				
HCNTi	¹ A'	58.94				
	³ A''	34.24				
	⁵ A''	25.61	31.52	39.44	36.67	36.01
HNCTi	¹ A'	59.26				
	³ A''	42.18				
	⁵ A''	33.22	40.38	47.72	44.67	43.90
TiHCN	¹ A'	85.66				
	³ Φ	44.20				
	⁵ A''	48.69				
TiHNC	¹ Γ	95.67				
	³ Φ	57.38				
	⁵ Φ	61.59				
HCTiN	³ A''	74.86				
	⁵ Δ	106.66				
HNTiC	³ A'	85.52				
	⁵ A''	93.34				

Notes. ZPV energies are included.

^a ZPV energies calculated at the B2PLYP level.

^b Calculated on the CCSD/aug-cc-pVTZ optimized geometries.

Calculations were carried out with the Gaussian 09 program package (Frisch et al. 2009) and CFOUR (Stanton et al. 2013).

3. Results and Discussion

3.1. [C, Ti, H, N] System

We have searched for different [C, Ti, H, N] isomers on the singlet, triplet, and quintet PES. These calculations were carried out at the B3LYP/aug-cc-pVTZ level as a premier approach. We have chosen this functional because in our previous study of cyanide/isocyanide of first-row transition metals (Rayón et al. 2007), we found that the B3LYP level gives stability results similar to that found at the CCSD(T) level. As an example, the relative energies $E(\text{TiNC}) - E(\text{TiCN})$ are -2.65 kcal mol⁻¹ and -2.54 kcal mol⁻¹ calculated at the B3LYP/6-311+G(3df) and CCSD(T)/6-311+G(3df) levels, respectively. Additional calculations are also done for the most stable isomers in their lowest-lying state. In Table 1, we have collected the relative energies for the 11 isomers located on the

3 PES and in Figure 1, the geometries of the ground state for each isomer are represented.

As can be seen in Figure 1, at the B3LYP level, the three most stable isomers of [C, Ti, H, N] system are obtained from the interaction of the titanium atom of TiH with the cyano radical, CN. This interaction can take place through the carbon atom, the nitrogen atom, or perpendicular to the C–N bond giving the hydrotitanium cyanide/isocyanide (HTiCN/HTiNC) open chains or the HTi-CN cyclic arrangement, respectively. The ground state is ³A'' for the three isomers. Singlet and quintet states for HTiCN/HTiNC are located higher in energy; about 30 kcal mol⁻¹ and 65 kcal mol⁻¹, respectively (see Table 1). It should be pointed out, that the cyclic structure, HTi-CN, is a true minimum only on the triplet surface. The most stable structure at the B3LYP/aug-cc-pVTZ level is hydrotitanium isocyanide, HTiNC (³A''). Hydrotitanium cyanide, HTiCN (³A'') and the cyclic arrangement are *quasi*-isoenergetic, being located only 4.62 kcal mol⁻¹ and 5.51 kcal mol⁻¹ above HTiNC, respectively.

The next six isomers are obtained by the interaction of the titanium atom with hydrogen cyanide/isocyanide through the terminal N/C atom giving HCNTi/HNCTi, the hydrogen atom giving TiHCN/TiHNC, or the C–N bond giving HC(Ti)N/HN(Ti)C. These cyclic structures that we have obtained via the perpendicular interaction of titanium with the CN unit of either HCN or HNC giving HC(Ti)N and HN(Ti)C, respectively, have a ³A'' ground state and are located 11.1 kcal mol⁻¹ and 35.4 kcal mol⁻¹ above the HTiNC (³A'') isomer at the B3LYP level, respectively. The ground state for the open chain isomers HCNTi and HNCTi is ⁵A'' and they are located 25.6 and 33.2 kcal mol⁻¹ higher in energy than HTiNC (³A'') at the B3LYP level, respectively. For both isomers, the triplet states are located above the quintet ones (around 9 kcal mol⁻¹ at the B3LYP level). The less stable isomers that correspond to the interaction between titanium and either hydrogen cyanide or hydrogen isocyanide at the hydrogen atom giving TiHCN, and TiHNC in their ³Φ ground state are located 44.20 kcal mol⁻¹ and 57.38 kcal mol⁻¹ higher in energy than HTiNC. Two important characteristics were found for the TiHCN/TiHNC (³Φ) isomers. First, they have large H–Ti distances. Second, they have an energetic gap (13.2 kcal mol⁻¹) similar to that found for HCN/HNC isomers (13.5 kcal mol⁻¹ at the B3LYP/aug-cc-pVTZ level of theory). These features indicate the TiHCN/TiHNC isomers can be seen as intermolecular complexes between the Ti atom and HCN/HNC molecules.

The last two isomers located at HCTiN and HNTiC involve the rupture of the CN bond, and are less stable. They are located more than 70 kcal mol⁻¹ above the most stable HTiNC isomer. The ground state is a triplet for both isomers and their corresponding singlet states have not been characterized.

For the seven more stable structures in their ground state, we have carried out additional optimizations at different theoretical levels (see Table 1). The most reliable ones are the CCSD(T) energies computed on the CCSD optimized geometries. The relative energies calculated at the B3LYP level for the three hydrotitanium isomers, HTiCN, HTiNC, and HTi-CN, are very close to that obtained at the CCSD(T). However, for the isomers obtained by interaction of titanium with HCN/HNC, the energies obtained at the B2PLYP level are the most similar to that calculated at the CCSD(T) level. The effect, on the relative energies, of the inclusion of triple excitations at the CCSD level, in general is less than 1 kcal mol⁻¹, with the

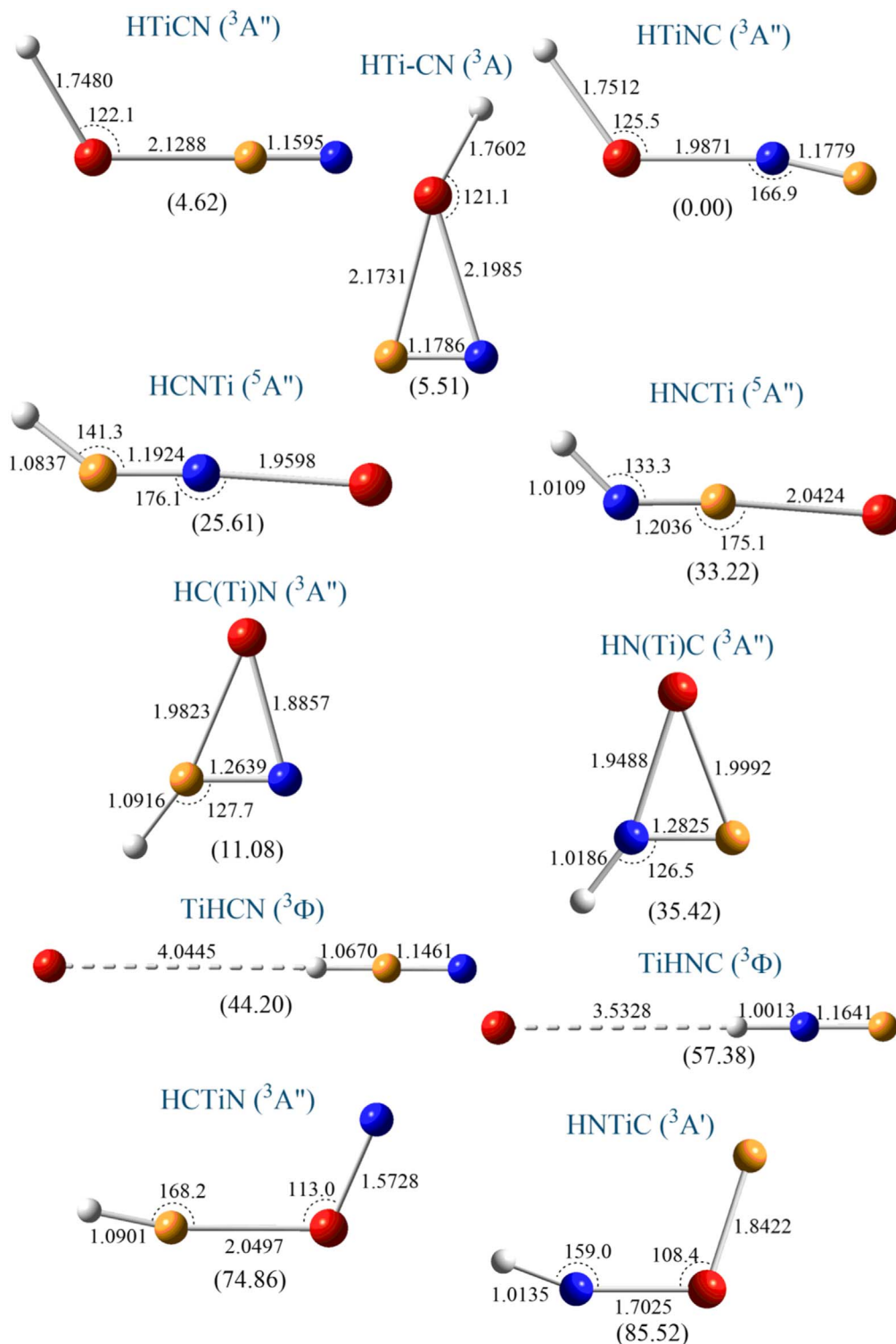


Figure 1. Structure and relative energy (in kcal mol⁻¹) of the lowest-lying states of the different [C, Ti, H, N] isomers at the B3LYP/aug-cc-pVTZ level. Distances are given in angstroms and angles are in degrees.

exception of the HC(Ti)N and HN(Ti)C cyclic structures (see Table 1).

3.2. Hydrotitanium Isomers: HTiCN, HTiNC, and HTi-CN

In this section we will focus on the three most stable isomers of the [C, Ti, H, N] system, which are obtained by interaction

of the titanium atom of HTi with CN, namely HTiCN, HTiNC, and HTi-CN.

The geometrical parameters obtained at different theoretical levels are collected in Table 2. At the MP2 level, the most stable isomer HTiNC is predicted to have a linear structure (³Σ symmetry); however, when we take into account the correlation of core electrons at the MP2 = full level, the geometry is an open chain (³A'' symmetry), this structure is also obtained at

Table 2

Optimized Geometries of Hydrotitanium Cyanide/Isocyanide [C, Ti, H, N] Isomers at Different Levels of Theory in Conjunction with the Aug-cc-pVTZ Basis Set

Isomer		Level						
		MP2	MP2 = full	B2PLYP	CCSD	CCSD(T)	CCSD(T) ^a	Composite
HTiCN (³ A'')	d(H-Ti)	1.7959	1.7827	1.7662	1.8021	1.7979	1.8001	1.7710
	d(Ti-C)	2.2039	2.1846	2.1504	2.1885	2.1856	2.1744	2.1339
	d(C-N)	1.1696	1.1597	1.1677	1.1646	1.1721	1.1689	1.1627
	∠H-Ti-C	141.8	140.3	127.5	136.6	134.9	132.8	129.5
HTiNC (³ A'')	d(H-Ti)	1.8520	1.7483	1.7674	1.8023	1.7985	1.7968	1.7623
	d(Ti-N)	2.1059	1.9895	2.0089	2.0395	2.0353	2.0349	2.0060
	d(N-C)	1.1877	1.185	1.1829	1.1809	1.1883	1.1848	1.1779
	<Ti-N-C	180.0	166.4	162.9	154.4	161.4	161.7	169.9
HTi-CN (³ A'')	<H-Ti-N	180.0	137.8	131.0	141.2	137.1	136.7	131.7
	d(H-Ti)	1.8401	1.7996	1.7838	1.8454	1.8433	1.8428	1.8049
	d(Ti-N)	2.2263	2.2612	2.2399	2.1931	2.2012	2.2013	2.2849
	d(Ti-C)	2.3658	2.1709	2.2088	2.411	2.3646	2.3787	2.1513
	d(N-C)	1.1934	1.1888	1.1831	1.1815	1.1894	1.1857	1.1769
	<H-Ti-C	158.6	169.1	141.4	164.2	163.5	164.3	169.8
	<H-Ti-C-N	80.0	105.3	85.8

Notes. Bond distances are in angstroms and angles are in degrees.^a Optimized geometries at the CCSD(T) level with the basis set aug-cc-pVQZ.

the other levels employed. On the other hand, the cyclic structure HTi-CN has a non-planar geometry at the MP2 and B2PLYP levels, but it is planar at the CCSD levels. In this regard, as is pointed out by DeYonker (2015) for correctly describing transition metal compounds, it is necessary to employ CC theory with post-CCSD(T) additive corrections. Therefore, we predict the geometries of the three isomers at the composite level, which includes relativistic, CV, and completeness of the basis set effects through additive corrections to those calculated at the CCSD(T)/aug-cc-pVQZ level. The general effect of these corrections is a shortening of the bond distances.

The relative energies of the three most stable isomers at different levels of theory are shown in Table 3. In addition, we display the effect of the different contributions on the relative stability in Figure 2. In Table 3, we also include the calculated T1 diagnostic, and the eigenvalues of the total spin-squared operator, S^2 values, of the UHF/aug-cc-pVTZ wave function, which can be used to determine the reliability of single-reference-based results. Spin contamination values are negligible and T1 diagnostics are less than 0.03 (Jiang et al. 2012), therefore single-reference methods are suitable for describing these isomers.

All levels of theory employed predict hydrotitanium isocyanide, HTiNC (³A''), as the most stable isomer (see Table 3). The hydrotitanium cyanide, HTiCN (³A'') and the cyclic isomer, HTi-CN (³A''), are located very close in energy, 3.67 kcal mol⁻¹ and 3.86 kcal mol⁻¹ above HTiNC at the composite level, respectively. We will analyze the relative stability in terms of the different contributions to the energy. In Figure 2, we can see that the inclusion of triple excitations on energy at the CCSD(T)/aug-cc-pVTZ level stabilizes HTiCN over HTiNC. When the size of the basis set is increased (see values TZ, QZ, and CBS), the HTi-CN isomer is slightly stabilized over HTiNC. The addition of CV correlation to the extrapolated CBS energy favors the stability of the HTiCN isomer and disfavors the stability of the cyclic structure HTi-CN with respect to the HTiNC isomer. The inclusion of relativistic effects mainly produces destabilization of HTi-CN. Finally, ZPV corrections (see the composite results) destabilize

Table 3Relative Energies in kcal mol⁻¹ of Hydrotitanium Isomers, HTiCN, HTiNC, and HTi-CN, and Transition States at Different Levels of Theory

Level	HTiC- N (³ A'')	HTiN- C (³ A'')	HTi- CN (³ A'')	TS1 (³ A'')	TS2 (³ A'')
ΔE					
CCSD/aug-cc-pVTZ	4.07	0.00	2.06	5.53	2.68
CCSD(T)/aug-cc-pVTZ	3.66	0.00	2.07
CCSD(T)/aug-cc-pVQZ	3.69	0.00	1.97
CCSD(T)/aug-cc-pVQZ ^a	3.71	0.00	2.03	4.97	2.50
Composite	3.67	0.00	3.86
T1	0.026	0.024	0.020	0.023	0.023
S^2	2.0291	2.0230	2.0064	2.0198	2.0244

Notes. Zero-point vibrational energy (ZPVE) corrections at the CCSD/aug-cc-pVTZ level are included. T1 diagnostic calculated at the CCSD/aug-cc-pVTZ level, and S^2 values of the UHF/aug-cc-pVTZ function are also included.^a Energies calculated on the optimized geometries at the CCSD/aug-cc-pVTZ level.

HTiCN and slightly stabilize HTi-CN over HTiNC. It should be noted that spin-orbit corrections (SOCs) have not been included in the composite procedure. We found similar SOC for HFeCN and HFeNC (Redondo et al. 2016). Given that iron is heavier than titanium, we have not computed the SOC in the titanium isomers because this correction does not change the relative energy.

Previous studies on the analogous systems [C, M, H, N], where M is Fe or Zn (Redondo et al. 2015, 2016), predict that HFeNC is slightly more stable than HFeCN (0.5 kcal mol⁻¹ at the composite level), whereas in the system with Zn HZnNC is located 5.13 kcal mol⁻¹ more stable than HZnCN at the CCSD(T)/aug-cc-pVQZ level. From these results, we can see that the stability of hydro-metal isocyanide decreases with respect to hydro-metal cyanide whenever going from early to late first-row transition metals. Similar trends were found for first-row transition metal cyanides/isocyanides (Rayón et al. 2007).

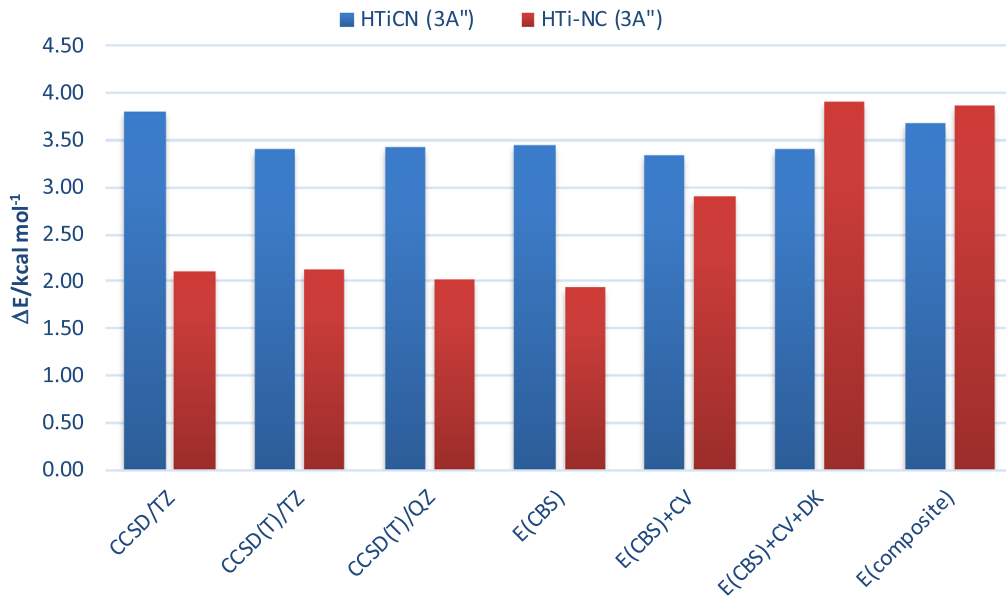


Figure 2. Relative energies, kcal mol^{-1} , of HTiCN and HTi-CN (with the HTiNC as reference) using different additive corrections to the couplet cluster energy in the composite method. A positive value indicates that HTiNC is more stable than HTiCN or HTi-CN.

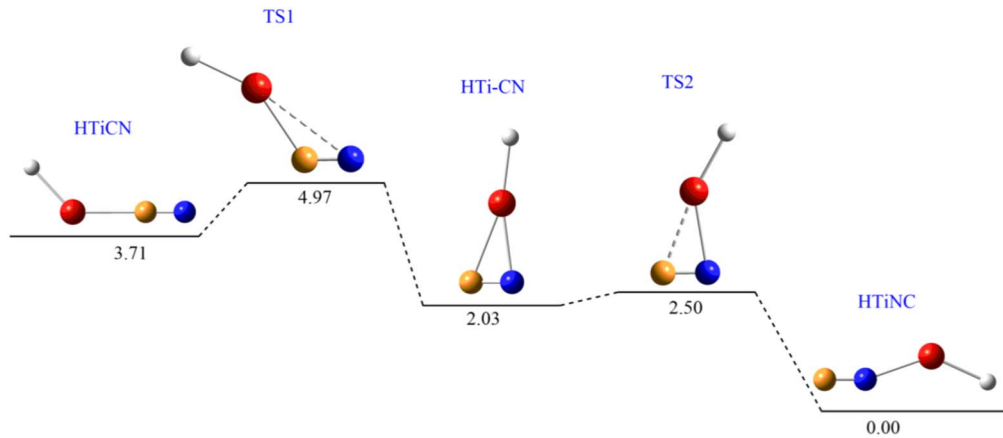


Figure 3. Interconversion barrier between the hydrotitanium isomers, HTiCN, HTiNC, and HTi-CN. Relative energies, in kcal mol^{-1} , are calculated with respect to HTiNC at the CCSD(T)/aug-cc-pVQZ//CCSD/cc-pVTZ level (ZPV energies are included).

Now we will analyze the isomerization processes between the HTiCN, HTiNC, and HTi-CN isomers shown in Figure 3. Relative energies of the transition states at different levels of theory are also included in Table 3. As can be seen in Figure 3, the interconversion between hydrotitanium cyanide, HTiCN, and hydrotitanium isocyanide, HTiNC, takes place through the cyclic structure HTi-CN. The isomerization process of HTiCN into the cyclic structure HTi-CN involves transition state TS1 that is located $1.26 \text{ kcal mol}^{-1}$ ($\sim 630 \text{ K}$) at the CCSD(T)/aug-cc-pVQZ level above HTiCN. This barrier suggests that the interconversion process between these isomers should have a slow rate at the low temperatures of the interstellar medium. Once the cyclic structure is reached, transition state TS2 connects this structure with the most stable isomer HTiNC. TS2 is only located $0.47 \text{ kcal mol}^{-1}$ ($\sim 237 \text{ K}$) at the CCSD(T)/aug-cc-pVQZ level over the cyclic structure. This small barrier shows that HTi-CN can easily isomerize into HTiNC even at low temperatures.

We have also analyzed the stability of these isomers in relation to the dissociation into $\text{TiH} + \text{CN}$. The dissociation energies for HTiCN, HTi-CN, and HTiNC obtained at the CCSD

Table 4
Spectroscopic Parameters for the HTiCN, HTiNC, and HTi-CN Isomers (in MHz)

	HTiCN	HTiNC	HTi-CN
A_e	298198.6	350729.1	54812.8
B_e	3574.4	4103.8	6048.8
C_e	3527.5	4048.9	5452.4
A_0	298198.6	372175.1	55781.4
B_0	3574.4	4122.3	5995.4
C_0	3527.5	4063.7	5388.7
$D_J \times 10^3$	1.162	2.795	6.300
D_{JK}	-0.0749	-1.957	0.171
D_K	396.620	943.324	0.575
$D_1 \times 10^6$	-27.283	-168.541	-591.617
$D_2 \times 10^6$	-2.340	-3.471	-151.239
μ	5.57	4.21	1.41

Note. Equilibrium rotational constants (A_e , B_e , and C_e) and rotational constants for the ground vibrational state (A_0 , B_0 , and C_0) are computed with the composite method and centrifugal distortion parameters in the symmetrically reduced Hamiltonian (D_J , D_{JK} , D_K , d_1 , and d_2) at the B2PLYP/aug-cc-pVTZ level. Dipole moments (μ in Debye) are computed at the CCSD/aug-cc-pVTZ level.

Table 5
Harmonic, ω , and Anharmonic, ν , Vibrational Frequencies (cm^{-1}) and IR Intensities (km mol^{-1}) for the HTiCN, HTiNC, and HTi-CN Isomers

Mode	HTiCN				HTiNC				HTi-CN			
	ω	I_{har}	ν	I_{anhar}	ω	I_{har}	ν	I_{anhar}	ω	I_{har}	ν	I_{anhar}
a' (CN stret.)	2252	37.2	2224	35.5	2118	293.3	2090	275.4	2087	18.0	2062	17.6
a' (TiH stret.)	1597	407.7	1557	381.5	1608	409.9	1551	380.2	1561	390.1	1517	355.3
a' (TiC(N) stret.)	428	187.8	439	114.8	503	183.4	499	162.1	406	83.4	385	19.6
a' (HTiC(N) bend.)	308	127.6	296	158.7	300	169.7	272	188.3	258	276.8	193	322.0
a' (TiCN(NC) bend.)	163	24.5	174	26.2	80	20.3	76	22.2	68	10.1	34i	2.4
a'' (TiCN(NC) bend.)	160	2.4	171	2.5	103	83.8	104	85.1	134	327.5	158	288.5

Note. Harmonic vibrational frequencies are calculated at the CCSD-rw/aug-cc-pVTZ level. Anharmonic contributions are computed at the B2PLYP/aug-cc-pVTZ level.

(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level including ZPVE corrections, are $110.75 \text{ kcal mol}^{-1}$, $112.44 \text{ kcal mol}^{-1}$, and $114.47 \text{ kcal mol}^{-1}$, respectively. The dissociation energy for HTiNC is very close to that obtained for HFeNC ($113.7 \text{ kcal mol}^{-1}$, at the same level of theory Redondo et al. 2016), indicating that both systems present similar stability toward fragmentation.

Based on the previous stability results, the most feasible targets from an experimental point of view are HTiNC, and HTiCN. The cyclic structure, HTi-CN, could easily isomerize into the lowest-lying isomer, HTiNC, and it is expected that this isomer could only be detected at very low temperatures. The relevant spectroscopic parameters to rotational spectroscopy, together with the dipole moments for the hydrotitanium isomers, are given in Table 4. The values of equilibrium rotational constants, A_e , B_e , C_e , were obtained from the bond distances computed at the composite level showed in Table 2. The corresponding constants for the ground vibrational state A_0 , B_0 , C_0 were computed from vibration-rotation coupling constants and degeneracy factors for the vibrational modes from anharmonic vibrational frequencies at the B2PLYP/aug-cc-pVTZ level. We can see in Table 4 that the three isomers have relative high dipole moments, in particular HTiCN and HTiNC (5.57 D and 4.21 D, respectively), that should favor their possible detection by rotational spectroscopy, provided they can be formed in the ISM.

In order to help an eventual detection in the gas phase of hydrotitanium isomers through IR spectroscopy, the predicted harmonic, anharmonic vibrational frequencies, and the corresponding IR intensities, computed at the CCSD-rw/aug-cc-pVTZ level, are collected in Table 5. Harmonic vibrational frequencies are calculated at the CCSD-rw level in order to take into account CV correlation effects in the geometries. The anharmonic contributions are computed at the B2PLYP/aug-cc-pVTZ level using a hybrid model (Barone et al. 2014). The calculated harmonic frequencies are in general slightly higher than the corresponding anharmonic ones and the absolute differences are more important in the largest frequencies corresponding to stretching modes. A positive anharmonic effect (the anharmonic frequencies are larger than the harmonic ones) is found for the a'' bending TiCN(NC) mode in the three isomers and for the stretching TiC and the a' TiCN bending in the isomer HTiCN. Considering IR intensities there are not straightforward variations when passing from the harmonic to the anharmonic approach. The IR spectrum predicted for HTiCN is dominated for the Ti-H and Ti-C stretching and the HTiC bending bands located at 1557 cm^{-1} , 439 cm^{-1} , and 296 cm^{-1} , respectively. For the lowest-lying isomer, HTiNC, all the

normal modes are intense, with the only exception being the a' TiNC bending. Finally, in the cyclic structure HTi-CN the more intense bands are located at 1517 cm^{-1} , 193 cm^{-1} , and 158 cm^{-1} and correspond to the Ti-H stretching, the bending HTi-CN, and the a'' TiCN bending modes respectively. As can be seen in Table 5, when we include anharmonic corrections the isomer HTi-CN has an imaginary frequency, indicating that it is not a true minimum on the corresponding PES. This result also suggests that the most feasible targets from an experimental point of view are HTiNC and HTiCN.

4. Conclusions

We have carried out a theoretical study of the [C, Ti, H, N] isomers, which are species of possible interstellar interest, employing different ab initio and DFT approaches. We have characterized 11 structures on the singlet, triplet, and quintet PES. Six isomers are obtained by the interaction of titanium atom with hydrogen cyanide/isocyanide through: the terminal N/C atom, giving HCNTi/HNCTi, the hydrogen atom, giving TiHCN/TiHNC; and perpendicular to the C-N bond, giving HC(Ti)N/HN(Ti)C. The interaction of the titanium atom of TiH with the cyano radical, CN, through the carbon atom, the nitrogen atom, or perpendicular to the C-N bond gives the hydrotitanium cyanide/isocyanide (HTiCN/HTiNC) open chains and the cyclic arrangement HTi-CN, respectively. Finally, the last two isomers, HCTiN and HNTiC, involving the rupture of the CN bond are less stable. We have found that hydrotitanium isomers, HTiCN, HTiNC, and HTi-CN, in their $^3A''$ state, are the most stable structures and they are located more than 19 kcal mol^{-1} , at the CCSD(T)/aug-cc-pVTZ level, below the rest of isomers.

To obtain accurate structures and relative energies, for the most stable isomers we apply a composite approach that considers the extrapolation to the CBS limit, relativistic, and CV electron correlation corrections at the CC level, including single and double excitations and a perturbative treatment of triple excitations (CCSD(T)). The lowest-lying isomer HTiNC ($^3A''$) is predicted to lie about $3.7 \text{ kcal mol}^{-1}$ and $3.9 \text{ kcal mol}^{-1}$ below both HTiCN ($^3A''$) and the cyclic structure HTi-CN ($^3A''$), respectively. The interconversion between hydrotitanium cyanide, HTiCN, and hydrotitanium isocyanide, HTiNC, takes place through the cyclic structure HTi-CN. The isomerization process of HTiCN into the cyclic structure HTi-CN involves a transition state located $1.26 \text{ kcal mol}^{-1}$ ($\sim 630 \text{ K}$) at the CCSD(T)/aug-cc-pVQZ level above HTiCN. The transition state that connects the cyclic structure, HTi-CN, with the most stable isomer HTiNC, is only located $0.47 \text{ kcal mol}^{-1}$ ($\sim 237 \text{ K}$) at the CCSD(T)/aug-cc-

pVQZ level over the cyclic structure. This small barrier shows that HTi-CN can easily isomerize into HTiNC even at low temperatures.

The relevant spectroscopic parameters to rotational spectroscopy, harmonic and anharmonic frequencies, and IR intensities are reported for the hydrotitanium isomers. This information could help in their laboratory or astronomical detection by radioastronomy or IR spectroscopy.

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