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Characterization Of The AzirinyI Cation And Its Isomers

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Abstract

The azirinyI cation ($C_2H_2N^+$) and its geometrical isomers could be present in the interstellar medium. The $C_2H_2N^+$ isomers are, however, difficult to identify in interstellar chemistry because of the lack of high-resolution spectroscopic data from laboratory experiments. *Ab initio* quantum chemical methods were used to characterize the structures, relative energies, and spectroscopic and physical properties of the low energy isomers of the azirinyI cation. We have employed second order Møller-Plesset perturbation theory (MP2), second order Z-averaged perturbation theory (ZAPT2), and coupled cluster theory with singles and doubles with perturbative triples CCSD(T) methods along with large correlation consistent basis sets such as cc-pVTZ, cc-pCVTZ, cc-pVQZ, cc-pCVQZ and cc-pV5Z. Harmonic vibrational frequencies, dipole moments, rotational constants, and proton affinities for the lowest energy isomers were calculated using the CCSD(T) method. AzirinyI cation, a cyclic isomer, is lowest in energy at all levels of theory employed. AzirinyI cation is followed by the cyanomethyl cation (H_2CCN^+), isocyanomethyl cation (H_2CNC^+), and a quasilinear $HCCNH^+$ cation which are 13.8, 17.3 and 21.5 kcal mol⁻¹ above the cyclic isomer, respectively, at the CCSD(T)/cc-pV5Z level of theory. The lowest three isomers all have C_{2v} symmetry and 1A_1 ground electronic states. The quasilinear $HCCNH^+$ cation has a C_s symmetry planar structure, and a $^3A''$ electronic ground state, unlike what some previous work suggested.

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Keywords

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Introduction

A variety of organic molecules have been observed in various astrophysical environments including interstellar clouds, planetary nebulae, outflows of carbon stars, and photodissociation regions, though only about two hundred molecules have been positively identified thus far.^{1,2} Recently our group has focused on identifying and characterizing small hydrocarbon molecules, including those with a nitrogen or oxygen heteroatom, that would be likely to form in the outflow from carbon stars.^{3–6} One interesting molecule, $c\text{-C}_2\text{HN}$, is a cyclic, aromatic molecule⁷ that is isoelectronic to cyclopropenylidene, $c\text{-C}_3\text{H}_2$, which has been observed in many astrophysical environments,^{8,9} and can be formed by replacing one of the C-H units with a N atom. Unlike $c\text{-C}_3\text{H}_2$ though, $c\text{-C}_2\text{HN}$ is not the global minimum for molecules with the HC_2N formula, but rather the global minimum is a quasi-linear triplet, HCCN , which has been observed in the interstellar medium (ISM).¹⁰ However, the structures are sufficiently different that both isomers should be observable if they are formed, similar to the situation for $c\text{-C}_3\text{H}_2$ and its linear isomer.⁸ The formation of $c\text{-C}_3\text{H}_2$ is believed to result from the dissociative attachment of an electron to $c\text{-C}_3\text{H}_3^+$,^{11–13} and by analogy the formation of $c\text{-C}_2\text{HN}$ is likely to result from dissociative attachment of an electron to $c\text{-C}_2\text{H}_2\text{N}^+$. There has been speculation that the azirinyl cation, $c\text{-C}_2\text{H}_2\text{N}^+$ could be present in the interstellar medium.^{14–17} There have been several theoretical and experimental studies aimed at characterizing isomers of $\text{C}_2\text{H}_2\text{N}^+$, though the theoretical studies have mostly been at low levels of theory.^{18–22} Thus, the purpose of the present study is to characterize the low-lying isomers of $\text{C}_2\text{H}_2\text{N}^+$ using high level *ab initio* quantum chemical coupled cluster methods.

Interestingly, azirinyl cation, Isomer 1 (Figure 1, C_{2v} , 1A_1), is the global minimum even though the lowest energy deprotonated neutral molecule is the quasi-linear triplet. Further, many of the previous theoretical studies have only examined the singlet isomers. In 1989, Harland et al.²³ examined nine different stationary points on the singlet potential energy surface (PES) using singles and doubles configuration interaction (CISD) and Møller-Plesset perturbation theories and found the lowest three to be azirinyl cation, cyanomethylene cation (Figure 2, C_{2v} , 1A_1), and isocyanomethylene cation (Figure 3, C_{2v} , 1A_1). In 1998, Mayer et al.²² reported the thermodynamic properties of the singlet $\text{C}_2\text{H}_2\text{N}^+$ isomers, and found the same ordering of the three lowest energy structures. They used Gaussian 2 (G2) theory as well as methods that include extrapolation to the one-particle basis set limit and found relative energies similar to those reported by Harland et al.²³ In 1999, Lau et al.²⁴ used G2 theory to examine the stability of $\text{C}_2\text{H}_2\text{N}^+$ isomers, including the lowest triplet structure (Figure 4, C_s , $^3A''$), and found the same order of stability for the singlet isomers, though the relative energies of the singlet isomers were somewhat different compared to the findings of Mayer et al.,²² with the lowest triplet isomer being slightly higher in energy than isocyanomethylene cation. In 2003, Di Stefano et al.²⁵ examined the production of cations containing C-N bonds both experimentally and theoretically, including $\text{C}_2\text{H}_2\text{N}^+$ isomers.

They again only considered the singlet species and found the same ordering for the three lowest energy isomers, but their B3LYP/6-31G* relative energies were different relative to either Harland et al.²³ or Lau et al.²⁴ In 2005, Frankowski et al.¹⁸ used Fourier Transform infrared (FT-IR) matrix isolation spectroscopy and density functional theory (DFT) to study the isomers of $C_2H_2N^+$ and found the same ordering for the singlet isomers, but this time the lowest triplet isomer was found to be slightly lower in energy than the isocyanomethylene cation. Not surprisingly, the relative energies of the singlet isomers were similar to that found by Di Stefano et al.²⁵ as B3LYP was used in both studies. Another significant difference between the Frankowski et al.¹⁸ and Lau et al.²⁴ studies concerning the triplet Isomer 4, is that Lau et al., using G2 theory, found the triplet to be quasi-linear while Frankowski et al., using B3LYP, found the triplet linear $HCCNH^+$ to be exactly linear.

Most of the studies mentioned above were mainly interested in the thermodynamic properties of $C_2H_2N^+$ isomers, and in particular to compare them to an experimental study by Holmes and Mayer¹⁹ and to try to resolve a difference in the computed and measured heat of formation of azirinyll cation. Even though the harmonic frequencies of the various isomers must have been computed in the G2 studies, they were not reported. Harmonic frequencies were reported by Harland et al. at the self-consistent field (SCF) level of theory with a polarized double zeta (DZP) basis set, and by Frankowski et al. at the B3LYP/6-311++G(3df,3pd) level of theory since they used these to help assign some of the FT-IR matrix isolation spectra they measured. Gray has studied extensively the reactions of acetonitrile and has shown that the CH_2CN radicals and cations are important products formed.²⁶ Ions are of particular interest in the dissociation of five-membered and six membered heterocycles containing nitrogen.^{3,19,27-29} Other theoretical studies of the azirinyll cation and some of its isomers have included calculations of magnetizability tensors.³⁰

In this work the azirinyll cation and its' other three lowest energy isomers have been investigated using high-level coupled cluster methods with very large correlation consistent basis sets. This will allow the determination of the relative energies, structures, and spectroscopic properties of the isomers accurately. In order to help identify the CH_2CN^+ isomers, the harmonic vibrational frequencies, rotational constants, and dipole moments will be determined at the MP2 and CCSD(T) levels of theory with several basis sets. The open shell isomer – only one isomer has a triplet ground electronic state – has been investigated using the second-order Z-averaged perturbation theory (ZAPT2) method with correlation consistent basis sets. Additionally, the proton affinities for the formation of the cations from their respective neutral isomers have been investigated. Our study will provide the most accurate structural and spectral parameters for these molecules to date. This work will provide data that can be used as foundation for further refinement of spectra in order to identify the $C_2H_2N^+$ isomers in future experimental work, and possibly in the interstellar medium.

Methods

The molecular geometries were fully optimized, and vibrational frequencies were calculated under the harmonic approximation. Second-order Møller-Plesset perturbation theory (MP2) along with Dunning's correlation consistent polar valence triple zeta (cc-pVTZ)³¹ basis set

were utilized. The isomer with a triplet state was investigated, in addition to UMP2, using second order Z-averaged perturbation theory (ZAPT2),^{32,33} which uses a symmetric spin orbital basis, as opposed to UMP2 based on unrestricted Hartree-Fock which uses different spatial orbitals for different spins. Starting with the MP2/cc-pVTZ optimized geometries, the lowest energy isomers were further optimized using the coupled cluster singles and doubles with perturbative triples correction method (CCSD(T)).^{34–37} The CCSD(T) optimized geometries and harmonic^{38,39} vibrational frequencies were determined using a series of correlation consistent basis sets, such as cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pCVTZ, and cc-pCVQZ. For all the calculations involving core-valence basis sets (cc-pCVTZ and cc-pCVQZ) we unfreeze the core, i.e. all electrons were correlated. The CCSD(T)/cc-pCVQZ level of theory has been shown previously⁴⁰ to produce very accurate structural parameters for small hydrocarbons, such as the ones considered here. For C and N the cc-pV5Z is a [6s5p4d3f2g1h] set and the cc-pCVQZ is a [8s7p5d3f1g] contracted set. All the MP2 and ZAPT2 calculations were performed using the Q-Chem 3.2 quantum chemistry package.⁴¹ All the coupled cluster calculations were carried out using the MOLPRO 2008.2 quantum chemistry package.⁴²

Results and Discussion

There are seven known isomers on the potential energy surface of $C_2H_2N^+$, of which we are doing a systematic study on the four lowest energy isomers. Azirinyll cation (Figure 1) is the global minimum. It is followed by cyanomethyl cation (Figure 2), isocyanomethyl cation (Figure 3) and the quasi-linear $HCCNH^+$ cation (Figure 4). All, but one of the four isomers have a singlet electronic ground state – $HCCNH^+$ has a triplet ground state.

The relative energies of the isomers are presented in Table 1. Each isomer's geometry was optimized using the HF/cc-pVTZ and MP2/cc-pVTZ levels of theory to start with. The four lowest energy isomers presented in Table 1 were then optimized using the CCSD(T) method with cc-pVTZ, cc-pCVTZ, cc-pVQZ, cc-pCVQZ, and cc-pV5Z basis sets for a systematic analysis.

At every level investigated, the relative energies of the isomers are azirinyll < cyanomethyl < isocyanomethyl < quasi-linear $HCCNH^+$. With the CCSD(T) method, several basis sets were used in the geometry optimization of the isomers, and there is slight variation in the relative energies of the isomers as expected. Relative ordering of the isomers differs slightly from previously published results. Harland et al. optimized geometries at the CISD/DZ+P level and reported the relative energies of the isomers as azirinyll < isocyanomethyl < cyanomethyl cations. In contrast, Lau et al.²⁴ using G2 theory order the relative energies as azirinyll < cyanomethyl < isocyanomethyl < $HCCNH^+$, in agreement with our findings. Frankowski et al.¹⁸ found the relative energies of the isomers to be azirinyll < cyanomethyl < linear $HCCNH^+$ ($C_{\infty v}$) < isocyanomethyl cation at the B3LYP/6-311++G(3df, 3pd) level of theory. In this work we employed higher levels of theory than those previously reported in order to predict the relative energy ordering definitively.

Azirinyl cation

The lowest energy isomer, azirinyl cation, is presented in Figure 1. The azirinyl cation has a three-membered cyclic arrangement with the two carbons and the nitrogen. The two hydrogen atoms are attached to the carbons. For all methods and basis sets used, the global minimum, azirinyl cation, has a C_{2v} symmetry, and 1A_1 electronic state, which is in agreement with previous work.^{24,22,18–21,23,43} There is a slightly elongated double bond between the two carbon atoms, and two similar carbon nitrogen linkages. At the CCSD(T)/cc-pV5Z level, the bond angles and bond lengths are $\angle HCN$ 141.2°, $\angle CNC$ 60.3°, $\angle NCC$ 59.9° $\angle HCC$ 158.9°, H-C 1.083 Å, C-N 1.338 Å, and C-C 1.343 Å. The largest difference in bond lengths occurs when one uses the cc-pVTZ basis and changes from the MP2 to CCSD(T) method. Between these methods, the bond angles are in agreement to 0.1°. Using the CCSD(T) method, the optimized geometries from calculation with cc-pVTZ, cc-pCVTZ, cc-pVQZ, cc-pCVQZ, and cc-pV5Z basis sets agree within 0.005 Å. The equilibrium structure's bond angles and bond lengths are shown in Figure 1 and are in general good agreement with other works, but are at a higher level of theory.^{43,44}

The dipole moments (computed with respect to the center of mass) and rotational constants were calculated with the very accurate optimized geometry obtained at the CCSD(T)/cc-pVQZ level and are given in Table 2. Proton affinities of the neutral species were calculated by taking the difference in energy between the protonated cation and the deprotonated neutral. In this case the energy of the azirinyl cation is subtracted from the energy of the neutral cyclic HC_2N . As shown in Table 2, the neutral HC_2N has a large proton affinity of 209.8 kcal mol⁻¹, as calculated at the CCSD(T)/cc-pVQZ level, for the formation of the azirinyl cation. As a comparison the proton affinity of H_2O is 165.1 kcal/mol.^{45,46} Therefore the formation of azirinyl cation by the protonation of the corresponding neutral species is likely to happen in an environment where both $HCCN$ and H^+ exist.

The harmonic vibrational frequencies were calculated at the CCSD(T) level of theory along with the cc-pVTZ, cc-pCVTZ, cc-pVQZ, cc-pCVQZ and cc-pV5Z basis sets. The vibrational frequencies can be found in Table 3. With the CCSD(T) method, as one improves the basis set from the cc-pVTZ to cc-pVQZ to cc-pV5Z, i.e. includes the effects of f, g, and h type functions in the basis set for the heavy atoms, the harmonic vibrational frequencies do not differ by more than 10 cm⁻¹. Addition of the g functions (triple zeta to quadruple zeta) in the basis set has a marginally larger effect than adding the h functions (quadruple zeta to 5-zeta). There is also a small but visible effect of adding core-correlation on each harmonic vibrational frequency, on going from the cc-pVTZ to cc-pCVTZ basis set or from the cc-pVQZ to cc-pCVQZ set. When the core electrons are incorporated into the model, the bond strengths increase which is reflected in the consistent increase in the harmonic vibrational frequencies. The symmetry assignments for two of the vibrational frequencies differs from that found in previous work, however our method simply found the b_2 vibrational mode to be lower than that reported previously.²³

Cyanomethyl cation

The second lowest energy isomer is the cyanomethyl cation in the 1A_1 electronic state. This isomer has C_{2v} symmetry, which is in agreement with previous results.^{18,24} At our best level

of theory, CCSD(T)/cc-pV5Z, the cyanomethyl isomer is 13.84 kcal mol⁻¹ above the global minimum.

The two hydrogen atoms are linked with the terminal carbon atom in this isomer. The bond angles and bond lengths at the CCSD(T)/cc-pV5Z level are <NCC 180.0°, <CCH 119.8°, <HCH 120.4°, N-C 1.181 Å, C-C 1.370 Å, and C-H 1.090 Å as shown in Figure 2. The C-C bond at 1.370 Å is intermediate between a single and double bond, while the C-N bond is essentially a triple bond. The bond distances and angles are presented in Figure 2 using the MP2 and the CCSD(T) methods along with very large basis sets. The bond lengths agree within 0.012 Å for each method and basis set used. The geometry optimization is in agreement with previously reported geometries with differences due to the higher level of theory used in the present study.^{18,23-25}

This isomer has the largest total dipole moment (5.21 Debye) due to having a nitrogen atom at one end at the CCSD(T)/cc-pVQZ level as shown in Table 2. The rotational constants calculated at the CCSD(T)/cc-pVQZ level can be found in Table 2. The rotational constants for this isomer are most similar to those of Isomer 3, isocyanomethylene cation. This is due to the fact that Isomers 2 and 3 have the most similar geometrical structures. As indicated in Table 2, the Isomer 2 has a proton affinity of 200.7 kcal mol⁻¹ at the CCSD(T)/cc-pVQZ level. The proton affinity is calculated by subtracting the energy of the neutral HCCN from the cationic H₂CCN⁺. Protonation of neutral HCCN can happen in either the CH end or in the N terminal. Protonation of the CH terminal, which gives us the cyanomethyl cation, has a larger proton affinity indicating that cyanomethyl cation will be a preferred product over the linear isomer.

Harmonic vibrational frequencies calculated at every level of theory considered here can be found in Table 3. Notice that CCSD(T)/cc-pVTZ gives good vibrational frequencies when compared to that obtained by superior CCSD(T)/cc-pVQZ method. With the CCSD(T)/cc-pVQZ method the vibrational frequencies are within 8 cm⁻¹ of those found with the cc-pVTZ basis set. Upon further improving the basis set to cc-pV5Z there is a visible, albeit small, change in harmonic vibrational frequencies. The harmonic vibrational frequencies when the core electrons are incorporated, and the cc-pCVTZ and cc-pCVQZ basis sets are used, are also consistent. Incorporation of the core electrons is important to get very accurate spectroscopic data. The vibrational frequencies and the symmetry assignments are in reasonable agreement with previous studies performed at lower levels of theory.^{18,23}

Isocyanomethyl cation

Isocyanomethyl cation is the third lowest energy isomer, shown in Figure 3. Isocyanomethyl cation can be produced by the ionization of isocyanomethyl radical, the laboratory rotational spectra of which has been recorded.⁴⁷ Isocyanomethyl cation has a C_{2v} symmetry and has a ¹A₁ electronic ground state, which is in agreement with other studies.^{23,24} At the CCSD(T)/cc-pV5Z level of theory, the isocyanomethyl isomer is 17.31 kcal mol⁻¹ higher in energy relative to azirinyli cation. Isocyanomethyl cation is only 3.47 kcal mol⁻¹ above the nearest isomer cyanomethyl cation.

The isocyanomethyl radical is structurally very similar to its' nearest isomer, the cyanomethyl cation. The optimized geometry of the isocyanomethyl cation can be found in Figure 3 with the bond angle and bond lengths shown for each level of theory. At the CCSD(T)/cc-pV5Z level, the bond angles and bond lengths are as follows: $\angle\text{CNC}$ 180.0°, $\angle\text{HCH}$ 122.0°, N-C 1.221 Å, C-N 1.284 Å, and C-H 1.090 Å. The terminal carbon makes a long carbon-nitrogen triple bond, while the methylene carbon forms essentially a double bond with the central nitrogen. With the cc-pVTZ basis set, the bond lengths increase when changing from the MP2 method to the CCSD(T) method. Using the CCSD(T) method, the $\angle\text{HCH}$ angle decreases and the (H)C-N bond length decreases as the basis set is improved from cc-pVTZ to cc-pVQZ. With the same levels of theory, the C-H and N-C bond lengths are in good agreement. The bond angles and bond lengths are in good agreement with those found previously.^{18,23–25}

The rotational constants and dipole moments can be found in Table 2. The rotational constants were computed with the very accurate geometries obtained at the CCSD(T)/cc-pVQZ level of theory. The proton affinity is calculated by subtracting the energy of the isocyanomethyl cation from the energy of the neutral HCNC. At the MP2/cc-pVTZ level of theory, the proton affinity for the neutral HCNC at the singly hydrogenated end, leading to the formation of isocyanomethyl cation, was found to be 211.6 kcal mol⁻¹. At the CCSD(T)/cc-pVQZ level the proton affinity is lowered by 1.7 kcal mol⁻¹ to 209.9 kcal mol⁻¹. This is larger than the proton affinity of HCCN by about 9 kcal mol⁻¹.

The harmonic vibrational frequencies are obtained using CCSD(T) and several correlation consistent basis sets as presented in Table 3. With the CCSD(T) method the vibrational frequencies obtained with the cc-pVTZ basis set are within 10 cm⁻¹ compared to those found with the cc-pVQZ basis set. Going to the cc-pV5Z basis set further improves the harmonic vibrational frequencies by a few wavenumbers. Additionally, the vibrational frequencies are in good agreement with those determined by Frankowski et al.¹⁸ The symmetries of the vibrational frequencies are also presented in Table 3, and the vibrational modes are arranged in order of their symmetry.

Quasi-linear HCCNH⁺, ³A''

The Isomer 4, HCCNH⁺ is planar. The lowest energy quasi-linear equilibrium structure for the HCCNH⁺ isomer was found to have a ³A'' electronic state and to be bent with C_s symmetry as shown in Figure 4 (the lowest singlet electronic state for the quasi-linear structure was found to be 16.6 kcal mol⁻¹ higher in energy at the CCSD(T)/cc-pVQZ level of theory). Using coupled cluster theory and a large basis set we find that there is a large difference in energy between the triplet excited state and the singlet ground state. At the CCSD(T)/cc-pV5Z level of theory the isomer 4 ³A'' is 21.45 kcal mol⁻¹ higher in energy relative to aziriny cation. With the CCSD(T) method, the relative energy decreases to 19.76 kcal mol⁻¹ when the core electrons are included and using the cc-pCVTZ basis set.

The optimized geometry of linear triplet HCCNH⁺ can be found in Figure 4. At the CCSD(T)/cc-pV5Z level the bond angles and lengths are as follows: $\angle\text{HNC}$ 178.5°, $\angle\text{NCC}$ 176.0°, $\angle\text{CCH}$ 158.9°, H-N 1.010 Å, N-C 1.168 Å, C-C 1.320 Å, and C-H 1.076 Å. The largest difference in bond angles and bond lengths from successive optimizations is seen

when one goes from the ZAPT2/cc-pVTZ level of theory to the CCSD(T)/cc-pVTZ level of theory. The C-C distance is a typical double bond distance. The central carbon is sp hybridized and essentially forms a C-N triple bond with a 1.168 Å bond distance.

The geometry of the $^3A''$ HNCCH⁺ isomer significantly differs from those found in other works. Frankowski et al.¹⁸ found that a linear HNCCH($^3\Sigma$, $C_{\infty v}$) isomer was the lowest energy isomer. In our research we have investigated both the singlet state and triplet state linear isomers at the CCSD(T)/cc-pVQZ level. The vibrational frequency analysis suggested that both the singlet state and the triplet state geometries should be bent. Other works did report a bent HNCCH⁺ isomer at the CISD+Q/DZ+P and MP2(Full)/6-31G(d) levels.^{23,24} The most notable differences between the reported structures and the optimized geometry in this work are the <CCH angles and the C-N bond lengths. Lau et al. reports a 110.2° <CCH angle and a 1.244 Å C-N bond length whereas Harland et al. report a 139.2° <CCH angle and a 1.141 Å C-N bond length. At the CCSD(T)/cc-pVQZ level, we found that the <CCH angle was 158.2° and the C-N bond length was 1.168 Å.

The total dipole moment and rotational constants were determined using the geometries obtained at the CCSD(T)/cc-pCVQZ level. This isomer has the smallest dipole moment 0.56 Debye of the isomers presented in Table 2. This isomer also has the largest rotational constant. Since the rotational constants depend on the geometry of the molecule, it is not surprising that the isomer in a different symmetry group has the rotational constants that differ drastically from the rotational constants of the other isomers investigated. Protonation of the nitrogen end of neutral HCCN leads to this isomer. The proton affinity for the hydrogen found on the nitrogen is 180.5 kcal mol⁻¹ at the ZAPT2/cc-pVDZ level of theory. This is much lower compared to the proton affinity for proton attachment to the other end of HCCN. These results indicate that a proton in the gas phase will likely attach on the carbon end and preferably produce the cyanomethyl cation, rather than this quasi-linear isomer.

The harmonic vibrational frequencies calculated using several different basis sets for Isomer 4 are in good agreement with each other except for ω_7 . The harmonic vibrational frequencies are presented in Table 3. Using the CCSD(T) method with different basis sets, the harmonic frequencies for the stretching modes increase when one improves the basis set from cc-pVTZ to cc-pVQZ, and when the core electrons were incorporated and change from the cc-pVTZ basis set to the cc-pCVTZ basis set, as is common. For ω_7 , which is the lowest energy in-plane bend, the harmonic frequency decreases on going from cc-pVTZ to cc-pV5Z as well as with the inclusion of core correlation. The difference between cc-pVQZ and cc-pV5Z is smaller than the difference between cc-pVTZ and cc-pVQZ, indicating that it is converging with respect to one-particle basis set. The behavior of ω_7 is probably indicative of a quasi-linear mode. Except for ω_7 , the harmonic frequencies computed with the cc-pVQZ basis set are in close agreement, within 10 cm⁻¹, compared to those found with the cc-pVTZ basis set, indicating that they are nearly converged with respect to one-particle basis set.

Conclusions

The four lowest energy isomers of $\text{H}_2\text{C}_2\text{N}^+$, the aziriny cation, cyanomethyl cation, isocyanomethyl cation and HCCNH^+ were systematically investigated using state-of-the-art *ab initio* quantum chemistry methods. Perturbation theory and coupled cluster theory methods along with very large correlation consistent basis sets were utilized to obtain very accurate structural and spectroscopic parameters that will be helpful in identifying these species in laboratory experiments.

The aziriny cation is the lowest in energy among all the isomers. Cyanomethyl, isocyanomethyl and the HCCNH^+ cations are 13.8, 17.3 and 21.5 kcal mol⁻¹ above the global minimum respectively at the CCSD(T)/cc-pV5Z level of theory. The three lowest energy isomers all have C_{2v} symmetry and $^1\text{A}_1$ ground electronic states. Isomer 4 has a planar quasi-linear structure with a $^3\text{A}''$ ground electronic state, unlike some previous work suggests. The triplet electronic state is 16.6 kcal mol⁻¹ below the singlet electronic state for the quasi-linear HCCNH^+ structure at the CCSD(T)/cc-pVQZ level of theory. The characterization of these isomers will give insight into the chemical pathways of their formation in the interstellar medium and hopefully will also aid in identifying them in both laboratory experiments and in astronomical observations.

As shown in Table 2, the three lowest energy isomers all have substantial dipole moments (computed with respect to the center of mass), especially the cyanomethyl and isocyanomethyl cations. As most molecules are identified through rotational spectroscopy, it is noteworthy that aziriny cation has rotational constants (Table 2) that are quite distinct from cyanomethyl and isocyanomethyl cations. While the rotational constants for cyanomethyl and isocyanomethyl cations are more similar, the differences are certainly large enough to be separately identified in high-resolution rotational spectroscopy. It is hoped that the data provided herein will prompt further laboratory and astronomical studies of these interesting cations.

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Figure 1.

Isomer (1), the optimized C_{2v} structure of Azirinyli cation is presented here using the MP2/cc-pVTZ and the CCSD(T)/cc-pVTZ/cc-pCVTZ/cc-pVQZ/cc-pCVQZ/cc-pV5Z levels of theory. See text for details.

Figure 2.

Isomer (2), the optimized C_{2v} structure of the cyanomethylene cation is shown here at the MP2/cc-pVTZ and the CCSD(T)/cc-pVTZ/cc-pCVTZ/cc-pVQZ levels of theory. See text for details.

Figure 3. Isomer (3), the optimized C_{2v} structure of the iso-cyanomethylene cation is pictured at the MP2/cc-pVTZ and the CCSD(T)/cc-pVTZ/cc-pCVTZ/cc-pVQZ/cc-pV5Z levels of theory.

Figure 4.

Isomer (4), the optimized structure of the $^3A''$ quasi-linear $HCCNH^+$ cation is pictured at the ZAPT2/cc-pVTZ and the CCSD(T)/cc-pVTZ/cc-pCVTZ/cc-pVQZ/cc-pV5Z levels of theory. See text for details.

Table 1

Relative energies (in kcal mol⁻¹) of Azirinyll cation, and its isomers, cyanomethylene cation, isocyanomethylene cation and the linear HCCNH⁺ are presented here at the MP2/cc-pVTZ and the CCSD(T)/cc-pVTZ/cc-pVQZ/cc-pV5Z/cc-pCVQZ/cc-pCVQZ levels of theory.

Isomer/ Figure	Isomer	MP2/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/cc-pCVQZ	CCSD(T)/ cc-pV5Z
Figure 1 (C ₂ N, ¹ A ₁)	Azirinyll	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Figure 2 (C ₂ N, ¹ A ₁)	Cyanomethylene	15.77	12.35	12.38	13.41	13.54	13.84	13.84
Figure 3 (C ₂ N, ¹ A ₁)	Isocyanomethylene	22.90	15.83	16.03	16.82	17.33	17.31	17.31
Figure 4 (C _s , ³ A ^{''})	Quasi-linear HCCNH ⁺	25.99 [*]	20.11	19.76	20.97	20.57	21.45	21.45

* The second-order Z-averaged perturbation theory (ZAPT2) in place of MP2, and RHF/UCCSD(T) in place of CCSD(T) were used for this open-shell isomer. See text for details.

Table 2

Rotational constants (in cm^{-1}) and dipole moments (Debye) in center of mass coordinate calculated at the CCSD(T)/cc-pVQZ level of theory. The proton affinity (in kcal mol^{-1}) of the corresponding neutral isomers of HC_2N calculated at the CCSD(T)/cc-pVQZ level of theory are presented in the last column.

Isomer/Figure	Isomer	Rotational Constants			Dipole Moment (Debye)	Proton Affinity kcal/mol
		A	B	C		
Figure 1 ($\text{C}_{2v}, {}^1\text{A}_1$)	Azirinyl ion	1.286	1.021	0.569	2.79	209.8
Figure 2 ($\text{C}_{2v}, {}^1\text{A}_1$)	Cyanomethylene cation	9.335	0.343	0.331	5.21	200.7
Figure 3 ($\text{C}_{2v}, {}^1\text{A}_1$)	Isocyanomethylene cation	9.212	0.384	0.369	4.07	209.9
Figure 4 ($\text{C}_s, {}^3\text{A}'$)	Quasi-linear HCCNH^+	114.319	0.338	0.337	0.56	180.5*

*The second-order Z-averaged perturbation theory (ZAPT2) was used for this open-shell isomer. See text for details.

Table 3

Harmonic vibrational frequencies (in cm^{-1}) determined with the CCSD(T) method in conjunction with the cc-pVTZ, cc-pVQZ, cc-pV5Z, and cc-pCVQZ basis sets.

Isomer	Sym	cc-pVTZ	cc-pCVTZ	cc-pVQZ	cc-pCVQZ	cc-pV5Z
Azirinyli ion Figure 1 C_{2v}	a_1 ω_1	3279	3280	3277	3283	3277
	a_1 ω_2	1648	1654	1656	1663	1657
	a_1 ω_3	1372	1378	1379	1385	1380
	a_1 ω_4	943	945	944	946	944
	b_1 ω_5	858	860	858	860	858
	a_2 ω_6	1000	1005	1002	1005	1005
	b_2 ω_7	3227	3232	3229	3235	3229
	b_2 ω_8	1157	1162	1167	1174	1169
	b_2 ω_9	992	996	995	999	996
Cyanomethylene cation Figure 2 C_{2v}	a_1 ω_1	3098	3102	3098	3103	3097
	a_1 ω_2	2161	2168	2169	2177	2171
	a_1 ω_3	1468	1471	1465	1468	1464
	a_1 ω_4	1084	1089	1088	1092	1088
	b_1 ω_5	1156	1158	1153	1155	1150
	b_1 ω_6	237	239	232	233	230
	b_2 ω_7	3212	3218	3215	3219	3215
	b_2 ω_8	1033	1036	1032	1035	1032
	b_2 ω_9	311	315	312	314	311
Isocyanomethylene cation Figure 3 C_{2v}	a_1 ω_1	3093	3097	3092	3097	3092
	a_1 ω_2	2018	2025	2025	2033	2025
	a_1 ω_3	1520	1523	1518	1521	1517
	a_1 ω_4	1203	1209	1208	1213	1209
	b_1 ω_5	1200	1202	1196	1199	1195
	b_1 ω_6	193	196	185	187	181
	b_2 ω_7	3218	3223	3220	3224	3219

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Isomer	Sym	cc-pVTZ	cc-pCVTZ	cc-pVQZ	cc-pCVQZ	cc-pV5Z
Quasi-linear HCCNH+ Figure 4 C _s	b_2	ω_8	1153	1155	1154	1154
	b_2	ω_9	225	230	223	220
	A'	ω_1	3650	3651	3655	3652
	A'	ω_2	3297	3302	3303	3304
	A'	ω_3	2049	2051	2048	2047
	A'	ω_4	1187	1195	1200	1203
	A'	ω_5	452	452	445	442
	A'	ω_6	394	394	379	374
	A'	ω_7	318	305	276	259
	A''	ω_8	438	440	438	437
	A''	ω_9	337	343	332	330