Accurate *ab initio* Quartic Force Fields of Cyclic and Bent HC$_2$N Isomers

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Abstract

Highly correlated *ab initio* quartic force field (QFFs) are used to calculate the equilibrium structures and predict the spectroscopic parameters of three HC$_2$N isomers. Specifically, the ground state quasilinear triplet and the lowest cyclic and bent singlet isomers are included in the present study. Extensive treatment of correlation effects were included using the singles and doubles coupled-cluster method that includes a perturbational estimate of the effects of connected triple excitations, denoted CCSD(T). Dunning's correlation-consistent basis sets cc-pVXZ, X=3,4,5, were used, and a three-point formula for extrapolation to the one-particle basis set limit was used. Core-correlation and scalar relativistic corrections were also included to yield highly accurate QFFs. The QFFs were used together with second-order perturbation theory (with proper treatment of Fermi resonances) and variational methods to solve the nuclear Schrödinger equation. The quasilinear nature of the triplet isomer is problematic, and it is concluded that a QFF is not adequate to describe properly all of the fundamental vibrational frequencies and spectroscopic constants (though some constants not dependent on the bending motion are well reproduced by perturbation theory). On the other hand, this procedure (a QFF together with either perturbation theory or variational methods) leads to highly accurate fundamental vibrational frequencies and spectroscopic constants for the cyclic and bent singlet isomers of HC$_2$N. All three isomers possess significant dipole moments, 3.05D, 3.06D, and 1.71D, for the quasilinear triplet, the cyclic singlet, and the bent singlet isomers, respectively. It is concluded that the spectroscopic constants determined for the cyclic and bent singlet isomers are the most accurate available, and it is hoped that these will be useful in the interpretation of high-resolution astronomical observations or laboratory experiments.

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I. INTRODUCTION

During the last 40 years a number of polyenes, in particular cyanopolyenes (HC_3N, HCN, HC_7N, HC_9N, $HC_{11}N$, HC_4N)[1-7] have been detected in interstellar space by radio telescopes. This class of molecule may play an important role in astronomy and interstellar chemistry due to their astrophysical abundance and rather large dipole moments.

One of the cyanopolyenes, the molecule HC_2N can be present as many isomers with different geometries such as a linear, bent, or cyclic structure in either a singlet or triplet electronic state. While the molecule that was detected in 1991[8] has a bent structure and a triplet electronic state, there is reason to expect that other isomers will be low lying. For example, the isoelectronic molecule, C_3H_2, possesses a cyclic singlet ground state (cyclopropenylidene)[9,10], and has been observed in many astronomical observations[11-13]. Further, cyclopropenylidene is essentially the smallest aromatic molecule, and thus the singlet, cyclic HC_2N molecule is the smallest aromatic molecule that contains a nitrogen atom. Thus one can make the follow analogy: cyclopropenylidene is thought to be formed by dissociative recombination of an electron with cyclic $C_3H_3^+$, which also commonly exist in two forms – cyclopropenyl cation and propargyl cation[14]. Hence the cyclic isomer of HC_2N could be formed by the same pathway – that is due to dissociative recombination of an electron to cyclic $H_2C_2N^+$ (which is the lowest energy form).

In addition, the cyclic HC_2N isomer was found to be an intermediate between the interconversion of the bent HCCN and the unknown bent HCNC on the hypersurface of neutral, anionic and cationic species where the barriers are feasible[15]. Thus the cyclic singlet isomer seems to be a good candidate for astrophysical detection, considering these various possible formation pathways and its large dipole moment. The purpose of our study is to provide accurate spectroscopic constants for the low-lying singlet isomers of cyclic and bent HC_2N which may be used to assign spectra from either high-resolution astronomical observations or laboratory experiments, and we include the quasilinear triplet ground state for comparison.

Previously, HC_2N has been the subject of many experimental and theoretical analyses. The main focus has been to determine the molecular structure of the ground state, that is, whether it is linear, quasilinear, or bent.

Early experiments by Dendramis and Leroi using matrix infrared (IR) and ultraviolet (UV) spectroscopy concluded the radical to be linear by performing a normal mode analysis[16]. Additionally,

Saito et. al[17] found a triplet linear ground state in the absence of K type satellite transitions, and these results were in agreement with earlier electron paramagnetic resonance (EPR)[18-21] studies. However, in 1990 Brown et. al slightly modified their previous experimental conclusion based on a microwave study, suggesting a quasilinear structure instead of a strict linear one[22]. More experimental evidence for the quasilinearity of cyanocarbene came from analysis of high-resolution rotational[23] and vibrational[24-29] spectra. McCarthy and co-workers[23] estimated the transition energies from relative intensity measurements in the microwave region. From that analysis they concluded that the HC_2N radical is not a normal bent or a well-behaved linear molecule. In addition, Morter et al.[24] through the high resolution infrared spectrum of HC_2N in the CH stretching region were able to deduce a very floppy HCX bending potential, which is characteristic of a quasilinear molecule.   The quasilinear nature of the triplet ground state of HC_2N has subsequently been studied further via photoelectron spectroscopy.[30]

Theoretical studies supported either a linear or quasilinear structure, where the difference between those two results was dependent on the level of theory. In 1987, Rice and Schaefer performed a multireference singles and doubles configuration interaction (MRSDCI) study on the triplet HC_2N, reporting that the bent-linear separation is only 0.8 kcal/mol[31]. Essentially the same value was obtained by Seidl and Schaefer[32] in 1992 using the coupled-cluster single and double excitation method that includes a perturbational estimate of connected triple excitations [CCSD(T)][33]. Malmqvist et al. used the complete-active-space self-consistent field (CASSCF) method[34] together with a polarized double zeta basis set (DZP) and found that the triplet cyanomethylene is bent[35] and more recently, Koput et al.[36] reported that the equilibrium structure of the molecule was found to be planar and bent using the coupled-cluster method, RCCSD(T), and basis sets cc-pVnZ (from double through-quintuple quality). In 2002, Nimlos et al.[30] performed *ab intio* and density functional theory calculations, mapping out the bending region and confirming the quasilinear nature of the ground state triplet.

Considering the results of the previous experimental and theoretical studies, there is consensus that the ground electronic state is a bent triplet with a quasilinear bending mode.   However, as discussed above, there is reason to expect that in astrophysical environments other isomers will exist, and to our knowledge there is no experimental evidence for these.   Aoki et al.[37] have studied various singlet and triplet isomers of HC_2N and were able to estimate the relative energies using the QCISD(T) method with the D95** basis set plus single point energy calculations at the SDCI+Q level

of theory with the general contraction scheme of the ANO basis set. Therein he found that the most stable singlet species corresponds to the cyclic isomer (7.7 kcal/mol above the ground state quasilinear triplet structure), followed by the bent singlet isomer at 13.8 kcal/mol above the quasilinear triplet cyanomethylene. In 2002, Park and Lee[38] studied isomers of HC_2N, but limited themselves to triplet electronic states.   More recently, Kassaee et al.[39] studied the singlet and triplet isomers of HC_2N and found that the only low energy isomers are the ground state quasilinear triplet, the cyclic singlet, and the bent singlet HCCN isomer.   Specifically, using G2 theory they found that the cyclic singlet was 5.0 kcal/mol higher in energy that the ground state triplet, and the bent singlet isomer is 7.6 kcal/mol higher than the ground state triplet.   All other isomers were at least 32 kcal/mol higher in energy than the ground state triplet.

The present work was undertaken with the aim of computing high-quality *ab initio* quartic force fields (QFFs) and spectroscopic constants for the cyclic and bent structures of cyanocarbene in the $^1A'$ electronic state.   We also compute a high-quality QFF for the $^3A'$ ground state bent structure and all of these possess C_s symmetry. The quasilinear triplet ground state is included for two reasons: 1) to determine how well a QFF performs for a quasilinear species, and 2) to compare with the bent singlet isomer and determine whether it also has a quasilinear nature.   We used the CCSD(T) method to compute highly accurate spectroscopic constants and vibrational fundamental frequencies for these isomers. To our knowledge, *ab initio* QFFs have never been reported for any of these electronic states of HC_2N. The theoretical approach is described in the next section, followed by results, discussion and conclusions.

II.   THEORY AND COMPUTATIONAL DETAILS

For the two singlet electronic states, we used the closed-shell CCSD(T) method that is based on restricted Hartree-Fock (RHF) molecular orbitals[40-42]. For the triplet electronic state, we used the spin-restricted coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T)[43,44] based on RHF molecular orbitals as a reference wave function. All electronic structure calculations were performed with the MOLPRO 2008.1 program[45]. The one-particle basis sets employed are the correlation-consistent polarized valence basis sets, cc-pVnZ[46], where n=T, Q, and 5.

The QFFs of cyanocarbene were calculated using the procedure outlined in Ref. 47. The reference geometry in this case was obtained by adding a core-correlation correction to the structure optimized at the CCSD(T)/cc-pV5Z or RCCSD(T)/cc-pV5Z level of theory. As outlined in Ref. 47, a

grid of points is constructed about the reference geometry and all electronic structure calculations are performed for each of these points. For each point, we include a scalar relativity correction, by means of the second order Douglas-Kroll-Hess method[48-50], and a core correlation correction, estimated using the Martin-Taylor core-correlation basis set[51]. The coupled cluster energies were extrapolated to the one-particle basis set limit using a two-point (1) and three-point (2) extrapolation formula[52,53]. Both formulas were tested in order to determine the best QFFs. The exact formulas we used are given here:

$$E(l) = E(\infty) + B(l)^{-3} \qquad (1)$$

$$E(l) = E(\infty) + B(l+1/2)^{-4} + C(l+1/2)^{-6} \qquad (2)$$

where l is the highest angular momentum used in the one particle basis set. The electronic energies of all points that have been used to fit the QFFs were computed in the same way, and the formula is given here:

$$E(l) = E(TQ5) + E(rel - nrel) + E(mtcc - nmtcc) \quad (3)$$

where $E_{(TQ5)}$ represents CCSD(T) or RCCSD(T) energies extrapolated to the one-particle basis set limit, the second term represents the contribution due to scalar relativistic effects, and the last term represents the core-correlation correction.

The grids for each electronic state consisted of 743 of distinct geometries and these were used to fit our best QFFs. These QFFs produced a new reference geometry called the "real minima," or in other words, the geometry where the gradient terms are zero. As described in the procedure outlined in Ref. 47, the QFFs are then transformed to the "real minima" and these represent the final QFFs. The sum of the squared residuals from the least squares fitting procedure were $1.3*10^{-16}$ a.u^2 for the 743 bent-triplet geometries, $1.2*10^{-16}$ for the bent-singlet and $1.0*10^{-16}$ a.u^2 for the 743 cyclic-singlet geometries. This level of precision is required in order to obtain reliable cubic and especially quartic force constants. The QFFs were used in the second-order vibrational perturbation theory program (PT) SPECTRO[54] to obtain spectroscopic constants and fundamental vibrational frequencies.

The simple internal coordinates, i.e, HC1, C1C2, C2N, for the quasilinear triplet and bent singlet structures are given in Figure 1a and 1b, respectively, while the formula for the two quasilinear

5

coordinates (A1 and A2) are:

$$\alpha^x_{abcd} = \cos\tau_{abcd} \cdot \sin\phi_{bcd}$$

$$\alpha^y_{abcd} = \sin\tau_{abcd} \cdot \sin\phi_{bcd}$$

where

$$\sin\tau_{abcd} = \vec{e}_{ba} \cdot (\vec{e}_{cb} \times \vec{e}_{cd})/(\sin\phi_{abc} \cdot \sin\phi_{bcd}), \quad -\pi/2 < \tau_{abcd} < 3\pi/2$$

The reference structure for the quasilinear triplet was obtained at the RCCSD(T)/cc-pV5Z level of theory, corrected for core-correlation, where the values are HC1=1.0699 Å, C1C2=1.3274 Å, C2N=1.1850 Å, A1($\angle$HC1C2)=145.07 and A2($\angle$C1C2N)=175.46°. The reference structure for the bent singlet was obtained using the CCSD(T)/cc-pV5Z level of theory, again corrected for core-correlation, which gave HC1 = 1.0960 Å, C1C2 = 1.3864 Å, C2N = 1.1756 Å, A1($\angle$HC1C2) = 109.65° and A2($\angle$C1C2N) = 172.42°.

For the cyclic isomer we choose the HC1, C1N2, C1C3 bond distances and bond angles A1($\angle$HC1N2), A2($\angle$N2C1C3), shown in figure 1c. The angle γ refers to the out-of-plane bending angle for the H-C bond with respect to the plane defined by the three C and N atoms, the formula is here:

$$\gamma_{abcd} = \sin^{-1}[\vec{e}_{ba} \cdot (\vec{e}_{bc} \times \vec{e}_{bd})/\sin\phi_{bcd}]$$

where $\vec{e}$ is a unit vector defined as $\vec{e}_{ab} = \vec{e}_b - \vec{e}_a$ with **b** at the center and **a** as H atom.

The reference structures was determined at the CCSD(T)/cc-pV5Z level of theory (corrected for core-correlation), where the values are HC1 = 1.0762 Å, C1N2 = 1.2937 Å, C1C3 = 1.3976 Å and A1($\angle$HC1N2) = 138.05°, A2($\angle$N2C1C3) = 62.11°.

Spectroscopic constants have been determined using standard second-order asymmetric top perturbation theory (PT) using the SPECTRO program[54]. Vibrational fundamental frequencies are also determined variationally (VCI), using the MULTIMODE program[55,56]. For the cyclic and bent singlet structures, tests were performed to ensure that the VCI calculations are converged to better than 1 cm^{-1} with respect to mode coupling (five mode coupling was used) and the size of the VCI basis set. As discussed more below, for the triplet state, the quasilinear nature causes a problem with the VCI calculations. For the variational calculations, QFFs are transformed to a Morse-cosine coordinate system[57]. All electronic structure calculations were performed with the MOLPRO

6

program suite[45].

III. RESULTS AND DISCUSSIONS

A. Equilibrium Structures, Harmonic Frequencies and Equilibrium Rotational Constants

The Tables 1-3 summarize the equilibrium geometries, equilibrium rotational constants, and harmonic vibrational frequencies for the quasilinear triplet, bent singlet and cyclic singlet, respectively. We have included various methods in order to compare different approximations. "2-pt" or "3-pt" are used to represent to the one particle basis set limit based on either the two-point (1) or three-point (2) formula described in the previous section, "core" for core correlation, "rel" for the scalar relativistic correction, "PT" for the second-order perturbation theory using the SPECTRO program, and "VCI" for vibrational configuration interaction using the MULTIMODE program. The results computed with the two-point, 2-pt(tz,qz), extrapolation formula are reported first, then we compare with the 2-pt(qz,5z) results and the three-point extrapolation formula, 3-pt(tz,qz,5z), results, followed by the 5z basis set (which means the cc-pv5Z basis) plus core-correlation and relativistic corrections.

The molecular structure of the quasilinear triplet and bent singlet are shown in Figures 1a and 1b, respectively. Here, bond distance coordinates are HC1, C1C2, and C2N, with two in-plane bending angles, ∠HC1C2 and ∠C1C2N, denoted respectively by A1 and A2. The coordinates for the cyclic singlet structure were defined in the previous section and are shown in Figure 1c.

Compared to the reference structure used to set up the generation of the QFFs, examination of our various results, we note that the best match is found at the 3-pt(tz,qz,5z)+core+rel level of theory, where the differences are less than 0.001 angstrom, between bond distance HC1, C1C2, and C2N, and 0.1 to 0.01 degrees, for angles A1 and A2. The same result is observed for all three isomers studied here as found by examining the results in Tables 1-3. As the reference geometry is confirmed to be very close to the minimum on our best QFF (3-pt(tz,qz,5z)+core+rel), we are able to assert that the highest level of theory QFF reported here, denoted as 3-pt(tz,qz,5z)+core+rel, should yield near quantitative accuracy.

For all three isomers, comparison of the 2-pt(tz,qz), 2-pt(qz,5z), and 3-pt(tz,qz,5z) results shows small differences between the first two methods and very small differences between the latter two approaches, consistent with our earlier studies[47,58]. That is, the difference between the 2-pt and 3-pt extrapolations is relatively small provided both include the 5z basis set, but the 2-pt(tz,qz) results are noticeably less converged. We note, however, that the 3-pt(tz,qz,5z) results are consistent with being

slightly more converged with respect to one-particle basis set completeness, and thus the 3-pt(tz,qz,5z) approach is preferred.

Comparison of the 3-pt(tz,qz,5z) and 3-pt(tz,qz,5z)+core results for all three isomers shows that core-correlation has the expected result of shortening bond lengths and increasing the stretching harmonic frequencies somewhat. Comparison of the 3-pt(tz,qz,5z)+core and 3-pt(tz,qz,5z)+core+rel results shows that scalar relativistic effects are relatively small for all three isomers, with the largest effect on a bond distance being only 0.0002 Å, and the largest effect on a harmonic frequency being less than 3 cm^{-1}. It is interesting that comparison of the 5z+core+rel and 3-pt(tz,qz,5z)+core+rel results for all three isomers shows relatively small differences, the effect on any harmonic frequency being less than 3 cm^{-1}, for example. This shows that for these molecular isomers, at least, convergence with respect to the one-particle basis set limit is rapid, which is not always the case. Our most complete results are those obtained at the 3-pt(tz,qz,5z)+core+rel level of theory, and the remainder of the discussion will focus on these.

In Table 1, our best results at the 3-pt(tz,qz,5z)+core+rel level are in good agreement with the available experimental data for the C1C2, and C2N bond lengths. With respect to the experimental HC1 bond distance, Brown et al.[22] found that this bond is shorter than all known C-H bond lengths previously determined in other hydrocarbon molecules, suggesting that an accurate study was necessary to understand the HCCN structure. However, they obtained this short CH bond distance by assuming a linear structure, but later studies have shown that the triplet ground state of HCCN is best viewed as quasilinear[23-29], and our results support that conclusion.

Comparison of our best equilibrium structure and harmonic frequency of the quasilinear triplet isomer with previous theoretical results shown in Table 1, not surprisingly we find better agreement with the study by Koput et al.[36] who used the CCSD(T)/cc-pVQz level of theory. The other previous theoretical results were obtained with the CCSD(T) [or QCISD(T)] method, but using only a polarized double zeta (DZP) quality basis set, leading to bond distances that are too long and harmonic stretching frequencies that are too low. While the differences between our best results and those of Koput et al.[36] are relatively small, the 3-pt(tz,qz,5z)+core+rel values for the equilibrium structure and harmonic frequencies should be the most reliable determined to date.

For the bent singlet and cyclic singlet isomers in Tables 2 and 3, respectively, there are no experimental data available, and the only previous theoretical results were obtained at the QCISD(T)/D95** level of theory[59] (Kassaee et al.[39] did not report equilibrium structures nor harmonic frequencies). Thus their bond distances are much too long and the stretching harmonic frequencies are

too high relative to our best results. The equilibrium structures and harmonic frequencies obtained here with the 3-pt(tz,qz,5z)+core+rel level of theory should be the most reliable available for the bent and cyclic singlet isomers of HCCN.

In the following section, we present and discuss our findings for the anharmonic fundamental vibrational frequencies and other spectroscopic constants of the quasilinear triplet, bent singlet, and cyclic singlet isomers of HCCN.

B. Fundamentals frequencies, Effective rotational constants and quartic and sextic centrifugal distortion constants.

Effective rotational constants, centrifugal distortion constants and fundamental vibrational frequencies are given in Tables 4 through 6 for the quasilinear triplet, bent singlet, and cyclic singlet isomers, respectively. These data allow us to compare different approximations applied in this work. For the quasilinear triplet isomer, see Table 4, the C_0 effective rotational constant from our best purely *ab initio* QFF is only 7 MHz lower than the experimental value obtained by McCarthy et al.[23] and Saito et al.[17], while the theoretical result of Mladenovic et al.[59] underestimates the experimental value by more than 47 MHz. Further, agreement between experiment and our best QFF for the B_0 vibrationally averaged rotational constant is also very good, being only 16 MHz too high. This agreement between the predicted and observed values of the effective B_0 and C_0 rotational constants is a strong confirmation of the accuracy of the calculated spectroscopic constants of cyanocarbene in this work. On the other hand, we note that for the quasilinear triplet isomer, there is an extremely large difference between the A_e and A_0 values, suggesting a very large vibrational contribution. This result can be attributed to the large corrections from the quartic and sextic centrifugal distortion constants, but this probably means that 2nd-order vibrational perturbation theory is not adequate. This result is consistent with the experimental studies showing that the triplet ground state is a quasilinear molecule. Interestingly, the bent singlet does not exhibit this behavior. That is, there is not an overly large vibrational contribution to the A_0 vibrationally averaged rotational constant as shown in Table 5. Quartic and sextic centrifugal distortion constants are also included in Tables 4-6. We note that for the triplet isomer, the computed value for D_J from our best QFF, 3-pt(tz,qz,5z)+core+rel, agrees very well with the experimental value of 0.0041 MHz given by Saito et al.[17]. The theoretical results presented here for the vibrationally averaged rotational constants of the bent and cyclic singlet isomers should facilitate future high-resolution astronomical or experimental analyses.

Table 4 shows the vibrational fundamental frequencies for the quasilinear triplet isomer using

the PT and VCI methods applied in this work. Several resonances have been detected in the PT analyses (indicated in the table) and these have been handled in the usual polyad formulation.[60] For the PT results, the agreement amongst the various approaches mostly mirrors that found for the harmonic frequencies. That is, the 2pt(qz,5z) results are similar to the 3pt(tz,qz,5z) values, while the 5z+core+rel quantities are similar to the 3pt(tz,qz,5z)+core+rel values. The one small exception, is that the variation for ν_4 amongst the various methods is larger, as large as 8.4 cm^{-1} between 5z+core+rel and 3pt(tz,qz,5z)+core+rel. The differences between PT and VCI, however, are significantly larger than we normally see, even for the CH stretching mode, ν_1. In fact, the discrepancy between PT and VCI is very large for ν_4 through ν_6, suggesting that a QFF is not really adequate to describe properly the anharmonic nature of the ground state triplet isomer. These results are, of course, consistent with the quasilinearity of the triplet state that has been noted previously. Agreement between our best fundamental vibrational frequencies, those arising from the 3pt(tz,qz,5z)+core+rel QFF, and the best previous theory from Mladenovic et al.[59] is mixed. The PT value for ν_1 agrees reasonably well (difference of only 3.7 cm^{-1}), but for υ_2 and υ_3 the agreement is less good, with differences of 10.9 and 19.3 cm^{-1}, respectively. On the other hand, if we compare our VCI results we find that the agreement for υ_3 is reasonable, but the agreement for υ_1 and υ_2 is poor, especially for υ_2 where we find a strong coupling with another state. Comparison of our best PT fundamental vibrational frequencies with experiment for the stretching modes (υ_1, υ_2, and υ_3) shows reasonable agreement with differences on the order of 10-20 cm^{-1}, though nowhere near as good as we have come to expect with this level of theory. The experimental results themselves for υ_4 through υ_6 are significantly varied, and so it is not a surprise that our results are in poor agreement. Again, all of this supports the previous conclusion that the ground state triplet isomer is a quasilinear molecule with significant coupling of its vibrational degrees of freedom, and our results show definitively that a QFF does not describe enough of the potential energy surface near the minimum to describe properly the vibrational fundamental frequencies. This is true even for VCI calculations where the QFF is transformed into a Morse-cosine coordinate system with better limiting behavior, or rather for the bending coordinate the cosine function ensures that the potential is multi-welled. This is in contrast to our earlier study on HNO, which possesses a very anharmonic H-N stretching motion.[60] There, the VCI calculations with a QFF transformed into the Morse-cosine coordinate system performed very well even though the PT results were relatively poor.

Tables 5 and 6 contain the vibrationally averaged rotational constants, the quartic and sextic centrifugal distortion constants, and the fundamental vibrational frequencies for the bent singlet and

the cyclic singlet isomers, respectively. Comparison of the PT results for the various levels of theory included shows similar behavior to that found for the equilibrium structures and harmonic frequencies. That is, differences between 2pt(qz,5z) and 3pt(tz,qz,5z) are small, while differences between 2pt(tz,qz) and 3pt(tz,qz,5z) are larger; for most vibrational fundamentals, differences between 5z+core+rel and 3pt(tz,qz,5z)+core+rel are relatively small, suggesting that one-particle basis set convergence is relatively rapid for these isomers; and scalar relativistic effects are relatively small (the largest effect on a given fundamental frequency is 1.5 and 1.4 cm^{-1} for the bent and cyclic isomers, respectively). Moreover, the agreement between the PT and VCI methodologies for the 3pt(tz,qz,5z)+core+rel QFF is very good for all six fundamental vibrational frequencies for both the bent and cyclic singlet isomers, with the largest differences being 9.5 cm^{-1} and 4.0 cm^{-1} for υ_5 and υ_2 of the cyclic singlet, respectively. The largest difference for the bent singlet is only 1.4 cm^{-1} for υ_4. There are no high-resolution experimental data with which to compare for the bent and cyclic singlet, but the agreement between PT and VCI together with the evidence that one-particle basis set convergence is nearly complete, suggests that the fundamental vibrational frequencies and other spectroscopic constants obtained from the 3pt(tz,qz,5z)+core+rel QFF should be very reliable. It is hoped that these will be useful in the interpretation of future high-resolution spectra obtained either from an astronomical observation or a laboratory experiment.

C. Force constants, anharmonic constants, and vibration-rotation interaction constants.

For completeness, the asymmetric top anharmonic constants for the quasilinear triplet, bent singlet, and cyclic singlet are presented in Tables 7-9, respectively, the quadratic, cubic and quartic force fields are given in Tables 10-12, respectively, and the α vibration-rotation interaction constants are given in Table 13. The respective 3pt(tz,qz,5z)+core+rel QFFs were used to generate the data in Tables 7-13. Also, constants which are affected by any included Fermi and/or Coriolis resonances are indicated in the Tables. As indicated, the QFFs and spectroscopic constants for the bent and cyclic singlet isomers should be very accurate and reliable. For the triplet isomer, constants involving the stretching modes will be more reliable than those involving bending or torsional motions, but higher-order force constants (i.e., beyond a QFF) are needed in order to describe more accurately the rovibrational properties of this isomer. Nonetheless, the 3pt(tz,qz,5z)+core+rel QFF we present for the triplet isomer should be the most accurate available and it should be a good place to start for construction of a larger potential function.

D. Isomeric energy differences and dipole moments.

Finally, the relative energies of the three HC_2N isomers included in the present study are collected in Table 14 together with their dipole moment values. The relative energies are presented with and without correction for zero-point energies. The zero-point energies are taken from the VCI calculations, but there was essentially no difference if PT zero-point energies were used instead. The first point to note is that consistent with earlier studies, we find the triplet isomer to be the lowest in energy, followed by the cyclic singlet 7.8 kcal/mol higher in energy (zero-point energies included), and then the bent singlet 11.1 kcal/mol higher in energy relative to the ground state triplet. The energy differences reported in Table 14 should be the most reliable available for these three isomers. Further, as there is likely a large barrier preventing interconversion, all three isomers should be long lived in an astrophysical environment with low collision rates and with negligible levels of ionizing radiation.

It is hoped that the data contained herein for the ground state triplet, and the cyclic and bent singlet isomers will aid in the interpretation of future laboratory experiments or astronomical observations. The large dipole moment values of 3.05 D, 3.06 D, and 1.71 D (computed at the CCSD(T)/cc-pVQZ level of theory) for the triplet, cyclic singlet, and bent singlet, respectively, mean that all three isomers should be easily observable in rotational spectroscopy provided there is a larger enough population.

IV. CONCLUSIONS

In the present contribution, we have characterized the quasilinear triplet, bent singlet, and cyclic singlet HC_2N isomers and determined their molecular properties. We have calculated a series of highly accurate *ab initio* QFFs based on the CCSD(T) level of theory together with extrapolation to the one-particle basis set limit and inclusion of core-correlation and scalar relativistic corrections. These are the most accurate purely *ab initio* QFFs available for these HC_2N isomers.

Consistent with earlier studies, we find that the most stable conformer of HC_2N is the quasilinear triplet cyanomethylene (figure 1a), followed by the cyclic singlet isomer (7.8 kcal/mol higher in energy), and then the bent singlet isomer 11.1 kcal/mol above the ground state triplet.

It was known that the ground state bent triplet species is quasilinear, and we find that a QFF is not adequate for describing all of the fundamental vibrational frequencies and spectroscopic constants. Specifically, the purely stretching fundamental frequencies and analogous spectroscopic constants are reasonably well described by 2nd-order perturbation theory (there is still a small effect due to coupling with the quasilinear modes), but the bending and torsion modes and related spectroscopic constants

are poorly described, especially those constants related to the A_0 rotational constant. Agreement with experiment for frequencies and spectroscopic constants involving the stretching modes is reasonable, while for the bending and torsion modes the agreement is significantly degraded due to the quasilinear nature of the triplet state.   On the other hand, VCI calculations using the QFF transformed into a Morse-cosine coordinate system (which has better limiting behavior) are relatively poor, even for the stretching fundamentals, indicating that a QFF is not adequate.

Interestingly, however, both the cyclic and bent singlet isomers are well described using a QFF. That is, the fundamental vibrational frequencies are well behaved as evidenced by the very good agreement between PT and VCI for solving the nuclear Schrödinger equation. The spectroscopic constants also exhibit reasonable behavior, with the A_0 constant having a reasonable value, but also consistent from one level of theory to another.

Fundamental vibrational frequencies and rovibrational spectroscopic constants from our best QFF, labeled 3pt(tz,qz,5z,)+core+rel, should be the most reliable available for the cyclic and bent singlet isomers, and it is hoped that these will be useful in the interpretation of a spectrum from a high-resolution astronomical observation or a laboratory experiment. Moreover, some of the data we report here for the quasilinear triplet species, such as the equilibrium structure and the harmonic frequencies, should also be the most accurate available – but the anharmonic analysis is lacking due to inadequacies in the use of a QFF for this quasilinear isomer.

Dipole moments were calculated using the best equilibrium geometry for each isomer at the CCSD(T)/cc-pVQZ level of theory (RCCSD(T)/cc-pVQZ for the ground state triplet). All three isomers possess a large dipole moment (3.05D, 3.06D, and 1.71D, for the triplet, cyclic singlet, and bent singlet isomers, respectively). Thus, all three should be easily observed and identified using modern telescopes such as Herschel, SOFIA, or ALMA, provided there is sufficient numbers of these isomers present.

 The quasilinear triplet isomer of HC_2N has already been identified in astronomical observations, but the cyclic and bent singlet geometrical isomers are also good candidates for astrophysical observation by microwave and infrared spectroscopy. This is due to the fact that both the cyclic and singlet isomers possess rather large dipole moments, but more importantly the cyclic isomer is isoelectronic to cyclopropenylidene, which has been identified in many different astrophysical environments. Moreover, the major formation pathway for cyclopropenylidene is thought to occur through dissociative attachment of an electron to the protonated form, and the analogous pathway for HC_2N again favors the cyclic isomer since the most stable form of $C_2H_2N^+$ is a cyclic isomer.

Due to the high probability of the existence of these isomers in astrophysical environments, especially the cyclic form, we have determined highly accurate QFFS and from these their fundamental vibrational frequencies and spectroscopic constants to aid in the interpretation of future astronomical observations from ALMA, Herschel, or SOFIA, or high-resolution laboratory experiments.

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Figure 1: Structure of 3 HC_2N Isomers. (a) X^3A'' Ground state triplet; (b) X^1A' Bent singlet; (c) X^1A' Cyclic singlet

(a)   (b)   (c)

Table 1. Equilibrium geometries (Å, degree), equilibrium rotational constants (MHz) and harmonic frequencies (cm^{-1}) of bent-triplet HC$_2$N at RCCSD(T) level of theory (see text for more details).

Ground State triplet	This work						Previous work		
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z) +core+rel	Exp	Theory	
HC1	1.0702	1.0704	1.0705	1.0691	1.0689	1.0689	0.998[a]	1.069[b]	1.082[c]
C1C2	1.3288	1.3299	1.3303	1.3273	1.3269	1.3267	1.323[a]	1.328[b]	1.357[c]
C2N	1.1862	1.1872	1.1876	1.1853	1.1852	1.1850	1.195[a]	1.186[b]	1.208[c]
A1(HC1C2)	144.89	144.61	144.53	144.99	145.03	144.95	-----	144.9[b]	147.0[c]
A2(C1C2N)	175.41	175.37	175.36	175.44	175.48	175.45	-----	175.4[b]	174.6[c]
A_e	1681210	1656675	1649291	1693550	1697149	1690595			1337775[d]
B_e	11037	11022	11016	11058	11061	11065			10687[d]
C_e	10965	10949	10943	10986	10989	10993			10603[d]
ω_1(A')	3343.8	3341.6	3341.0	3350.0	3349.8	3349.0			3340[b] 3333[d]
ω_2(A')	1865.8	1864.5	1864.0	1869.0	1870.1	1869.2			1863[b] 1818[d]
ω_3(A')	1144.3	1141.7	1140.8	1145.6	1146.2	1145.8			1139[b] 1123[d]
ω_4(A')	574.5	578.7	580.4	574.7	571.3	572.8			581[b] 689[d]
ω_5(A')	384.5	383.5	383.4	385.4	384.4	384.2			380[b] 376[d]
ω_6(A'')	427.0	426.7	426.6	428.8	429.4	428.8			425[b] 408[d]

a) From microwave spectra ref. [22] considered as linear structure;
b) From ref. [36] at CCSD(T)/cc-pVQZ level of theory;
c) From ref. [32] at CCSD(T)/DZP; d) From ref. [37] at QCISD(T)/D95** level of theory.

Table 2. Equilibrium geometries (Å, degree), equilibrium rotational constants (MHz) and harmonic frequencies (cm^{-1}) of bent-Singlet HC$_2$N at CCSD(T) level of theory (see text for more details).

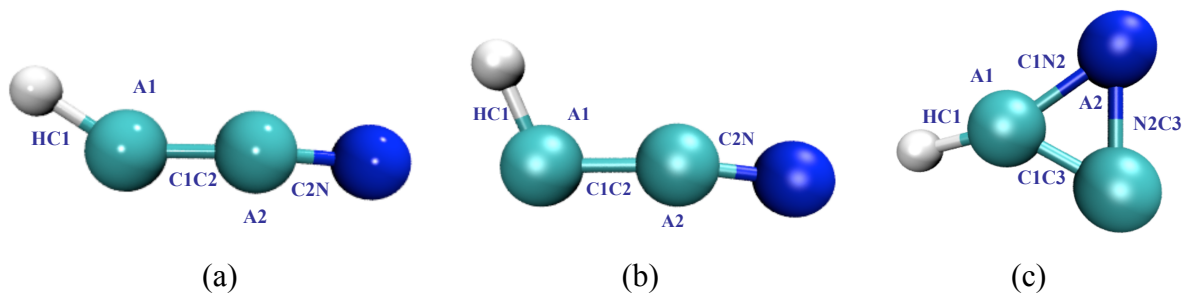| Bent Singlet	This work						Previous work
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z)+ core+rel	Theory
HC1	1.0974	1.0976	1.0977	1.0961	1.0957	1.0958	1.106[a]
C1C2	1.3888	1.3897	1.3901	1.3865	1.3858	1.3858	1.419[a]
C2N	1.1761	1.1773	1.1778	1.1754	1.1754	1.1752	1.198[a]
A1(HC1C2)	109.48	109.43	109.40	109.59	109.71	109.66	107.4[a]
A2(C1C2N)	172.36	172.35	172.35	172.39	172.44	172.41	171.6[a]
A_e	537230	536569	536177	539478	54020	540376	510262[a]
B_e	11081	11064	11057	11105	11109	11112	10725[a]
C_e	10857	10840	10833	10881	10886	10888	10505[a]
ω_1(A')	3066.1	3064.1	3063.2	3071.3	3074.3	3072.8	
ω_2(A')	2065.0	2062.0	2061.1	2068.5	2068.8	2067.9	
ω_3(A')	1057.1	1057.1	1057.1	1060.2	1060.7	1060.7	
ω_4(A')	971.7	973.2	973.5	974.2	974.5	974.9	
ω_5(A')	293.7	292.9	292.9	295.7	295.6	294.6	
ω_6(A'')	429.6	427.8	427.3	430.7	430.7	430.2	

a) From ref. [37] at QCISD(T)/D95** level of theory.

Table 3. Equilibrium geometries (Å, degree), equilibrium rotational constants (MHz) and harmonic frequencies (cm^{-1}) of cyclic-Singlet HC$_2$N.(see text for more details).

Cyclic singlet	This work						Previous work
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z)+ core+rel	Theory
HC1	1.0774	1.0775	1.0775	1.0762	1.0761	1.0761	1.083[a]
C1N2	1.2943	1.2959	1.2964	1.2937	1.2935	1.2935	1.314[a]
N2C3	1.4089	1.4108	1.4116	1.4085	1.4075	1.4077	1.436[a]
C1C3	1.3988	1.4003	1.4008	1.3974	1.3971	1.3969	1.422[a]
A1(HC1N2)	137.98	137.95	137.93	138.02	138.06	138.04	137.8[a]
A1(C1N2C3)	62.15	62.14	62.13	62.11	62.13	62.11	62.09[a]
A_e	40835	40726	40684	40842	40883	40872	39493[a]
B_e	34647	34582	34556	34722	34732	34741	33615[a]
C_e	18744	18702	18685	18767	18779	18779	18159[a]
$\omega_1(A')$	3263.1	3262.4	3262.2	3268.8	3269.2	3268.5	
$\omega_2(A')$	1611.4	1607.3	1606.0	1613.3	1614.2	1612.9	
$\omega_3(A')$	1324.3	1320.5	1319.4	1326.5	1326.2	1325.7	
$\omega_4(A')$	1035.9	1034.0	1033.2	1036.3	1037.9	1037.0	
$\omega_5(A')$	845.1	844.8	844.5	848.4	850.2	849.6	
$\omega_6(A'')$	910.2	908.9	908.5	912.3	911.8	911.9	

a) From ref [37] (QCISD(T)/D95**).

Table 4. Rotational constants, vibrationally averaged structure (Å, degree), quartic D and sextic H centrifugal distortion constants (MHz) and vibrational fundamentals frequencies (cm^{-1}) computed on selected QFFs with a second order PT(S reduced Hamiltonian) of the ground state triplet HC$_2$N.

Ground State triplet	PT						VCI	Previous work	
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z) +core+rel	3-pt (tz,qz,5z) +core+rel	Experiment	Theory
A_o	2586574	2518363	2496121	2611229	2632677	2614091		4350000[b]	
B_o	11016	11001	10995	11037	11040	11043		11027[b]	
C_o	10951	10935	10928	10972	10975	10979		10986.41[a]10986.4[b]	10938.6[e]
HC1	1.0681	1.0684	1.0686	1.0669	1.0666	1.0666			
C1C2	1.3202	1.3215	1.3221	1.3187	1.3182	1.3181			
C2N	1.1926	1.1925	1.1939	1.1917	1.1917	1.1915			
A1(HC1C2)	150.35	148.22	149.75	150.45	150.61	150.49			
A2(C1C2N)	175.77	175.70	175.71	175.80	175.84	175.81			
$10^{10}H_J$	-4.8164	-5.1048	-5.1889	5.1257	-5.1405	-5.1787			
H_K	8819.37	7823.79	7509.36	9170.48	9601.03	9266.62			
$10^6 H_{JK}$	-24.083	-22.765	-22.292	-24.450	-25.183	-24.780			
H_{KJ}	0.4180	0.3861	0.3748	0.4355	0.4546	0.4433			
$10^{10}h_1$	2.1872	2.1620	2.1475	2.1904	2.2312	2.2248			
$10^{11}h_2$	4.5841	4.6375	4.6370	4.5601	4.6372	4.6559			
$10^{11}h_3$	2.5398	2.5027	2.4804	2.5391	2.6037	2.5960			
D_J	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042		0.0041[b]	
D_K	58897.4	55082.1	53865.8	60321.2	61689.4	60484.5			
D_{JK}	2.6957	2.6450	2.6287	2.7399	2.7493	2.7397			
$10^3 d_1$	-0.0215	-0.0218	-0.0219	-0.0211	-0.0213	-0.0214			
$10^3 d_2$	-0.0058	-0.0058	-0.0058	-0.0058	-0.0058	-0.0058			
$\upsilon_1(A')$	3241.1	3236.9	3235.9	3244.6	3244.1	3243.2	3271.2	3229.0[c]- 3247[d]	3246.66[e]3245.2[f]
$\upsilon_2(A')$	1723.7	1725.1	1725.5	1723.2	1723.6	1722.8	1615.5[&]	1735[c]-1727, 1735,	1733.71[e]1851.0[f]
$\upsilon_3(A')$[#]	1157.8	1154.9	1153.9	1158.8	1159.8	1159.3	1177.4	1757[d]	1178.57[e]1113.9[f]
$\upsilon_4(A')$[a1]	292.3	298.6	302.1	285.0	274.4	276.6	305.8	1178[c]	610.4[f]
$\upsilon_5(A')$	487.0	489.5	490.2	488.1	489.5	489.0	556.2	458[c]-383[d]-365[a]	336.2[f]
$\upsilon_6(A'')$	480.3	477.4	476.8	478.3	477.4	476.8	561.4	369[c]-187[d]-145[a]	362.1[f]

a)From microwave spectra ref. [23]; b) From microwave spectra ref. [17]; c) From argon matrix IR spectra ref. [16] d) From High resolution infrared spectra ref. [25];e) From ref.[59] at MR-ACPF/cc-pVQZ; f) From ref. [35] at CASSCF/DZP. [#]υ_3 affected by resonance polyad with $2\upsilon_4$, $\upsilon_4+\upsilon_5$, υ_4, υ_5, $2\upsilon_5$, $2\upsilon_6$, ; [a2]Fermi resonance type 1 $\upsilon_4=2\upsilon_5$. [&] In resonance with another state at 1992.5 cm^{-1}.

Table 5. Rotational constants, vibrationally averaged structure (Å, degree), quartic D and sextic H centrifugal distortion constants (MHz) and vibrational fundamentals frequencies (cm^{-1}), computed on selected QFFs with a second order PT(S reduced Hamiltonian) of bent singlet HC$_2$N

Bent Singlet	PT						VCI
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z) +core+rel	3-pt (tz,qz,5z) +core+rel
A_o	540126	539186	538717	542306	543795	543130	
B_o	11069	11052	11045	11093	11098	11099	
C_o	10833	10816	10809	10857	10861	10863	
HC1	1.1065	1.1067	1.1069	1.1406	1.1048	1.1049	
C1C2	1.3910	1.3920	1.3924	1.3913	1.3881	1.3881	
C2N	1.1765	1.1777	1.1782	1.1755	1.1758	1.1756	
A1(HC1C2)	109.49	109.41	109.38	108.59	109.70	109.64	
A2(C1C2N)	172.44	172.43	172.43	172.46	172.52	172.49	
$10^9 H_J$	-1.9452	-1.9856	-1.9954	-1.9573	-1.9578	-1.9741	
H_K	0.4942	0.4802	0.4749	0.5040	0.5156	0.5083	
$10^6 H_{JK}$	2.4776	2.5099	2.5173	2.4845	2.4918	2.5012	
H_{KJ}	-0.0020	-0.0021	-0.0021	-0.0021	-0.0021	-0.0021	
$10^{11} h_1$	6.7268	6.5112	6.4392	6.7592	6.8086	6.7709	
$10^{10} h_2$	1.5934	1.5959	1.5957	1.5935	1.5925	1.5988	
$10^{11} h_3$	3.2622	3.2423	3.2350	3.2604	3.2545	3.2630	
D_J	0.0050	0.0050	0.0050	0.0051	0.0050	0.0051	
D_K	228.25	225.56	224.45	231.19	233.91	232.41	
D_{JK}	0.9403	0.9373	0.9360	0.9444	0.9461	0.9459	
$10^3 d_1$	-0.0868	-0.0868	-0.0868	-0.0867	-0.0864	-0.0867	
$10^3 d_2$	-0.0214	-0.0213	-0.0212	-0.0214	-0.0213	-0.0213	
$\upsilon_1(A')$[a1]	2928.8	2926.7	2925.8	2932.9	2935.3	2933.8	2934.9
$\upsilon_2(A')$[#]	2043.3	2045.1	2045.3	2048.7	2050.9	2050.7	2050.0
$\upsilon_3(A')$	1040.4	1042.5	1042.8	1044.4	1045.0	1046.9	1046.9
$\upsilon_4(A')$[a2]	949.1	956.8	958.3	953.8	957.5	958.4	957.0
$\upsilon_5(A')$	310.4	321.1	323.3	318.3	325.9	325.1	323.9
$\upsilon_6(A'')$	443.2	442.6	442.3	445.4	446.1	445.7	444.2

[a1] Fermi resonance type 2 $\upsilon_1= \upsilon_2+ \upsilon_4$.
[#] υ_2 affected by resonance polyad with $2\upsilon_3$, $2\upsilon_4$, $\upsilon_3+ \upsilon_4$
[a2] Fermi resonance type 1 $\upsilon_4= 2\upsilon_6$.

Table 6. Rotational constants, vibrationally averaged structure (Å, degree), quartic D and sextic H centrifugal distortion constants (MHz) and vibrational fundamentals frequencies (cm^{-1}) computed on selected QFFs with a second order PT(s reduced Hamiltonian) of cyclic singlet HC_2N

Cyclic Singlet	PT						VCI
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z) +core+rel	3-pt (tz,qz,5z)+ core+rel
A_o	40710	40599	40557	40715	40755	40744	
B_o	34414	34347	34322	34489	34497	34505	
C_o	18584	18541	18525	18607	18618	18618	
HC1	1.0798	1.0799	1.0800	1.0787	1.0786	1.0786	
C1N2	1.3005	1.3020	1.3026	1.2998	1.2997	1.2996	
N2C3	1.4152	1.4171	1.4179	1.4148	1.4138	1.4141	
C1C3	1.4066	1.4082	1.4087	1.4052	1.4050	1.4047	
A1(HC1N2)	137.87	137.84	137.84	137.93	137.97	137.94	
A2(C1N2C3)	62.22	62.21	62.20	62.18	62.20	62.18	
10^7H_J	-2.8738	-2.9026	-2.9074	-2.8896	-2.9053	-2.9132	
10^6H_K	18.495	18.533	18.596	18.619	18.153	18.336	
10^6H_{JK}	6.5936	6.6283	6.6488	6.6516	6.5510	6.6001	
10^6H_{KJ}	-21.723	-21.796	-21.876	-21.910	-21.399	-21.605	
$10^{10}h_1$	801.93	792.82	793.75	810.24	781.45	789.14	
$10^{10}h_2$	1886.4	1886.4	1885.4	1891.1	1892.1	1895.6	
$10^{10}h_3$	-347.91	-353.36	-357.60	-359.28	-337.83	-345.77	
D_J	0.0471	0.0469	0.0469	0.0470	0.0472	0.0472	
D_K	0.0904	0.0885	0.0876	0.0882	0.0902	0.0893	
D_{JK}	0.0954	0.0961	0.0966	0.0970	0.0949	0.0960	
d_1	-0.0263	-0.0263	-0.0263	-0.0264	-0.0264	-0.0264	
d_2	-0.0090	-0.0090	-0.0090	-0.0090	-0.0090	-0.0090	
$\upsilon_1(A')$[a1]	3122.7	3118.6	3117.4	3126.1	3125.8	3124.7	3126.0
$\upsilon_2(A')$[a2]	1571.1	1567.0	1565.7	1572.8	1573.9	1572.5	1576.5
$\upsilon_3(A')$	1292.0	1288.6	1287.6	1294.4	1294.1	1293.6	1294.1
$\upsilon_4(A')$	1012.5	1012.0	1011.6	1013.7	1015.9	1015.1	1014.4
$\upsilon_5(A')$	823.9	821.3	820.4	825.1	825.9	824.9	832.4
$\upsilon_6(A'')$	899.6	894.5	893.3	898.8	896.4	896.0	901.3

[a1]Fermi resonance type 1 $\upsilon_1 = 2\upsilon_2$;
[a2]Fermi resonance type 1 $\upsilon_2 = 2\upsilon_5$.

Table 7. Anharmonic constants (cm^{-1}) X_{ij} using second order PT of ground state triplet HC_2N

X_{ij}	3-pt(tz,qz,5z)+core+rel					
	1	2	3	4	5	6
1	-61.465					
2	13.944	-50.113				
3	-8.108	14.163*	-6.800			
4	31.217	-100.021*	29.339*	-94.294*		
5	-1.368	-12.715	4.792 *	-27.770 *	-1.187*	
6	-1.436	-7.656	6.595	18.391	86.801	-1.644

*)Constants are affected by Fermi resonance

Table 8. Anharmonic constants (cm^{-1}) X_{ij} using second order PT of bent singlet HC_2N

X_{ij}	3-pt(tz,qz,5z)+core+rel					
	1	2	3	4	5	6
1	-66.238					
2	2.655*	-14.469				
3	-14.622	-3.506*	-2.534*			
4	4.766 *	-7.103*	-14.900*	-9.029*		
5	-1.322	-4.844	13.485	17.358	-0.310	
6	-3.616	-3.242	2.222	1.072*	37.720	-0.810*

*)Constants are affected by Fermi resonance

Table 9. Anharmonic constants X_{ij} (cm^{-1}) using second order PT of cyclic singlet HC$_2$N

X_{ij}	3-pt(tz,qz,5z)+core+rel					
	1	*2*	*3*	*4*	*5*	*6*
1	-59.814					
2	-0.187*	-6.770*				
3	6.009	-13.684	-9.301			
4	-7.839	-11.05	-4.418	-6.014		
5	-12.097	-8.185*	-12.693	0.432	-4.278*	
6	-18.906	-4.260	-2.235	3.292	0.186	-2.471

*)Constants are affected by Fermi resonance

Table 10. Force constants of ground state triplet HC_2N

Quadratic		Cubic		Quartic					
F_{11}	6.099718	F_{111}	-35.0216	F_{1111}	178.13	F_{5321}	-0.08	F_{6651}	0.27
F_{21}	-0.103938	F_{211}	0.0314	F_{2111}	-0.66	F_{5322}	-0.31	F_{6652}	0.06
F_{22}	6.869360	F_{221}	-0.0878	F_{2211}	-0.50	F_{5331}	-0.03	F_{6653}	-0.24
F_{31}	-0.020148	F_{222}	-39.8088	F_{2221}	-0.17	F_{5332}	-0.21	F_{6654}	-0.05
F_{32}	2.547680	F_{311}	0.1146	F_{2222}	208.28	F_{5333}	0.63	F_{6655}	0.54
F_{33}	13.804232	F_{321}	-0.0750	F_{3111}	0.10	F_{5411}	0.15	F_{6666}	1.99
F_{41}	0.107727	F_{322}	-12.1467	F_{3211}	-0.50	F_{5421}	0.09		
F_{42}	0.497186	F_{331}	0.0586	F_{3221}	0.33	F_{5422}	-0.17		
F_{43}	-0.194265	F_{332}	6.7619	F_{3222}	51.85	F_{5431}	-0.07		
F_{44}	0.198258	F_{333}	-108.4164	F_{3311}	0.42	F_{5432}	0.15		
F_{51}	0.09182	F_{411}	0.0745	F_{3321}	-0.15	F_{5433}	0.06		
F_{52}	0.042316	F_{421}	-0.1607	F_{3322}	-44.35	F_{5441}	0.13		
F_{53}	0.099894	F_{422}	-1.1752	F_{3331}	0.35	F_{5442}	-0.11		
F_{54}	0.003399	F_{431}	-0.0122	F_{3332}	33.10	F_{5443}	-0.07		
F_{55}	0.370815	F_{432}	0.9678	F_{3333}	545.73	F_{5444}	-0.06		
F_{66}	0.384813	F_{433}	-0.6078	F_{4111}	-0.36	F_{5511}	-0.02		
		F_{441}	-0.1227	F_{4211}	-0.04	F_{5521}	0.09		
		F_{442}	-0.0570	F_{4221}	-0.08	F_{5522}	1.09		
		F_{443}	-0.1822	F_{4222}	3.46	F_{5531}	0.17		
		F_{444}	-0.7923	F_{4311}	0.17	F_{5532}	0.01		
		F_{511}	0.0035	F_{4321}	0.27	F_{5533}	1.02		
		F_{521}	-0.0223	F_{4322}	-3.85	F_{5541}	0.15		
		F_{522}	-0.2417	F_{4331}	-0.05	F_{5542}	-0.04		
		F_{531}	-0.0195	F_{4332}	3.04	F_{5543}	-0.36		
		F_{532}	-0.1100	F_{4333}	-2.34	F_{5544}	0.12		
		F_{533}	0.1245	F_{4411}	-0.05	F_{5551}	-0.10		
		F_{541}	0.0004	F_{4421}	0.65	F_{5552}	0.57		
		F_{542}	0.0660	F_{4422}	0.78	F_{5553}	0.25		
		F_{543}	-0.0936	F_{4431}	-0.09	F_{5554}	0.18		
		F_{544}	-0.1878	F_{4432}	0.23	F_{5555}	2.49		
		F_{551}	-0.0250	F_{4433}	-0.56	F_{6611}	-0.16		
		F_{552}	-0.5696	F_{4441}	0.08	F_{6621}	0.09		
		F_{553}	-0.6664	F_{4442}	-1.83	F_{6622}	0.66		
		F_{554}	0.0543	F_{4443}	1.22	F_{6631}	-0.04		
		F_{555}	-0.1372	F_{4444}	0.12	F_{6632}	2.00		
		F_{661}	-0.0167	F_{5111}	-0.12	F_{6633}	0.43		
		F_{662}	-0.5635	F_{5211}	-0.03	F_{6641}	0.10		
		F_{663}	-0.7123	F_{5221}	-0.12	F_{6642}	0.08		
		F_{664}	0.0042	F_{5222}	1.45	F_{6643}	0.09		
		F_{665}	-0.0456	F_{5311}	-0.20	F_{6644}	-0.25		

3-pt(tz,qz,5z)+core+rel

* Units of the force constants are mdyn/$Å^n rad^m$ appropiate for an energy unit of mdyn Å (1 mdyn Å=1 aJ).

Table 11. Force constants of bent singlet HC_2N

3-pt(tz,qz,5z)+core+rel									
Quadratic		**Cubic**		**Quartic**					
F_{11}	5.177931	F_{111}	-30.3037	F_{1111}	153.39	F_{5321}	0.03	F_{6651}	-0.02
F_{21}	-0.078059	F_{211}	-0.0546	F_{2111}	-0.42	F_{5322}	-0.73	F_{6652}	0.22
F_{22}	5.686484	F_{221}	-0.1827	F_{2211}	0.12	F_{5331}	0.004	F_{6653}	0.04
F_{31}	0.016299	F_{222}	-34.8266	F_{2221}	-0.41	F_{5332}	0.34	F_{6654}	0.75
F_{32}	1.248974	F_{311}	0.0800	F_{2222}	189.14	F_{5333}	-0.20	F_{6655}	1.19
F_{33}	15.696256	F_{321}	-0.1485	F_{3111}	-0.42	F_{5411}	-0.02	F_{6666}	*1.29*
F_{41}	0.256731	F_{322}	-4.6015	F_{3211}	-0.47	F_{5421}	0.27		
F_{42}	0.598469	F_{331}	0.0460	F_{3221}	0.18	F_{5422}	-0.45		
F_{43}	-0.096386	F_{332}	1.0410	F_{3222}	4.45	F_{5431}	0.04		
F_{44}	0.618229	F_{333}	-110.1983	F_{3311}	0.28	F_{5432}	0.16		
F_{51}	0.044490	F_{411}	-0.0473	F_{3321}	-0.12	F_{5433}	0.08		
F_{52}	0.092149	F_{421}	-0.4747	F_{3322}	2.91	F_{5441}	0.18		
F_{53}	0.127001	F_{422}	-0.9156	F_{3331}	-0.02	F_{5442}	0.33		
F_{54}	0.090590	F_{431}	0.0451	F_{3332}	-7.13	F_{5443}	0.02		
F_{55}	0.454490	F_{432}	0.5959	F_{3333}	599.39	F_{5444}	-0.08		
F_{66}	0.176844	F_{433}	-0.3576	F_{4111}	-1.14	F_{5511}	-0.13		
		F_{441}	-0.3082	F_{4211}	-0.04	F_{5521}	0.09		
		F_{442}	0.3516	F_{4221}	-0.36	F_{5522}	1.82		
		F_{443}	-0.5044	F_{4222}	-0.33	F_{5531}	0.04		
		F_{444}	-0.8951	F_{4311}	-0.00	F_{5532}	0.30		
		F_{511}	-0.0119	F_{4321}	-0.10	F_{5533}	0.47		
		F_{521}	-0.1458	F_{4322}	-1.32	F_{5541}	-0.10		
		F_{522}	-0.5268	F_{4331}	0.09	F_{5542}	0.01		
		F_{531}	-0.0478	F_{4332}	0.61	F_{5543}	-0.08		
		F_{532}	-0.1084	F_{4333}	-0.24	F_{5544}	0.37		
		F_{533}	-0.0208	F_{4411}	0.09	F_{5551}	0.13		
		F_{541}	-0.0398	F_{4421}	0.75	F_{5552}	0.51		
		F_{542}	0.0398	F_{4422}	-1.68	F_{5553}	0.14		
		F_{543}	-0.0683	F_{4431}	-0.16	F_{5554}	-0.03		
		F_{544}	-0.2001	F_{4432}	1.38	F_{5555}	2.73		
		F_{551}	-0.0452	F_{4433}	-0.75	F_{6611}	0.12		
		F_{552}	-0.8930	F_{4441}	0.79	F_{6621}	0.03		
		F_{553}	-0.5875	F_{4442}	-0.44	F_{6622}	0.55		
		F_{554}	0.0273	F_{4443}	0.54	F_{6631}	-0.06		
		F_{555}	-0.2939	F_{4444}	-0.39	F_{6632}	-0.13		
		F_{661}	-0.0411	F_{5111}	-0.19	F_{6633}	1.15		
		F_{662}	-0.1594	F_{5211}	-0.04	F_{6641}	-0.92		
		F_{663}	-0.4751	F_{5221}	0.31	F_{6642}	-0.14		
		F_{664}	0.0355	F_{5222}	1.74	F_{6643}	-0.17		
		F_{665}	-0.1267	F_{5311}	0.01	F_{6644}	0.91		

*Units of the force constants are $mdyn/Å^n rad^m$ appropiate for an energy unit of mdyn Å (1 mdyn Å=1 aJ).

Table 12. Force constants of cyclic singlet HC_2N

3-pt(tz,qz,5z)+core+rel									
Quadratic		**Cubic**		**Quartic**					
F_{11}	5.794836	F_{111}	-33.6249	F_{1111}	172.40	F_{5321}	-0.66	F_{6651}	-0.28
F_{21}	0.089307	F_{211}	0.3365	F_{2111}	-0.88	F_{5322}	15.21	F_{6652}	-0.24
F_{22}	10.266993	F_{221}	-0.5971	F_{2211}	-1.18	F_{5331}	-0.11	F_{6653}	-0.74
F_{31}	-0.068733	F_{222}	-59.4398	F_{2221}	2.45	F_{5332}	27.33	F_{6654}	0.78
F_{32}	0.788188	F_{311}	0.0216	F_{2222}	294.28	F_{5333}	-3.57	F_{6655}	1.40
F_{33}	7.615518	F_{321}	-0.1056	F_{3111}	-0.52	F_{5411}	-0.25	F_{6666}	*1.95*
F_{41}	0.029753	F_{322}	-3.3018	F_{3211}	0.21	F_{5421}	0.10		
F_{42}	0.101387	F_{331}	-0.0115	F_{3221}	-0.06	F_{5422}	-1.12		
F_{43}	0.072597	F_{332}	-2.7149	F_{3222}	12.25	F_{5431}	-0.01		
F_{44}	0.546874	F_{333}	-39.9175	F_{3311}	-0.56	F_{5432}	-0.31		
F_{51}	-0.117645	F_{411}	0.0292	F_{3321}	-0.27	F_{5433}	1.81		
F_{52}	2.625797	F_{421}	-0.3208	F_{3322}	3.25	F_{5441}	-0.13		
F_{53}	2.724999	F_{422}	-0.0491	F_{3331}	1.24	F_{5442}	0.57		
F_{54}	0.023056	F_{431}	0.2592	F_{3332}	15.47	F_{5443}	-1.12		
F_{55}	5.707030	F_{432}	0.0567	F_{3333}	170.01	F_{5444}	0.35		
F_{66}	0.425536	F_{433}	-0.2563	F_{4111}	-0.20	F_{5511}	-0.38		
		F_{441}	-0.1263	F_{4211}	-0.23	F_{5521}	0.60		
		F_{442}	-0.7306	F_{4221}	0.76	F_{5522}	0.47		
		F_{443}	-0.2954	F_{4222}	1.23	F_{5531}	-0.04		
		F_{444}	-0.2603	F_{4311}	0.13	F_{5532}	53.50		
		F_{511}	-0.1860	F_{4321}	0.07	F_{5533}	33.17		
		F_{521}	0.0620	F_{4322}	-1.92	F_{5541}	0.14		
		F_{522}	-5.8720	F_{4331}	-0.46	F_{5542}	-0.99		
		F_{531}	0.2778	F_{4332}	1.52	F_{5543}	0.39		
		F_{532}	-6.0349	F_{4333}	-0.98	F_{5544}	-1.90		
		F_{533}	-8.5677	F_{4411}	-0.38	F_{5551}	0.50		
		F_{541}	-0.0755	F_{4421}	0.14	F_{5552}	77.33		
		F_{542}	0.2102	F_{4422}	0.85	F_{5553}	125.07		
		F_{543}	-0.6873	F_{4431}	0.21	F_{5554}	-4.50		
		F_{544}	0.9470	F_{4432}	0.22	F_{5555}	345.77		
		F_{551}	0.0091	F_{4433}	0.15	F_{6611}	-0.24		
		F_{552}	-15.3923	F_{4441}	0.10	F_{6621}	-0.13		
		F_{553}	-20.7043	F_{4442}	1.24	F_{6622}	-0.19		
		F_{554}	1.2424	F_{4443}	-0.87	F_{6631}	0.52		
		F_{555}	-46.7521	F_{4444}	-0.09	F_{6632}	0.35		
		F_{661}	-0.1333	F_{5111}	0.47	F_{6633}	-0.39		
		F_{662}	-0.2581	F_{5211}	-0.19	F_{6641}	-0.04		
		F_{663}	-0.2352	F_{5221}	0.70	F_{6642}	-0.63		
		F_{664}	0.5859	F_{5222}	-11.44	F_{6643}	-0.11		
		F_{665}	-0.0324	F_{5311}	0.34	F_{6644}	1.71		

* U*nits of the force constants are* mdyn/Å^{n}rad^m *appropiate for an energy unit of mdyn* Å (1 mdyn Å=1 aJ).

Table 13. Alpha-rovibrational constants (MHz) using second order PT of HC$_2$N Isomers

	Bent Triplet	Bent Singlet	Cyclic Singlet
α_{1A}	-202538.7	26548.6	43.8
α_{2A}	-300037.4	-2561.8	195.1
α_{3A}	-118621.8	-8510.0	-289.9
α_{4A}	-1561849.3*	-32431.9	316.4*
α_{5A}	-310272.7*	14143.9*	-182.7*
α_{6A}	-4008.5*	-2697.1*	174.0*
α_{1B}	-24.4	14.7	177.1
α_{2B}	-50.5	59.9	92.2
α_{3B}	-47.6	15.3	232.4
α_{4B}	10.9	25.2	-226.4
α_{5B}	46.6	-48.7	99.4
α_{6B}	22.0	-42.0	95.6
α_{1C}	-32.4	23.8	60.2
α_{2C}	-37.3	55.9	59.0
α_{3C}	-51.8	12.8	2.7
α_{4C}	26.0*	45.9	149.5*
α_{5C}	21.2*	-76.3	72.9*
α_{6C}	45.7	-12.6	-21.7

*)Modes for which Coriolis resonance has been taken into account.

Table 14. Relative energies (in Kcal/mol) and dipole moments (μ, in Debye). These energies are given with respect to the X^3A'' ground state triplet structure.

HC$_2$N	$\Delta E^{(1)}$	$\Delta E^{(2)}$	$\mu^{(3)}$
Ground State triplet	0.0	0.0	3.05
Cyclic singlet	5.7	7.8	3.06
Bent singlet	10.6	11.1	1.71

1)Energies came from the best *ab intio* QFFs, 3-pt(tz,qz,5z)+core+rel.
2) Includes anharmonic Zero-point energies corrections.
3) Dipole moments computed at CCSD(T)/cc-pVQZ level of theory.