Structure and spectroscopic properties of neutral and cationic tetratomic [C,H,N,Zn] isomers: A theoretical study

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The structure and spectroscopic parameters of the most relevant [C,H,N,Zn] isomers have been studied employing high-level quantum chemical methods. For each isomer, we provide predictions for their molecular structure, thermodynamic stabilities as well as vibrational and rotational spectroscopic parameters which could eventually help in their experimental detection. In addition, we have carried out a detailed study of the bonding situations by means of a topological analysis of the electron density in the framework of the Bader's quantum theory of atoms in molecules. The analysis of the relative stabilities and spectroscopic parameters suggests two linear isomers of the neutral [C,H,N,Zn] composition, namely, cyanidehydridezinc HZnCN ($^1\Sigma$) and hydrideisocyanidezinc HZnNC ($^1\Sigma$), as possible candidates for experimental detections. For the cationic $[C,H,N,Zn]^+$ composition, the most stable isomers are the ion-molecule complexes arising from the direct interaction of the zinc cation with either the nitrogen or carbon atom of either hydrogen cyanide or hydrogen isocyanide, namely, $HCNZn^+$ ($^2\Sigma$) and $HCNZn^+$ ($^2\Sigma$). © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4919879]

I. INTRODUCTION

The study of metal-cyanide compounds has received growing attention in recent years. The cyanide unit is one of the most interesting ligands in chemistry. Cyanide units can be linked together to give novel framework materials with important applications in a number of fields including supramolecular chemistry, crystal engineering, and hydrogen storage.[1–4] Besides, the cyanide group shows curious properties such as a quasi-isotropic charge distribution in such a way that some metal cyanides MCN (M = Na and K) are polytopic systems, where the M^+ cation orbits the CN^- ligand, while other metals show linear cyanide (MCN) or isocyanide (MNC) geometries.[5–7] On the other hand, cyanogen (CN) is the simplest molecule including carbon and nitrogen, essential elements in the chemistry of life.

Besides this intrinsic interest, the observation of several metal cyanides and isocyanides in space, in the past few years, has attracted additional attention to these systems. To date, MgCN, MgNC, AlNC, NaCN, SiCN, SiNC, and FeCN have been detected in space.[8–16] In particular, magnesium cyanide and isocyanide molecules were observed in relatively dense and hot environments.[8–11] These conditions favour the formation of molecules that are not even observed in cold interstellar gas clouds. In this context, theoretical studies have suggested the radiative association of Mg^+ with HCN/HNC, followed by the dissociative recombination of hydromagnesium cyanide/isocyanide cation with an electron as a possible source of interstellar MgCN and MgNC.[17] Thus hydro-cyanides and -isocyanides could play an important role in the synthesis of metal cyanides.

In contrast to metal-cyanide complexes, few investigations have been devoted to the study of hydrides of the metal cyanides. Recently, a high-level *ab initio* study has been carried out on tetratomic structural isomers comprising H, C, N, and Mg atoms.[18] In this study, the HMgNC compound was identified as being the most stable isomer. The second most stable species, HMgCN, was found to be only 2.44 kcal/mol (at the coupled-cluster with single and double excitations and a perturbative inclusion of triple excitations with the augmented-correlation-consistent polarized valence triple-zeta basis set (CCSD(T))/aug-cc-pVQZ level) more energetic than the former. A transition state connecting the two minima was located 6.46 kcal/mol higher in energy than the most stable isomer. Thus, the two linear molecules, HMgNC and HMgCN, could be probable candidates for future detections at microwave or IR wavelengths.[18] Almost simultaneously to that theoretical study, the detection of hydromagnesium isocyanide, HMgNC, in both the laboratory and in the carbon rich evolved star intrinsic reaction coordinate (IRC)+10216 has been reported.[19]

Transition metals such as iron, manganese, nickel, or zinc are relatively abundant in space.[20] Consequently, one should expect that hydro-cyanides or -isocyanides containing transition metals could be good candidates for detection in the interstellar medium. Zinc cyanide, ZnCN, and its hydride, HZnCN, were synthesised in the gas phase.[21,22] Their structures were also characterized using pulsed Fourier transform microwave (FTMW) techniques.[21,22]

Recently, we have carried out a theoretical study of cyanides and isocyanides of first-row transition metals M(CN) (M = Sc–Zn) providing predictions for their molecular

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properties.[23] Regarding zinc compounds, we found that the cyanide isomer ZnCN was 5.11 kcal/mol (at the CCSD(T) level) more stable than the corresponding isocyanide arrangement in agreement with the experimental evidence.[21,22] Concerning [C,H,N,Zn] compounds, the only theoretical work, to date, has been a Modified Neglect of Diatomic Overlap (MNDO) study on the structures of $[ZnNCH]^+$ ions.[24] However, the neutral analogous were not investigated. It should be noted in this point that there are also two theoretical works devoted to determine the molecular and electronic structures of zinc carbenes and their positive and dipositive ions.[25,26]

In this study, we present a theoretical analysis of neutral and cationic tetratomic [C,H,N,Zn] isomers making use of accurate quantum chemistry approaches. Our main goal is to provide information about thermodynamic stabilities as well as electronic, vibrational, and rotational spectroscopic parameters. In addition, we will characterize the nature of the bonds in the different isomers through the topological analysis of the electron density in the framework of the Bader's Quantum Theory of Atoms in Molecules (QTAIM).[27]

The paper is structured as follows: In Sec. II, we introduce the computational methods used in our study. Section III presents, first, the thermochemistry, structural aspects, spectroscopic parameters, and analysis of the bonding for the neutral [C,H,N,Zn] compounds and second, the corresponding cationic compounds will be analyzed. In both cases, a special attention will be given to the most stable isomers. In Sec. IV, we will summarize the main findings of our study.

II. COMPUTATIONAL METHODS

Structural parameters for the [C,H,N,Zn] and $[C,H,N,Zn]^+$ compounds have been obtained by using different theoretical methodologies. Preliminary optimized geometries were obtained at the Density Functional Theory (DFT) level. In particular, we have first used the B3LYP (Becke 3-parameter Lee-Yang-Parr) exchange-correlation functional[28,29] which includes the Lee-Yang-Parr[30] correlation functional in conjunction with a hybrid exchange functional initially proposed by Becke.[31] Within the context of the DFT, we have, second, employed the M06-HF[32,33] functional that has full Hartree-Fock exchange, thereby eliminating long-range self-interaction error, but also has overall average performance as good as or better than B3LYP. Geometries were also optimized employing different *ab initio* methods: second order Møller–Plesset (MP2),[34] quadratic configuration interaction including single and double (QCISD) excitations,[35] CCSD, and CCSD(T).[36] In the CCSD(T) calculations, we checked the T1 diagnostic.[37] In all cases, it was found below the 0.04 value.[38] Thus, these values do not suggest a multireference character.

Concerning basis sets, we have used the Dunning's aug-cc-pVTZ (correlation-consistent polarized valence triple-zeta including diffuse functions) basis set.[39,40] In coupled cluster calculations, we have also employed the aug-cc-pVQZ basis set[39,40] which has a quadruple-zeta character and includes both diffuse and polarization functions.

Harmonic vibrational frequencies were computed within the coupled cluster theory (CCSD level) with aug-cc-pVTZ basis sets. The nature of the compounds has been determined by the number of negative eigenvalues of the analytical Hessian (zero in minimum and one in first-order saddle points). The connection between transition-state structures and minima has been checked through the IRC[41] formalism. In order to aid in a possible experimental detection by IR spectroscopy, anharmonic vibrational frequencies and IR intensities have been predicted at CCSD/aug-cc-pVTZ level of theory by means of the vibrational second-order perturbation theory (VPT2)[42] as implemented in the CFOUR program package.[43] The VPT2 calculations imply the evaluation of the full cubic force field together with the semidiagonal part of the quartic force field, which are usually enough for obtaining anharmonic corrections to the vibrational frequencies. The cubic force field calculations also serve for estimating vibration-rotation interaction constants, and therefore to correct rotational constants including vibrational effects.

Equilibrium spectroscopic parameters were obtained at the CCSD(T)/aug-cc-pVQZ level. In order to obtain an estimate of B_0 rotational constants, vibration-rotation interaction constants were estimated using second-order perturbation theory at the MP2/aug-cc-pVTZ level.

Electronic energies were computed at the same levels of calculation than those used in geometry optimizations. In addition, for comparative purposes, single point calculations on the CCSD/aug-cc-pVTZ geometry at the CCSD(T)/aug-cc-pVQZ level were also performed.

In all correlated computations, the valence electrons of the carbon and nitrogen atoms and the 4s and 3d electrons of zinc were included. Quantum calculations were carried out with the GAUSSIAN 09 package of programs.[44]

The nature of the bonding for the most stable [C,H,N,Zn] and $[C,H,N,Zn]^+$ isomers was characterized through the topological analysis of the electronic density in the framework of the Bader's QTAIM.[27] In this context, two limiting types of interactions can be identified, namely, shared and closed-shell interactions.[45] In shared interactions, typical of covalent compounds, the nuclei are bound as a consequence of the lowering of the potential energy associated with the concentration of electronic charge shared between the nuclei; this is reflected in relatively large values of $\rho(r)$ and negative values of the Laplacian, $\nabla^2\rho(r)$, at the critical point. The second limiting type of atomic interaction is that occurring between closed-shell systems, such as those found in ionic bonds or van der Waals molecules, for instance. In these interactions, $\rho(r)$ is relatively low in value and the Laplacian, $\nabla^2\rho(r)$, is positive. Nevertheless, between these limiting types, there is a whole spectrum of intermediate interactions. It should be noted that for elements with more than half-filled valence shells, a lack of the expected density accumulations along the bonds can be found.[46,47] Typical examples are the F–F bond in the F_2 molecule and the O–O bond in H_2O_2.

Another useful property to characterize the degree of covalence of a bond is the total energy density $H(r)$. It is defined as the sum of the potential energy density $V(r)$ and the gradient kinetic energy density $G(r)$ at a critical point. In covalent interactions, $H(r)$ is negative in value and the system is stabilized by the accumulation of electronic charge in the internuclear region.[48] If the value of $H(r)$ is positive, accumulation of charge density in the region between the

nuclei leads to a destabilization of the system, which is the typical characteristic of ionic interactions and van der Waals systems.[45] The covalent character of an interaction can also be quantitatively analyzed by taking into account the $|V(r)|/G(r)$ ratio. In covalent interactions, the value of this relationship is greater than 2. It is smaller than 1 for non-covalent interactions and between 1 and 2 for partially covalent bonds.

Total electron densities were computed at CCSD/aug-cc-pVTZ. In all calculations, we assessed the accuracy of the integration over the atomic basin (Ω) by the magnitude of the corresponding Lagrangian function $L(\Omega)$ ($-(1/4)$ times the atomic integral of the Laplacian of the electron density), which, in all cases, was lower than 10^{-4} a.u. The topological analysis of electron charge density was performed for each neutral and cationic isomers using the Keith's AIMAll package[49] including standard thresholds.

III. RESULTS AND DISCUSSION

We have searched for different possible [C,H,N,Zn] and $[C,H,N,Zn]^+$ isomers with both cyanide and isocyanide arrangements. In particular, we have included in this study open-chain (linear and bent) structures with the zinc atom located at one end of the chain and in a middle position. It should be also noted that we have not found stable cyclic (three-member ring) structures with the zinc atom bonded to the carbon and nitrogen atoms.

A. [C,H,N,Zn] isomers

1. Energetics

In Table I, we present relative (with respect to the most stable isomer) energies at different levels of theory for the neutral [C,H,N,Zn] isomers. In addition, in Figure 1, we show the structures of the neutral isomers considered in the present study. In this figure, we have included the B3LYP/aug-cc-pVTZ relative energies.

For each isomer, we have considered singlet and triplet states; however, in all cases, the triplet isomers were clearly higher in energy than the corresponding singlet ones (with the only exception of the two isomers that derivate from the insertion of the zinc atom between the carbon-nitrogen bond) and they will not be considered in our study. Thus, for instance, both triplet HZnCN and HZnNC are 113 kcal/mol and 119 kcal/mol (at the B3LYP/aug-cc-pVTZ level of theory), respectively, above the corresponding singlet HZnCN and HZnNC isomers.

Our preliminary B3LYP calculations showed that the most stable isomer of the [C,H,N,Zn] composition was cyanidehydridezinc, HZnCN ($^1\Sigma$ state). It should be noted in this point, as we already mentioned in the Introduction, that this isomer has been characterized experimentally using rotational spectroscopy.[21] The corresponding isocyanide counterpart hydrideisocyanidezinc HZnNC ($^1\Sigma$) is located just 4.89 kcal/mol higher in energy at the B3LYP level. These isomers can be seen as the result of the insertion of zinc atom into either the H–C or H–N bonds of either hydrogen cyanide or hydrogen isocyanide. The two isomers that correspond to the interaction between zinc and either hydrogen cyanide or hydrogen isocyanide at the hydrogen atom, H-type isomers, namely, (hydrogen cyanide-κH)zinc, ZnHCN ($^1\Sigma$ state), and (hydrogen isocyanide-κH)zinc, ZnHNC ($^1\Sigma$ state), are located 4.83 kcal/mol and 18.14 kcal/mol higher in energy than HZnCN. In a similar way, we have considered the intermolecular complexes that arise from the interaction between the zinc atom and either HCN or HNC at either the nitrogen or carbon ends, N/C type isomers, namely, (hydrogen cyanide-κN)zinc, HCNZn ($^1A'$), and (hydrogen isocyanide-κC)zinc, HNCZn ($^1A'$). These two isomers are located 4.85 and 18.38 kcal/mol, respectively, higher in energy than HZnCN. It should be noted that the energetic gaps between the intramolecular complexes ZnHCN/ZnHNC (13.31 kcal/mol) and HCNZn/HNCZn (13.53 kcal/mol) are attributable to the energy difference between HCN and HNC (13.52 kcal/mol at the B3LYP/aug-cc-pVTZ level of theory). Finally, we have considered the two isomers that derivate from the insertion of the zinc atom between the carbon-nitrogen bond of either HCN or HNC, namely, hydrogencarbidenitridezinc, HCZnN ($^3\Delta$), and carbidehydrogennitridezinc, HNZnC ($^3A'$). These compounds have triplet ground states and are, as expected, by far less stable than HZnCN (155.12 kcal/mol and 156.96 kcal/mol, respectively).

Just focusing on the six most stable isomers, we can infer, from Table I, that regardless of the level of calculation, the most stable isomer of the [C,H,N,Zn] composition is found to be cyanidehydridezinc. Hydrideisocyanidezinc is located 5.13 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) higher in energy. Therefore, HZnCN and HZnNC will be the primary targets for experimental observation. Following in energy are the intermolecular complexes that

TABLE I. Relative energies in kcal/mol of the different [C,H,N,Zn] isomers at different levels of theory. ZPVE corrections are included.

	Isomer					
Level	HZnCN	HZnNC	ZnHCN	ZnHNC	HCNZn	HNCZn
B3LYP/aug-cc-pVTZ	0.0	4.89	4.83	18.14	4.85	18.38
M06-HF/aug-cc-pVTZ	0.0	1.95	19.63	30.73	19.23	30.49
MP2/aug-cc-pVTZ	0.0	8.13	12.18	29.37	12.21	29.98
QCISD/aug-cc-pVTZ	0.0	4.48	8.27	22.15	8.30	22.38
CCSD/aug-cc-pVTZ	0.0	4.59	8.07	22.02	8.10	22.24
CCSD(T)/aug-cc-pVTZ	0.0	5.23				
CCSD(T)/aug-cc-pVQZ	0.0	5.13				
CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ	0.0	5.13	9.03	23.22	9.04	23.45

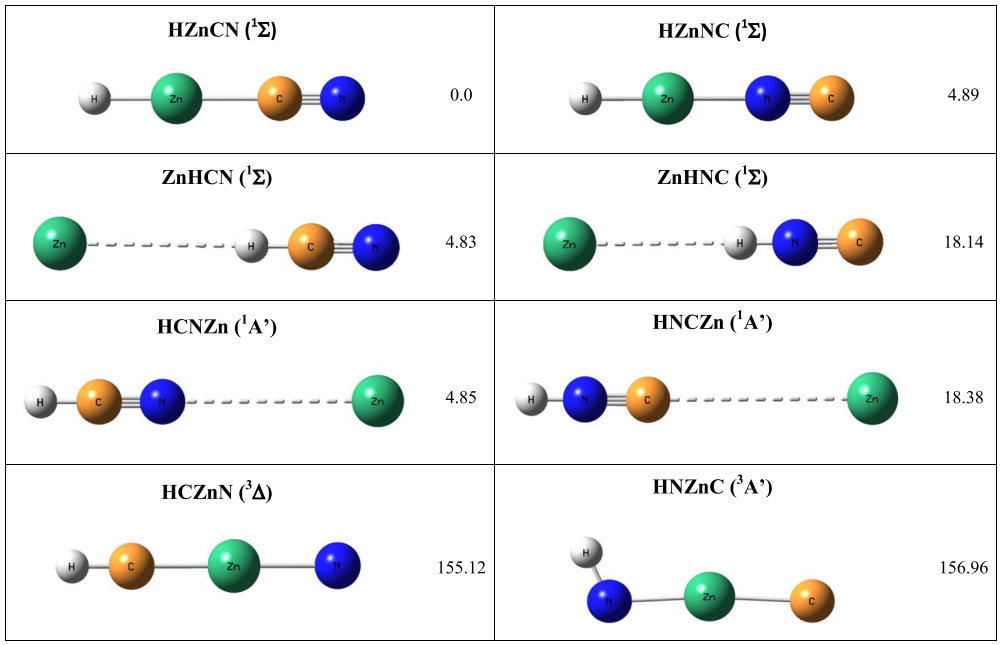

FIG. 1. Relative energies (in kcal/mol) for the [C,H,N,Zn] isomers calculated at the B3LYP/aug-cc-pVTZ level (Zero-point Vibrational Energy (ZPVE) corrections are included).

arise from the interaction between the zinc atom and hydrogen cyanide at either the hydrogen (ZnHCN) or nitrogen (HCNZn) atoms. These isomers are found nearly isoenergetic, especially at the most reliable levels of theory, and are located approximately 9 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) above HZnCN. Finally, the less stable isomers are the corresponding isocyanide derivatives of zinc, namely, ZnHNC and HNCZn which are again almost isoenergetic and lie around 23 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) above cyanidehydridezinc.

In general, a good agreement is observed for the stability order of isomers provided by the different methodologies employed in the present work. In particular, CCSD(T)/aug-cc-pVQZ level predicts identical relative energies than the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level. The MP2, QCISD, CCSD, and CCSD(T) results suggest that the stability of the [C,H,N,Zn] compounds follows the order: HZnCN > HZnNC > ZnHCN ≈ HCNZn > ZnHNC ≈ HNCZn. However, at B3LYP level, hydrideisocyanidezinc and the intermolecular complexes that derive from the interaction between the zinc atom and hydrogen cyanide (ZnHCN and HCNZn) are almost isoenergetic. The M06-HF stability order is similar to the CCSD(T) one, although relative energies differ quantitatively. These results suggest that high-level methodologies, rather than DFT, should be used for predicting relative stabilities in this type of compounds.

Let us now briefly make a comment on the possible interconversion processes between isomers. The transition states for the different isomerization processes between isomers, namely, HZnNC → HZnCN, ZnHCN → HZnCN, and ZnHNC → HZnNC are shown in Figure 2. The isomerization barrier for the HZnNC → HZnCN reaction is estimated to be 6.41 kcal/mol (at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ). This small barrier suggests a relatively low degree of covalency (see Table VI *vide infra*) in the metal-cyanide/

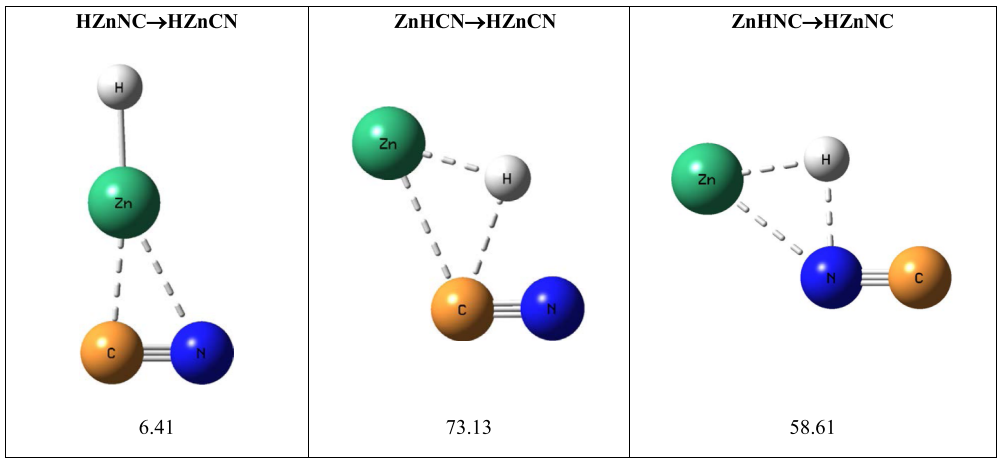

FIG. 2. Transition states corresponding to the different isomerization processes between isomers. Isomerization barriers are given in kcal/mol.

TABLE II. Dissociation energies calculated at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ.

Process	ΔE (kcal/mol)
HZnCN → HZn + CN	114.06
HZnNC → HZn + CN	108.93
ZnHCN → Zn + HCN	0.36
ZnHNC → Zn + HNC	0.63
HCNZn → Zn + HCN	0.35
HNCZn → Zn + HNC	0.40

isocyanide bonds.[50,51] On the other hand, as expected, the isomerization barriers corresponding to insertion of the zinc atom into the H–C/N bonds in hydrogen cyanide/isocyanide are rather high (73.13 kcal/mol for the ZnHCN → HZnCN isomerization and 58.61 kcal/mol for the ZnHNC → HZnNC one at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level of theory). Therefore, ZnHCN and ZnHNC intermolecular complexes could not be considered as possible precursors for HZnCN and HZnNC molecules because their respective isomerization barriers are very high.

In order to analyze the stability of the isomers, we have also computed dissociation energies. For the most stable isomers, the dissociation energy is the energy associated to the HZn(CN) → HZn + CN process. Whereas for the intermolecular complexes, this quantity corresponds to the energy involved in either ZnH(CN) → Zn + H(CN) or H(CN)Zn → Zn + H(CN) process. The results obtained at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level including ZPE corrections are shown in Table II. It is readily seen that both cyanidehydridezinc and hydrideisocyanidezinc are stable toward fragmentation into HZn + CN moieties (dissociation energies are 114 and 109 kcal/mol, respectively). Therefore, as we already mentioned, it is expected that HZnCN and HZnNC could be reasonable experimental targets. On the opposite, the intermolecular complexes, ZnHCN, ZnHNC, HCNZn, and HNCZn, exhibit extremely low dissociation energies; thus, as expected, they will easily dissociate to give the zinc atom and either hydrogen cyanide or hydrogen isocyanide.

2. Structure

The geometrical parameters for the [C,H,N,Zn] isomers, corresponding to minima on the singlet potential energy surface are shown in Table III. Because HZnCN and HZnNC are the primary targets for experimental observation, their bond lengths have been refined employing higher-level theoretical methods. Extrapolated values have been obtained employing CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ bond lengths. As it can be seen, the agreement between the geometrical parameters computed with the different methodologies is rather good. Just regarding the most stable isomer, HZnCN, it can be noted that its CCSD(T) geometrical parameters are in reasonable agreement with the available experimental measures from Fourier transform microwave rotational spectroscopy.[21] In Table III, r_0 stands for the bond length obtained directly from a least-squares fit to the moments of inertia, r_s is calculated using Kraitchman's equations and accounts in part for the zero-point vibrational effects,[52,53] and the $r_m^{(1)}$ bond lengths were computed by the method developed by

TABLE III. Optimized geometries of the different [C,H,N,Zn] isomers at different levels of theory in conjunction with the aug-cc-pVTZ basis set. Bond distances are given in angstroms and angles in degrees.

		Level								Experimental[a]		
Isomer		B3LYP	M06-HF	MP2	QCISD	CCSD	CCSD(T)	CCSD(T)[b]	CCSD(T)[c]	r_0	r_s	$r_m^{(1)}$
	d(H–Zn)	1.519	1.5489	1.4975	1.5193	1.52	1.5177	1.5173	1.5170	1.4965(13)	1.4972	1.4950(3)
HZnCN ($^1\Sigma$)	d(Zn–C)	1.9149	1.9504	1.8881	1.9151	1.9163	1.9114	1.9083	1.9060	1.9014(37)	1.8994	1.8966(6)
	d(C–N)	1.1546	1.1411	1.1764	1.1617	1.1606	1.1686	1.1651	1.1625	1.1504(54)	1.1476	1.1459(6)
	d(H–Zn)	1.5095	1.542	1.489	1.5114	1.5122	1.5108	1.5105	1.5103			
HZnNC ($^1\Sigma$)	d(Zn–N)	1.8353	1.8656	1.8172	1.8326	1.8342	1.8325	1.8293	1.8270			
	d(N–C)	1.1722	1.161	1.1857	1.1778	1.1761	1.1836	1.1802	1.1777			
	d(Zn–H)	3.5255	3.4628	3.0846	3.4127	3.4212						
ZnHCN ($^1\Sigma$)	d(H–C)	1.0665	1.0658	1.0664	1.066	1.0658						
	d(C–N)	1.1461	1.1331	1.1674	1.154	1.1527						
	d(Zn–H)	3.0346	2.9772	2.8005	3.082	3.0889						
ZnHNC ($^1\Sigma$)	d(H–N)	1.0001	1.0018	1.0018	0.9971	0.9971						
	d(N–C)	1.1642	1.1537	1.1771	1.1702	1.1685						
	d(Zn–N)	5.9701	4.0566	3.5697	3.9229	3.9303						
HCNZn($^1A'$)	d(N–C)	1.146	1.1333	1.1674	1.1538	1.1526						
	d(C–H)	1.0656	1.0653	1.0648	1.0656	1.0654						
	<Zn–N–C	174.7	177.8	129.4	180.	180.						
	d(Zn–C)	7.0733	4.546	3.883	4.1789	4.1897						
HNCZn($^1A'$)	d(C–N)	1.1644	1.154	1.1767	1.1701	1.1684						
	d(N–H)	0.9969	0.9982	0.9978	0.9954	0.9953						
	<Zn–C–N	177.0	180.	179.8	179.5	179.6						

[a]Reference 21.
[b]aug-cc-pVQZ basis set.
[c]Extrapolated.

TABLE IV. Rotational constants, in megahertz, for HZnCN and HZnNC.

	HZnCN ($^1\Sigma$)		HZnNC ($^1\Sigma$)	
Level	B_e/MHz	B_o/MHz	B_e/MHz	B_o/MHz
CCSD/aug-cc-pVTZ	3795.7	3796.0	4275.8	4286.4
CCSD(T)/aug-cc-pVTZ	3794.2	3794.5	4266.3	4276.9
CCSD(T)/aug-cc-pVQZ	3809.4	3809.7	4283.6	4294.2
CCSD(T)[a]	3820.3	3820.6	4296.2	4306.8
Experimental[b]		3859.1758(12)		

[a]Extrapolated.
[b]Reference 21.

Watson *et al.*[54] and are believed to be closer to the equilibrium structure than the r_s or r_0 geometries. Our CCSD(T) predictions on interatomic distances are slightly larger (1.49% in d(H–Zn), 0.62% in d(Zn–C), and 1.68% in d(C–N)) than those reported experimentally. However, it should be noted in this point that the flat bending in cyanides may lead to the prediction of somewhat short C–N distances from the experimental data.[55–60]

Finally, as it can be inferred from Table III, the C–N bond distances in isomers with a cyanide arrangement are slightly shorter than that in cyanogen (1.1705 Å at CCSD(T)/aug-cc-pVQZ level). And the opposite is true for the corresponding isomers with an isocyanide arrangement. Therefore, it seems from the geometrical parameters that bonding to the CN moiety of a zinc atom through the carbon atom slightly reinforces the C–N bond, whereas it is slightly weakened if the bonding occurs through the nitrogen atom. This effect was also found on cyanides and isocyanides of first-row transition metals.[23]

3. Spectroscopic parameters

Table IV lists the most relevant spectroscopic parameters to the rotational spectroscopy of cyanidehydridezinc and hydrideisocyanidezinc. The values of equilibrium rotational constants, B_e, were obtained from the bond distances showed in Table III and the corresponding constants for the ground vibrational state B_0, were computed from vibration-rotation coupling constants and degeneracy factors for the vibrational modes from anharmonic vibrational frequencies. The differences between B_0 and B_e rotational constants are on the order of 0.275 MHz (HZnCN) and 0.55 MHz (HZnNC). In cyanidehydridezinc, the experimental value for the rotational constant,[17] 3859.1758(12) MHz, matches reasonably well with that predicted theoretically at the best level of calculation (3809.68 MHz).

The CCSD/aug-cc-pVTZ harmonic and anharmonic vibrational frequencies for cyanidehydridezinc and hydrideisocyanidezinc are given in Table V. In HZnCN, the π HZnC bending mode is the most intense in IR. The HZn stretching mode also gives rise to a strong IR absorption band. However, in the hydrideisocyanidezinc isomer, the most intense band corresponds to the σ CN stretching mode and the π HZnN bending mode presents also a high intensity band. As expected, the IR intensities of the frequencies associated to the C–N stretching mode for HZnCN and HZnNC are clearly different being the IR band for HZnNC much stronger than that for the HZnCN compound. These discrepancies arise from the different natures of the CN bond in HZnCN and HZnNC.

If we compare harmonic and anharmonic frequencies, we observe that, in general, harmonic frequencies are slightly higher than the corresponding anharmonic ones and the absolute differences are more important in the stretching frequencies than in the bending ones. The only exception is the negative anharmonicity found in the σ ZnN stretching mode in HZnNC. Similar results have been reported for the SiC stretching mode[61] in SiC_4 and in σ MgN and σ MgC stretching modes[18] in HMgNC and HMgCN, respectively. In both isomers, the higher difference between harmonic and anharmonic frequencies corresponds to the σ HZn stretching mode (77 cm^{-1} and 72 cm^{-1} in HZnCN and HZnNC, respectively.)

4. Bonding situations

Let us make now a brief discussion on the nature of the bond for the [C,H,N,Zn] isomers. Table VI collects the main results of the QTAIM analysis for the neutral isomers. For

TABLE V. CCSD/aug-cc-pVTZ harmonic and anharmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of the HZnCN and HZnNC isomers.

HZnCN					HZnNC				
	Harmonic		Anharmonic			Harmonic		Anharmonic	
Symmetry	ν	I	ν	I	Symmetry	ν	I	ν	I
σ CN stretching	2266	25.4	2240	25.6	σ CN stretching	2163	264.3	2135	253.7
σ HZn stretching	2008	84.7	1931	82.4	σ HZn stretching	2027	61.6	1955	62.1
π HZnC bending	475	105.2	462	103.4	σ ZnN stretching	521	56.0	523	56.7
σ ZnC stretching	468	39.3	459	14.0	π HZnN bending	466	112.2	456	109.8
π ZnCN bending	215	11.1	207	10.3	π ZnNC bending	135	3.1	127	2.6

TABLE VI. Local topological properties (in a.u.) of the electronic charge density distribution calculated at the position of the bond critical points for the different [C,H,N,Zn] species.[a]

Species	Bond	$\rho(r)$	$\nabla^2\rho(r)$	$\lvert V(r)\rvert/G(r)$	$H(r) = -K$
	Zn–H	0.125	0.111	1.727	−0.0735
HZnCN	Zn–C	0.117	0.298	1.404	−0.0505
	C–N	0.487	−0.153	2.042	−0.9424
	Zn–H	0.127	0.104	1.745	−0.0760
HZnNC	Zn–N	0.127	0.538	1.281	−0.0526
	C–N	0.460	−0.361	2.116	−0.8686
	Zn–C	0.002	0.004	0.664	0.0003
HNCZn	C–N	0.443	0.039	1.988	−0.8173
	N–H	0.344	−2.328	12.492	−0.6374
	Zn–N	0.002	0.005	0.727	0.0003
HCNZn	C–N	0.487	0.017	1.995	−0.9324
	C–H	0.298	−1.283	9.906	−0.3612
	Zn–H	0.002	0.005	0.766	0.0003
ZnHCN	C–H	0.298	−1.281	9.917	−0.3607
	C–N	0.486	0.014	1.996	−0.9309
	Zn–H	0.004	0.009	0.846	0.0003
ZnHNC	N–H	0.342	−2.319	12.497	−0.6350
	C–N	0.444	0.039	1.988	−0.8180
CN	C–N	0.434	0.569	1.848	−0.9393
HZn	Zn–H	0.101	0.119	1.627	−0.0501
HCN	C–N	0.486	0.018	1.995	−0.9312
	C–H	0.298	−1.284	9.878	−0.3616
HNC	C–N	0.443	0.034	1.989	−0.8170
	N–H	0.344	−2.326	12.454	−0.6372

[a]The electronic charge density [$\rho(r)$], the Laplacian [$\nabla^2\rho(r)$], the relationship between the potential energy density [$V(r)$] and the lagrangian form of kinetic energy density [$G(r)$], and the total energy density, [$H(r)$].

comparative purposes, we have included in the table the local topological properties of the electronic charge distribution for the CN and ZnH moieties as well as for HCN and HNC. The corresponding contour maps of the Laplacian of electron density, besides molecular graphs of electron density, are shown in Figure S1 of the supplementary material.[62]

For the most stable isomers, namely, cyanidehydridezinc and hydrideisocyanidezinc, the local topological properties of the carbon-nitrogen bond critical points (BCPs) are indicative of shared interactions: large values of electron density, negatives values of its Laplacian, |V(r)|/G(r) ratios greater than 2, and negative values of the total energy densities H(r). Zinc-carbon, zinc-nitrogen, and zinc-hydrogen interactions have moderate values of ρ(r) and slightly negative values of H(r); however, the Laplacian at these BCPs is positive and the |V(r)|/G(r) ratios are between one and two. Thus, these binding can be classified as partially covalent closed shell interactions.[60]

TABLE VII. Relative energies in kcal/mol of the different $[C,H,N,Zn]^+$ isomers at different levels of theory. ZPVE corrections are included.

	Isomer			
Level	$HCNZn^+$	$HNCZn^+$	$HZnCN^+$	$HZnNC^+$
B3LYP/aug-cc-pVTZ	0.0	10.36	91.70	74.40
M06-HF/aug-cc-pVTZ	0.0	11.02		
MP2/aug-cc-pVTZ	0.0	12.49		
QCISD/aug-cc-pVTZ	0.0	11.56		
CCSD/aug-cc-pVTZ	0.0	13.77		
CCSD(T)/aug-cc-pVTZ	0.0	13.59		
CCSD(T)/aug-cc-pVQZ	0.0	13.47		
CCSD(T)/aug-cc-pVQZ// CCSD/aug-cc-pVTZ	0.0	13.49		

As we above mentioned the H-type: ZnHCN and ZnHNC and N/C type: HCNZn and HNCZn, intermolecular complexes arise from the interaction between the zinc atom and either HCN and HNC at hydrogen or nitrogen/carbon ends. Thus, as expected, the topological characteristics of the carbon-nitrogen, carbon-hydrogen, and nitrogen-hydrogen bonds are identical to those found for isolated HCN and HNC molecules (see Table VI). On the other hand, all the BCPs involving the zinc atom, namely, the zinc-nitrogen, zinc-carbon, or zinc-hydrogen links show characteristics typical of van der Waals interactions:[63] extremely low values of the electronic charge density, slightly positive values of its Laplacian, the |V(r)|/G(r) ratios are lesser than one, and the total energy densities have slightly positive values.

It should be noted that the bond critical point data for carbon-nitrogen bonds reflect the general trend pointed out in the preceding comments on the molecular structure of these isomers. The electronic densities for C–N bond critical points are always slightly larger for cyanides arrangements than for those of corresponding isocyanides counterparts, a trend that

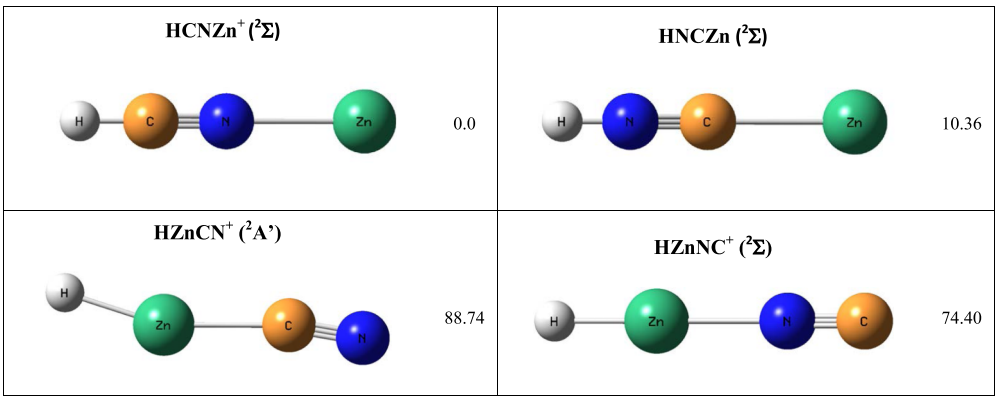

FIG. 3. Relative energies (in kcal/mol) for the $[C,H,N,Zn]^+$ isomers calculated at the B3LYP/aug-cc-pVTZ level (ZPVE corrections are included).

TABLE VIII. Dissociation energies for $HCNZn^+$ and $HNCZn^+$ calculated at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ.

Process	ΔE (kcal/mol)
$HCNZn^+ \rightarrow Zn^+ + HCN$	36.45
$HNCZn^+ \rightarrow Zn^+ + HNC$	37.41

is also followed by the absolute value of the total energy density. These observations reflect the strengthening/weakening of the C–N bond upon formation of the cyanides/isocyanides arrangements.

B. $[C,H,N,Zn]^+$ isomers

1. Energetics

As in the neutral counterparts, for each isomer, we have considered doublet and quartet states. However, the quartet isomers were in all cases no competitive in energy against the corresponding doublet ones and they were not included in our study. The relative energies for charged [C,H,N,Zn] isomers computed at different levels of theory are shown in Table VII and in addition, Figure 3 depicts the structures of these isomers together with B3LYP/aug-cc-pVQZ relative energies.

Regardless of the level of theory used, the most stable isomer of the $[C,H,N,Zn]^+$ composition was the ion-molecule complex arising from direct interaction of zinc cation with the nitrogen atom of HCN, namely, (hydrogen cyanide-κ*N*)zinc(1+) ion, $HCNZn^+$. The corresponding isocyanide counterpart (hydrogen isocyanide-κ*C*)zinc(1+) ion, $HNCZn^+$, was located 13.49 kcal/mol higher in energy (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level). Hydrideisocyanidezinc(1+) ion, $HZnNC^+$ (74.40 kcal/mol above $HCNZn^+$ at B3LYP level), and cyanidehydridezinc(1+) ion, $HZnCN^+$ (88.74 kcal/mol above $HCNZn^+$ at B3LYP level) follow in stability order. We have also considered other possible arrangements like those isomers that arise from the insertion of the zinc cation into the C–N bond of either hydrogen cyanide or hydrogen isocyanide; however, they are by far less stable and were not included in the table. It should be noted that in all isomers, the positive charge is located on the zinc atom.

Our results on the stability order of $[Zn,N,C,H]^+$ ions are in good agreement with the previous study by Palii *et al.*[24] However, our calculations predict a higher stabilization (13.47 kcal/mol at the CCSD(T)/aug-cc-pVQZ level of theory) of $HCNZn^+$ over $HNCZn^+$ than the MNDO calculations[24] (around 3 kcal/mol).

Regarding stability of $[Zn,N,C,H]^+$ isomers, and as we did for the neural isomers, we have computed the energies associated to the $Zn(CN)H^+ \rightarrow Zn^+ + H(CN)$ process. In Table VIII, we have summarized the results obtained at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level including ZPE corrections. Both $HCNZn^+$ and $HNCZn^+$ are stable toward formation of zinc cation and either hydrogen cyanide or hydrogen isocyanide (dissociation energies are 36.45 and 37.41 kcal/mol, respectively). Thus, it seems that both isomers could be reasonable experimental targets.

TABLE X. Rotational constants, in megahertz, for $HCNZn^+$ and $HNCZn^+$.

	$HCNZn^+$ ($^2\Sigma$)		$HNCZn^+$ ($^2\Sigma$)
Level	B_e/MHz	B_o/MHz	B_e/MHz
CCSD/aug-cc-pVTZ	3451.9	3446.1	3088.3
CCSD(T)/aug-cc-pVTZ	3451.8	3446.0	3098.6
CCSD(T)/aug-cc-pVQZ	3491.2	3485.4	3123.2
CCSD(T)[a]	3518.7	3512.9	3141.7

[a]Extrapolated.

2. Structure

Table IX collects the geometrical parameters for the two most stable $[C,H,N,Zn]^+$ isomers. First, the agreement among the results obtained at different levels of theory is rather good. Second, Zn–C or Zn–N bond distances are found to be significantly shorter than those found for the neutral counterparts. At the CCSD/aug-cc-pVTZ level of theory, the Zn–N bond distance in $HCNZn^+$ is 2.0759 Å whereas in the corresponding neutral counterpart, this distance enlarges to 3.9303 Å. In a similar way, the Zn–C bond distance is 2.1571 Å in $HNCZn^+$ and as long as 4.1897 Å in HNCZn. This is directly related to the different natures of the Zn–C and Zn–N bonds in neutral and cationic compounds.

3. Spectroscopic parameters

Rotational constants for $HCNZn^+$ and $HNCZn^+$ are listed in Table X. For $HCNZn^+$, the difference between B_0 and B_e

TABLE IX. Optimized geometries of the different $[C,H,N,Zn]^+$ isomers at different levels of theory in conjunction with the aug-cc-pVTZ basis set. Bond distances are given in angstroms and angles in degrees.

		Level							
Isomer		B3LYP	M06-HF	MP2	QCISD	CCSD	CCSD(T)	CCSD(T)[a]	CCSD(T)[b]
$HCNZn^+(^2\Sigma)$	d(Zn–N)	2.0878	2.0871	2.0570	2.0728	2.0759	2.0707	2.0569	2.0468
	d(N–C)	1.1405	1.1295	1.1541	1.1475	1.1460	1.1527	1.1501	1.1482
	d(C–H)	1.0743	1.0758	1.0731	1.0739	1.0738	1.0754	1.0751	1.0749
$HNCZn^+(^2\Sigma)$	d(Zn–C)	2.1765	2.1897	2.1233	2.1571	2.1580	2.1504	2.1408	2.1338
	d(C–N)	1.1449	1.1349	1.1576	1.1508	1.1493	1.1565	1.1531	1.1506
	d(N–H)	1.0079	1.0124	1.0088	1.0061	1.0061	1.0083	1.0071	1.0062

[a]aug-cc-pVQZ basis set.
[b]Extrapolated.

TABLE XI. Harmonic and anharmonic vibrational frequencies (ω, cm^{-1}) and IR intensities (I, km/mol) for $HCNZn^+$ and $HNCZn^+$ evaluated at the CCSD/aug-cc-pVTZ level.

$HCNZn^+$					$HNCZn^+$		
	Harmonic		Anharmonic			Harmonic	
Symmetry	ν	I	ν	I	Symmetry	ν	I
σ HC stretching	3391	143	3266	133	σ HN stretching	3943	1020
σ CN stretching	2234	117	2210	112	σ NC stretching	2270	8.6
π HCN bending	818	24	807	25	π HNC bending	857	111
σ NZn stretching	289	44	275	10	π NCZn bending	604	11
π CNZn bending	166	20	162	15	σ CZn stretching	290	3.5

rotational constants is on the order of 5.77 MHz. The harmonic and anharmonic (just for the most stable isomer) vibrational frequencies for $HCNZn^+$ and $HNCZn^+$ are shown in Table XI. Upon lowering $HNCZn^+$ to Cs point group symmetry, variational collapse of the reference ROHF (Restricted open-shell Hartree–Fock) wavefunction to a different electronic state took place. This orbital instability gave nonsensical results for fittings of anharmonic CCSD force fields. Therefore, for $HNCZn^+$, only harmonic vibrational frequencies were computed. In both isomers, the most intense IR absorption band corresponds to either σ HC or σ HN stretching mode. In $HCNZn^+$, the σ CN stretching mode also gives rise to a strong IR absorption band (117 km/mol), whereas in its isocyanide counterpart, this σ CN stretching mode presents a low intensity band (8.6 km/mol). As it was observed in neutral isomers, harmonic frequencies are slightly higher than the corresponding anharmonic ones and the absolute differences are more important in the stretching frequencies than in the bending ones. Even though a direct comparison between $HCNZn^+/HNCZn^+$ and HCN/HNC isomers is not straightforward due to the presence of the zinc atom, it could be interesting to compare our computed harmonic vibrational frequencies for the $HCNZn^+/HNCZn^+$ isomers with those computed for the HCN/HNC compounds. At CCSD/aug-cc-pVTZ level of theory, the harmonic frequency for the σ CN stretching mode was found to be 2173 cm^{-1} for HCN and 2102 cm^{-1} for HNC and the corresponding σ HC/σ HN stretching frequencies were 3473 cm^{-1} and 3846 cm^{-1}, respectively. The σ CN stretching modes in $HCNZn^+$ are around 60 cm^{-1} higher than in the HCN isomer. And a similar trend was found when comparing the σ CN stretching frequency of $HNCZn^+$ with that computed for HNC (in this case, the difference is around 68 cm^{-1}). This result suggests that the σ CN stretching frequency is only slightly modified upon formation of $HCNZn^+/HNCZn^+$ isomers.

TABLE XII. Local topological properties (in a.u.) of the electronic charge density distribution calculated at the position of the bond critical points for the different [C,H,N,Zn] species.[a]

Species	Bond	$\rho(r)$	$\nabla^2\rho(r)$	$\lvert V(r)\rvert/G(r)$	$H(r) = -K$
	Zn–N	0.071	0.286	1.208	−0.0187
$HCNZn^+$	N–C	0.487	0.077	1.980	−0.934
	C–H	0.296	−1.340	12.768	−0.366
	Zn–C	0.069	0.185	1.308	−0.0206
$HNCZn^+$	C–N	0.464	0.256	1.932	−0.874
	N–H	0.332	−2.430	16.246	−0.650

[a]The electronic charge density $\rho(r)$, the Laplacian $[\nabla^2\rho(r)]$, the relationship between the potential energy density $[V(r)]$ and the lagrangian form of kinetic energy density $[G(r)]$, and the total energy density, $[H(r)]$.

4. Bonding situations

A summary of the most relevant topological properties of the critical points for $HCNZn^+$ and $HNCZn^+$ is collected in Table XII. In addition, the contour maps of the Laplacian of the electron density are shown in Figure S2 of the supplementary material.[62] C–H and N–H bonds exhibit typical characteristics of shared interactions: large electron density, negative values of its laplacian, $|V(r)|/G(r)$ ratios greater than 2, and negative total energy densities H(r). The nature of the Zn–C or Zn–N bonds is different. These interactions have low values of ρ(r) and slightly negative values of the total energy density; however, the Laplacian is positive and the $|V(r)|/G(r)$ ratios are between one and two. This type of binding has been attributed to partially covalent closed-shell interactions.[60] On the other hand, Zn–C bond has slightly lower electron density and absolute H(r) values than the Zn–N bond, suggesting that Zn–C bond in $HNCZn^+$ could be considered to have a slightly larger ionic (less covalent) character than the Zn–N bond in the $HCNZn^+$.

Carbon-nitrogen bonds in both $HCNZn^+$ and $HNCZn^+$ show some characteristics of covalent bonds: relatively large values of electron density and negative values of the total energy density. However, the Laplacian of the electron density is positive and the $|V(r)|/G(r)$ ratio is slightly lower than two suggesting some ionic character. Again, it was observed that the electron density for the C–N BCP in $HCNZn^+$ is slightly larger than for that found in $HNCZn^+$, a trend that is also followed by the absolute value of the total energy density. These observations reflect the strengthening/weakening of the C–N bond upon formation of the cyanides/isocyanides arrangements.

IV. CONCLUSIONS

The most stable isomer of the [C,H,N,Zn] composition is cyanidehydridezinc HZnCN ($^1\Sigma$) with the corresponding isocyanide counterpart, hydrideisocyanidezinc, HZnNC($^1\Sigma$), located 5.13 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) higher in energy. Both HZnCN and HZnNC are stable toward fragmentation into HZn + CN moieties (dissociation energies are 114 and

109 kcal/mol, respectively, at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level). Therefore, HZnCN and HZnNC will be possible candidates for microwave or IR interstellar detections. In fact, HZnCN has already been observed by rotational spectroscopy.[17] Following in energy are the almost isoenergetic intermolecular complexes, ZnHCN and HCNZn that arise from the interaction between the zinc atom and hydrogen cyanide at either the hydrogen or nitrogen atoms. These isomers are located approximately 9 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) higher in energy than HZnCN. The corresponding isocyanide derivatives of zinc, namely, ZnHNC and HNCZn correspond to van der Waals complexes and are also isoenergetic and lying approximately 23 kcal/mol (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level) above cyanidehydridezinc.

We conclude that ZnHCN and ZnHNC intermolecular complexes could not be considered as possible precursors for HZnCN and HZnNC molecules because their respective isomerization barriers are very high. The low isomerization barrier for the HZnNC → HZnCN process (6.41 kcal/mol at the CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ) suggests a relatively low degree of covalency in the metal-cyanide/isocyanide bonds.[50,51]

Topological analysis of electron density for HZnCN and HZnNC allows us to characterize C–N BCPs as shared interactions typical of covalent compounds. Whereas Zn–C, Zn–N, and Zn–H interactions can be classified as partially covalent closed shell interactions. BCPs involving the zinc atom for the intermolecular complexes (ZnHCN, ZnHNC, HCNZn, and HNCZn) show characteristics typical of van der Waals interactions.

Concerning cationic $[C,H,N,Zn]^+$ compounds, the most stable isomer is the ion-molecule complex that arises from the direct interaction of zinc cation with the nitrogen atom of HCN (hydrogen cyanide-κ*N*)zinc(1+) ion, $HCNZn^+$ ($^2\Sigma$). The corresponding isocyanide counterpart (hydrogen isocyanide-κ*C*)zinc(1+) ion, $HNCZn^+$ ($^2\Sigma$), is located 13.49 kcal/mol higher in energy (at CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVTZ level). Both $HCNZn^+$ and $HNCZn^+$ could be reasonable experimental targets since they are stable toward formation of zinc cation and either hydrogen cyanide or hydrogen isocyanide (dissociation energies are 36.45 and 37.41 kcal/mol, respectively).

The analysis of the bonding situation in the cationic isomers shows that C–H and N–H bonds exhibit typical characteristic of shared interactions whereas Zn–C or Zn–N binding has been attributed to partially covalent closed-shell interactions. Carbon-nitrogen bonds exhibit some characteristics of covalent bonds: relatively large values of electron density and negative values of the total energy density. However, the Laplacian of the electron density is positive and the $|V(r)|/G(r)$ ratio is slightly lower than two suggesting some ionic character.

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