**Rotational spectra and nitrogen nuclear quadrupole coupling for the cyanoacetylene dimer:
 $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}\cdots\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$**

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Abstract

The rotational spectra of cyanoacetylene dimer, $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N} \cdots \text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, were recorded using Balle-Flygare type Fourier transform microwave (FTMW) spectrometers. The low J transitions were measured down to 1.3 GHz at very high resolution, FWHM ~ 1 kHz. The spectral hyperfine structure due to the ^{14}N nuclear quadrupole coupling interactions is well-resolved below 4 GHz using a low frequency spectrometer at the University of Arizona. The experimental spectroscopic constants were fitted as: $B_0 = 339.2923310(79)$ MHz, $D_J = 32.152(82)$ Hz, $H = -0.00147(20)$ Hz, $eqQ(^{14}\text{N}_1) = -3.9902(14)$ MHz, and $eqQ(^{14}\text{N}_2) = -4.1712(13)$ MHz. The vibrationally averaged dimer configuration is $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N} \cdots \text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$. Using a simple linear model, the vibrational ground state and the equilibrium hydrogen bond lengths are determined to be: $r_0(\text{N} \cdots \text{H}) = 2.2489(3)$ Å and $r_e(\text{N} \cdots \text{H}) = 2.2315$ Å. The equilibrium center-of-mass distance between the two HCCCN subunits is $r_{com} = 7.0366$ Å. Using the rigid precession model, the vibrational ground state center-of-mass distance and the pivot angles which HCCCN subunits make with the a -axis of $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N} \cdots \text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ are $r_{c.m.} = 7.0603$ Å, $\theta_1 = 13.0^\circ$, and $\theta_2 = 8.7^\circ$, respectively. The calculated hydrogen bond energy of $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N} \cdots \text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ is 1466 cm^{-1} using the MP2/aug-cc-PVTZ method in present work.

1. Introduction

There have been many spectroscopic measurements on cyanoacetylene, $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, since 1970, when it was detected in interstellar clouds.¹ Since it is a species of astrophysical interest, various HCCCN isotopologues have been studied. Lafferty and Lovas summarized numerous spectroscopy results and published them in their review article.² The abundant experimental data of HCCCN allow us to determine its spectroscopic constants and molecular structure accurately. For example, Botschwina *et al*³ used spectroscopic measurements in combination with *ab initio* calculations to determine the equilibrium (r_e) structure of HCCCN; Huckauf and Jäger *et al*^{4,5} determined the vibrational ground state (r_0) structure based on experimental rotational constants of fourteen HCCCN isotopologues. The hyperfine structure of the spectra arising from ^{14}N and D quadrupole coupling interactions was measured using a beam maser by Tack and Kukolich.⁶ A thorough understanding of the structure and the large dipole moment of 3.73172 D⁷ make HCCCN an ideal binding partner for weakly-bounded complexes.

The complexes of HCCCN with Ar ⁴, Ne ⁵, He ⁸, H_2 ⁹, HF ¹⁰, CO ¹¹, H_2O ¹², NH_3 ¹², and SO_3 ¹³ have been measured by microwave spectroscopy. The complexes of HCCCN with HF ^{14,15}, HCN ¹⁵, N_2 ¹⁶, CO_2 ¹⁶, HCCH ¹⁷, and BF_3 ¹⁸ have been observed by infrared spectroscopy. Numerous studies on weakly bounded HCCCN complexes not only improved our understanding of weak intermolecular interactions but also encouraged scientists to develop efficient modeling to describe the intermolecular force fields and the potential energy surfaces (PESs) of HCCCN complexes. Callegari *et al*¹⁹, Stiles *et al*²⁰, and Akin-Ojo *et al*²¹ have worked on $\text{He} \cdots \text{HCCCN}$ complex in various ambient environments. Zhou *et al*^{22,23} performed CCSD(T) and MP4 calculations to obtain the PESs of $\text{Ne} \cdots \text{HCCCN}$ and $\text{Ar} \cdots \text{HCCCN}$. Huckauf *et al*⁴ also predicted the r_e structure of $\text{Ar} \cdots \text{HCCCN}$ using CCSD(T) method and observed its rotational

transitions with an FTMW spectrometer. Those experimental measurements agreed with the theoretical predictions quite well. These studies greatly enhanced our understanding of the weakly bounded van der Waal complexes.

In contrast to the abundant studies of HCCCN with other binding partners, few were performed on the HCCCN polymers, (HCCCN)_n. Only the infrared spectra of HCCCN ... HCCCN and (HCCCN)₃ were observed by Yang *et al*^{24,25}, yet no microwave spectra were measured. Our aim is to partially fill in this gap and present our work on the pure rotational spectra of HCCCN ... HCCCN.

2. Experimental

Cyanoacetylene, HCCCN, was synthesized by a modified method which is originated from Moureu and Bongrand.²⁶ Briefly, commercially available propiolamide, HCCC(O)NH₂, and excess P₂O₅ were baked in a sand bath at 120 – 140 °C for two hours. P₂O₅ was used to absorb the water produced in the reaction. Sand was used to dissipate the heat and dilute the reagents to slow down the reaction. The product was extracted from the reaction vessel and collected using a “dry ice – acetone” trap, where the frozen sample appears as a white frost. Then the crude HCCCN product was sublimed at room temperature into a holding cylinder without further purification. Second run neon, a mixture of 80% Ne and 20% He, was used as purging gas to transfer HCCCN sample to a gas tank under slightly positive gauge pressure. This avoided the contamination from ambient environment.

The cyanoacetylene dimer complex, H–C≡C–C≡N ... H–C≡C–C≡N, was produced in a pulsed supersonic jet beam by expanding 0.3% HCCCN seeded in Ne buffer with a General Valve nozzle (series 9). The stagnation pressure was ~5 psi above the atmospheric pressure. Two

FTMW spectrometers were used for measurements. The one at Wesleyan University is operable between 4 GHz and 26.5 GHz with a resolution capability of full-width-at-half-maximum (FWHM) ≤ 5 kHz.²⁷ The one at the University of Arizona is a low frequency spectrometer with frequency range from 1 GHz to 6 GHz.²⁸ Both spectrometers employ the Coaxially Oriented Beam Resonator Arrangement (COBRA) to improve sensitivity and resolution.²⁹

3. Results

The $J = 2 \leftarrow 1$ to $J = 19 \leftarrow 18$ transitions of HCCCN $\cdots$ HCCCN were measured from 1.3 to 13 GHz. The transitions above 4 GHz were initially recorded at Wesleyan University in 2006. However, the ^{14}N nuclear quadrupole coupling hyperfine structures (*hfs*) of the spectra were not clearly resolved even at 4 GHz – the low frequency limit of a regularly designed FTMW spectrometer. Except for a few weak lines on the side branches which could be distinguished, most strong lines are congested to form only partially resolved broad transitions in the high frequency bands. Only the center frequencies from each of the *hfs* contours could be determined. The importance of that work lies in the fact that a crude rotational constant was obtained from fitting high J transitions. We can use these results and the ^{14}N nuclear quadrupole coupling constant of a HCCCN monomer, $\chi_0(^{14}\text{N}) = -4.31806(38)$ MHz,⁴ to predict the *hfs* of the spectra below 4 GHz. For low J transitions in the low frequency bands, the larger hyperfine splittings and better resolution allowed us to resolve the complex *hfs*. The low frequency spectrometer at the University of Arizona was used to measure the transitions between 1 GHz and 6 GHz. The state-of-the-art high resolution, FWHM ~ 1 kHz, made it possible to resolve the *hfs* of the spectra. Figure 1 presents the *hfs* of the $J = 5 \leftarrow 4$ transition of HCCCN $\cdots$ HCCCN.

For convenience, we denote the respective H and N atoms on the first and the second subunits as H₁, N₁ and H₂, N₂. We label ₂ as H₁CCCN₁ ... H₂CCCN₂ whenever it is necessary to discuss the hydrogen bonding atoms (*i.e.*, N₁ and H₂) or compare the corresponding properties of H and N of the two HCCCN subunits.

Since the nuclear spin of ¹⁴N nuclei is 1, the interaction of its nuclear quadrupole moment and the electric field gradients cause hyperfine splittings of spectra. The coupling scheme of angular momenta is shown in Eq. (1):

$$\mathbf{J} + \mathbf{I}_1 = \mathbf{F}_1 \quad \text{and} \quad \mathbf{F}_1 + \mathbf{I}_2 = \mathbf{F} \quad (1)$$

where $\mathbf{I}_1$ and $\mathbf{I}_2$ are the nuclear spins of the respective ¹⁴N₁ and ¹⁴N₂ atoms of HCCCN ... HCCCN₂. The Hamiltonian that we used to fit the data is given in Eq. (2). It is very similar to the one given by Buxton *et al*³⁰ for (HCN)₂ except that we introduce a sextic centrifugal distortion constant, H , in this work.

$$\hat{\mathbf{H}} = B_0 \mathbf{J}^2 - D_J \mathbf{J}^4 + H \mathbf{J}^6 - \sum_{i=1}^2 eqQ(^{14}\text{N}_i) \frac{3(\mathbf{I}_i \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_i \cdot \mathbf{J}) - \mathbf{I}_i^2 \mathbf{J}^2}{2I_i(2I_i - 1)(2J - 1)(2J + 3)} \quad (2)$$

where $i = 1, 2$ is an index for the N atoms in the subunits of HCCCN ... HCCCN. In the rigid precession model discussed in the following paragraphs, the $eqQ(^{14}\text{N}_i)$ will be labelled as $\chi_{aa}(^{14}\text{N}_i)$.

Pickett's SPFIT program was used to fit the spectroscopic constants.³¹ Except for a few weak transitions that are masked by the neighboring strong lines, almost all measurable hyperfine transitions below 6 GHz were included in the fit. Quite a few high frequency transitions beyond 6 GHz were also included in the fit because they are critical to determine the centrifugal distortion constants. To ensure the quality of the fit, great efforts were made in this work to avoid contaminations. All high frequency lines were carefully selected in case their peak frequencies

slightly shifted by the overlaps of condensed *hfs*. Only 122 clearly resolved transitions were put in Pickett's input file. The root-mean-square (*rms*) error, 0.44 kHz, is a perfect match of our instrumental limit, FWHM $\sim$ 1 kHz. Table 1 lists the assignments of fitted transitions; Table 2 gives the fitted spectroscopic constants of (HCCCN)₂.

We include further discussion on the fit of the two quadrupole coupling constants of the N atoms because $eqQ(^{14}\text{N}_1)$ and $eqQ(^{14}\text{N}_2)$ are close in value and have a large correlation coefficient, 0.9817 (according to our fit results). Initially, it was difficult to fit the two values simultaneously, or distinguish them from each other. The difference between the $eqQ(^{14}\text{N}_1)$ and $eqQ(^{14}\text{N}_2)$ values is due to two effects, a) the difference in the bending vibrational amplitudes (pivot angles) of the HCCCN subunits, and b) small polarization effects arising from forming the hydrogen bond. We believe that (a) is most important and the bending vibrational amplitude is greater for the sub unit containing N₁ so that $eqQ(^{14}\text{N}_1)$ will be smaller than $eqQ(^{14}\text{N}_2)$. The same trend was observed by Buxton *et al*³⁰ in the study of (HCN)₂, with a difference of $\sim$ 0.35 MHz. The structures from the *ab initio* calculations in present work do not include effects of the bending vibrations and gave a small but noticeable gap, 0.15 MHz – 0.20 MHz, between $eqQ(^{14}\text{N}_1)$ and $eqQ(^{14}\text{N}_2)$, and give an indication of the magnitude of the polarization effects. In addition, $eqQ(^{14}\text{N}_2)$ may be closer to the $eqQ(^{14}\text{N})$ value of HCCCN, free monomer because that N atom is not involved in the hydrogen bond.

A small gap, $eqQ(^{14}\text{N}_1) - eqQ(^{14}\text{N}_2) = 0.18$ MHz, was fixed in our initial fit to obtain the spectroscopic constants. This allowed us to remove many wrong assignments. The initial fit was improved and the *rms* error reduced down to the instrumental limit and we believe that the wrong assignments were eliminated. Then the constraint between $eqQ(^{14}\text{N}_1)$ and $eqQ(^{14}\text{N}_2)$ was released to fit them individually and simultaneously, giving the present results.

Normal mode vibrational atom displacements were calculated using Gaussian (G09)(freq) with B3LYP (aug-cc-pVTZ) in order to further support the assignment of the smaller eQq value to N₁. The resulting 3 lowest vibrational modes, $\tilde{\nu}_1 = 17.3 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 35.0 \text{ cm}^{-1}$, and $\tilde{\nu}_3 = 66.6 \text{ cm}^{-1}$, are all bending modes involving primarily changes in θ_1 and θ_2 (see Fig. 3). The approximate r.m.s. angular deviations of θ_1 for both $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are larger than r.m.s deviations of θ_2 . These modes will make the most important contributions to the reductions of eQq by vibrational averaging because the lower frequency modes (with corresponding lower force constants) will have larger amplitudes for the zero-point motions. These results support the present assignments of eQq values to N₁ and N₂ nitrogen atoms.

4. Discussion

4.1 The simple linear model for HCCCN ... HCCCN

The vibrational ground state (r_0) structure of H—C≡C—C≡N has been determined from the recent experimental data by Jäger *et al*⁵ as: $r_0(\text{H—C}) = 1.0575(1) \text{ \AA}$, $r_0(\text{C}\equiv\text{C}) = 1.2044(3) \text{ \AA}$, $r_0(\text{C—C}) = 1.3796(3) \text{ \AA}$, and $r_0(\text{C}\equiv\text{N}) = 1.1586(3) \text{ \AA}$. If the structures of HCCCN monomers do not change upon dimerization and the moieties of HCCCN ... HCCCN preserve a linear geometry, the hydrogen bond length can be derived from its rotational constant, $B_0 = 339.2923310(79) \text{ MHz}$. The moment of inertia of HCCCN ... HCCCN can be calculated by $I_0 = K/B_0 = 1489.5093(18) \text{ amu}\cdot\text{\AA}^2$, where conversion factor $K = h/8\pi^2 = 505379.07(61) \text{ amu}\cdot\text{\AA}^2\cdot\text{MHz}$.³² A simple linear model yields a complex bond length of HCCCN ... HCCCN, $r_0(\text{N} \cdots \text{H}) = 2.2489(3) \text{ \AA}$. This agrees with the experimental bond length measured by IR spectroscopy, $2.266 \text{ \AA}$ ²⁴, and the equilibrium bond length obtained by *ab initio* calculations, $2.277 \text{ \AA}$ ^{33,34}. We also predicted the HCCCN ... HCCCN structure with MP2/cc-pvQZ method while fixing the HCCCN subunits at

their r_e structures.³ This makes $r_e(\text{N} \cdots \text{H})$ the only parameter for optimization. The calculated complex bond length is 2.217 Å. Such a short bond length implies that there exists an intensive intermolecular interactions between the two binding partners. Our MP2/aug-cc-PVTZ calculation predicted the hydrogen bond energy of $\text{HCCCN} \cdots \text{HCCCN}$ to be 1466 cm^{-1} , which is in good agreement with the calculated $(\text{HCN})_2$ hydrogen bond energy, 1500 cm^{-1} .³⁵ Various studies on the “ $\text{R} - \text{C} \equiv \text{N} \cdots \text{H} - \text{X}$ ” ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{NC}, \text{CCH}, \text{etc.}$) complexes showed that their hydrogen bond energies, $\epsilon(\text{N} \cdots \text{H})$, can vary from 1000 cm^{-1} to 2400 cm^{-1} .^{35,36,37,38} Our calculated hydrogen bond energy, 1466 cm^{-1} , is well within this range. It seems that there exists a moderately strong hydrogen bond in $\text{HCCCN} \cdots \text{HCCCN}$.

The fitted centrifugal distortion constants of a complex allow us to estimate the strength of intermolecular force interaction provided that the coupling between intermolecular stretching and normal mode vibrations of the complex binding partners can be ignored. Under the assumption that the centrifugal distortion of a weakly bound complex can be attributed to its van der Waals vibrations, Novick³⁹ proposed a pseudo-diatomic approximation to treat the quadratic centrifugal distortion constant, D_J , of a simple rod-ball system as a function of the van der Waals stretching frequency, ν_s . Millen⁴⁰ extended this model to deal with various types of complexes. We can use it to calculate the van der Waals stretching force constant, k_s , from fitted D_J . This model requires the rigidity of binding partners and assumes no large amplitude motions involved in a complex. The $\text{HCCCN} \cdots \text{HCCCN}$ dimer approximately satisfies these requirements. Following the derivations of Ref. [36], k_s can be calculated by Eq. (3):

$$k_s = \frac{16\pi^2 \mu_D (B_e^D)^3}{D_J} \left(1 - 2 \frac{B_e^D}{B_e^M} \right) \quad (3)$$

where $\mu_D = 25.5054495 \text{ amu}$ is the pseudo-diatomic reduced mass of $\text{HCCCN} \cdots \text{HCCCN}$; $D_J = 32.152(82) \text{ Hz}$ is the fitted quadratic centrifugal distortion constant; B_e^M and B_e^D are the equilibrium rotational constants of HCCCN and $(\text{HCCCN})_2$, respectively. $B_e^M = 4549.688 \text{ MHz}$ is calculated from the r_e structure of HCCCN .³ Since $B_0 \approx B_e$ in a complex without large amplitude motions, replacing B_e^D in Eq. (3) with $B_0^D = 339.2923310(79) \text{ MHz}$ does not introduce a big error to determine $k_s(\text{N} \cdots \text{H}) = 6.854 \text{ N/m}$. Using Eq. (4) we obtain the van der Waals stretching frequency, $\nu_s(\text{N} \cdots \text{H}) = 2.025 \times 10^{12} \text{ Hz}$. Eq. (5) provides us with a means to estimate B_e from B_0 for a complex.^{41,42} Therefore, $B_e^D = 340.322 \text{ MHz}$ can be calculated from B_0^D . Their relative difference, $|B_0^D - B_e^D|/B_e^D = 0.3\%$, is roughly the same as the uncertainty of fitted D_J , 0.26%. This convinced us of the validity of using the $B_e \approx B_0$ approximation in Eq. (3).

$$\nu_s = \frac{1}{2\pi} \sqrt{\frac{k_s}{\mu_D}} \quad (4)$$

$$B_e = \frac{1}{2} \left(\frac{\nu_s}{18} - \sqrt{\left(\frac{\nu_s}{18} \right)^2 - 4B_0 \left(\frac{\nu_s}{18} \right)} \right) \quad (5)$$

Interestingly, Eqs. (3), (4), and (5) form a recursive cycle. After a few loops of recursion, the results converged at: $k_s(\text{N} \cdots \text{H}) = 6.9124 \text{ N/m}$, $\nu_s(\text{N} \cdots \text{H}) = 2.0333 \times 10^{12} \text{ Hz}$, *i.e.*, 67.822 cm^{-1} , and $B_e^D = 340.3176 \text{ MHz}$. They are within 1% differences from their initial values. The uncertainties were not reported because they rely on the rigidity of binding partners and the validity of pseudo-diatomic model, not on the measurement errors. It is our educated guess that those converged calculation results are within $\sim 1\%$ from their actual values. Hence we report $k_s(\text{N} \cdots \text{H}) = 6.91 \text{ N/m}$, $\nu_s(\text{N} \cdots \text{H}) = 67.8 \text{ cm}^{-1}$, and $B_e^D = 340.3 \text{ MHz}$ in this work. Please notice that the k_s and ν_s calculations in the pseudo-diatomic model are based on the analysis assuming harmonic vibrations. There may 10% - 25% errors in this type of calculations.

Since the equilibrium structure of HCCCN has been determined by Botschwina *et al*³ as:
 $r_e(\text{H—C}) = 1.0624 \text{ \AA}$, $r_e(\text{C}\equiv\text{C}) = 1.2058 \text{ \AA}$, $r_e(\text{C—C}) = 1.3764 \text{ \AA}$, and $r_e(\text{C}\equiv\text{N}) = 1.1605 \text{ \AA}$, the
equilibrium center-of-mass (*com*) distance between the two subunits of HCCCN ... HCCCN ,
 r_{com} , can be calculated by the parallel axis theorem:

$$I_e^D = 2I_e^M + \mu_D r_{com}^2 \quad (6)$$

where μ_D is the pseudo-diatomic reduced mass of HCCCN ... HCCCN ; $I_e^D = 1485.0217$
 $\text{amu}\cdot\text{\AA}^2\cdot\text{MHz}$ is derived from B_e^D ; $I_e^M = 111.07994 \text{ amu}\cdot\text{\AA}^2\cdot\text{MHz}$ is obtained from the r_e structure
of HCCCN.³ $r_{com} = 7.0366 \text{ \AA}$ is calculated from Eq. (6). The equilibrium hydrogen bond length,
 $r_e(\text{N} \cdots \text{H}) = 2.2315 \text{ \AA}$, can be calculated from r_{com} . Figure 2 shows the geometric structures of
 $(\text{HCCCN})_2$ in the simple linear model.

4.2 The rigid precession model of HCCCN ... HCCCN

While HCCCN monomer is a linear molecule, its dimer complex might not preserve a linear
orientation. A more sophisticated but possible non-linear configuration of a dimer complex was
invoked by Goodwin and Legon.⁴³ In their rigid precession model, the two binding partners act
as rigid rotors, pivot about their own *coms*, , and make an isotropic pivot motion about the
equilibrium *a*-axis of the dimer . To a good approximation, assuming that HCCCN monomers are
not changed upon complexation, the rigid precession model can be used to describe the
geometric structures of HCCCN ... HCCCN . Since the r_0 structure of HCCCN was accurately
determined, only three parameters are necessary to depict the structures of HCCCN ... HCCCN :
 $r_{c.m.}$ – the distance between the *coms* of HCCCN subunits; θ_1 and θ_2 – the pivot angles of
 H_1CCCN_1 and H_2CCCN_2 make with the *a*-axis of complex, respectively. Notice that the

coupling of torsional vibrations and molecular overall rotations might shift the a -axis of a complex slightly away from its center-of-mass axis – a line which crosses the two *coms* of binding partners. This introduces a new structural parameter and adds to the complexity of geometric analysis. Fortunately, for a near collinearly orientation, the angle made between the a -axis and the center-of-mass axis, α , is usually small enough to be ignored. For instance, the α 's of four (HCN)₂ isotopologues are $\sim 0.2^\circ$.³⁰ The α for HCCCN ... HCCCN should be comparable to or even less than that. The overlap of a -axis and center-of-mass axis of HCCCN ... HCCCN will not introduce noticeable changes to the structural analysis.

Although only three parameters can determine the structure of HCCCN ... HCCCN, extracting them from the measurement results is not straight-forward. Only the rotational constant, B_0 , obviously relates to HCCCN ... HCCCN structure. We need more clues to solve this puzzle. Assuming that the electric field gradients upon ¹⁴N nuclei are nearly unaffected by the complexation of HCCCN monomers, the pivot angles, θ_1 and θ_2 , can be calculated from the fitted $eqQ(^{14}\text{N})$ values. Using the $r_{c.m.}$ which can be derived from B_0 , the geometric structure of HCCCN ... HCCCN can be determined from the measured spectroscopic constants.

The ¹⁴N nuclear quadrupole coupling constant of HCCCN is $\chi_0(^{14}\text{N}) = -4.31806(38) \text{ MHz}^4$. Since $eqQ(^{14}\text{N})$ is a projection of $\chi_0(^{14}\text{N})$ upon the a -axis of (HCCCN)₂, the $eqQ(^{14}\text{N})$ given in the simple linear model can be denoted as $\chi_{aa}(^{14}\text{N})$ in the rigid precession model. The pivot angle, θ , can be derived from Eq. (8)⁴⁴

$$\chi_{aa} = \frac{1}{2} \chi_0 \langle 3 \cos^2 \theta - 1 \rangle \quad (8)$$

In theory, the uncertainty of a pivot angle, $d\theta$, can be estimated using Eq. (9):

$$d\theta = \left| \left(\frac{\partial \theta}{\partial \chi_{aa}} \right)_{\chi_0} d\chi_{aa} \right| + \left| \left(\frac{\partial \theta}{\partial \chi_0} \right)_{\chi_{aa}} d\chi_0 \right| \quad (9)$$

where $d\chi_{aa}$ and $d\chi_0$ are the standard deviations of the $\chi_{aa}({}^{14}\text{N})$ for $(\text{HCCCN})_2$ and the $\chi_0({}^{14}\text{N})$ for HCCCN, respectively. Since $\chi_{aa}({}^{14}\text{N}_1) = -3.9902(14)$ MHz and $\chi_{aa}({}^{14}\text{N}_2) = -4.1712(13)$ MHz were fitted to the *hfs* of spectra, the pivot angles of $\text{HCCCN} \cdots \text{HCCCN}$, $\theta_1 = 13.0^\circ$ and $\theta_2 = 8.7^\circ$, can be calculated using Eq. (8). They agree very well with the pivot angles of $(\text{HCN})_2$: $\theta_{1, \text{HCN}} = 13.7^\circ$ and $\theta_{2, \text{HCN}} = 8.7^\circ$.³⁰ This angular agreement further supports the assignments of which χ_{aa} belongs to which nitrogen in $\text{HCCCN} \cdots \text{HCCCN}$. We hesitate to report the standard deviations of pivot angles because they depend more on the validity of pseudo-diatomic model and/or rigid precession model than the experimental errors. Given the rigidity of the HCCCN subunits and the weak hydrogen bonding between them, the two models should be good approximations for $\text{HCCCN} \cdots \text{HCCCN}$. Our best guess on the uncertainty of pivot angles are $\sim 1\%$. Figure 3 shows the geometric structures to the scale of $\text{HCCCN} \cdots \text{HCCCN}$ in the rigid precession model.

The parallel axis theorem can be used to calculate the vibrational ground state center-of-mass distance of the two HCCCN subunits, $r_{c.m.}$, provided that we know the pivot angles, θ_1 and θ_2 .

$$I_0^D = \frac{1}{2} \langle 1 + \cos^2 \theta_1 \rangle I_0^M + \frac{1}{2} \langle 1 + \cos^2 \theta_2 \rangle I_0^M + \mu_D r_{c.m.}^2 \quad (10)$$

where μ_D is the pseudo-diatomic reduced mass of $(\text{HCCCN})_2$, $I_0^D = 1489.5093 \text{ amu} \cdot \text{\AA}^2 \cdot \text{MHz}$ is calculated from the B_0 of $(\text{HCCCN})_2$, and $I_0^M = 111.09530 \text{ amu} \cdot \text{\AA}^2 \cdot \text{MHz}$ is calculated from the B_0 of HCCCN. Then from Eq. (10), we obtain $r_{c.m.} = 7.0603 \text{ \AA}$. For ease of structural comparisons between simple linear model and rigid precession model, and between $(\text{HCN})_2$ and $(\text{HCCCN})_2$, we can project the subunits onto the *a*-axis of their dimer complexes and calculate the “projected distance between N and H”, $\overline{r_0(\text{N} \cdots \text{H})}$, based on their θ_1 , θ_2 and $r_{c.m.}$ values as well as the bond

lengths of monomers. The $\overline{r_0(\text{N} \cdots \text{H})}$ for $\text{HCCCN} \cdots \text{HCCCN}$ is determined to be 2.3415 Å in this work, which is longer than that of the $(\text{HCN})_2$ analog, 2.2647 Å. A comparison between $\text{HCCCN} \cdots \text{HCCCN}$ and $(\text{HCN})_2$ can be found in Table 3.

The rigid procession model treatment requires that electric field gradients be invariant upon the complexation of HCCCN monomers. This assumption is better for the H_2CCCN_2 subunit since that $^{14}\text{N}_2$ is not involved in the hydrogen bond, which makes its ambient environment similar to that of a free HCCCN molecule. This does not apply to the H_1CCCN_1 subunit in that $^{14}\text{N}_1$ which is hydrogen bonded to H_2CCCN_2 . The moderately strong hydrogen bonding energy, $\epsilon(\text{N} \cdots \text{H})$, implies that there exists a fairly strong intermolecular interaction between the two subunits of $\text{HCCCN} \cdots \text{HCCCN}$. This might induce intermolecular charge redistribution between $^{14}\text{N}_1$ and H_2 nuclei, which will affect their electric field gradients and result in a different $eqQ(^{14}\text{N}_1)$ from its $eqQ(^{14}\text{N}_2)$ counterpart. A demonstration of this came from our MP2/aug-cc-PVQZ calculation. In this work we fix the structure of two subunits as the r_e structure of a free HCCCN monomer. Then apply the Hirshfeld analysis to obtain the charge densities on each nuclei. The results are presented on top of the molecular formula in Figure 2. We notice that the hydrogen bonded $^{14}\text{N}_1$ is less negative than its unbounded counterpart $^{14}\text{N}_2$ by -0.1667 vs. -0.2097; the hydrogen bonded H_1 is less positive than its unbonded H_2 counterpart by 0.0832 vs. 0.1222. This implies an intermolecular charge transfer from $^{14}\text{N}_1$ to H_2 , which lower down the electron density on $^{14}\text{N}_1$ (being less negative than $^{14}\text{N}_2$) and enhance the electron density on H_2 (being less positive than H_1). A similar study on $(\text{HCN})_2$ showed that 40% of the difference in $\chi_{aa}(^{14}\text{N})$ between a free HCN monomer and $(\text{HCN})_2$ can be attributed to the intermolecular charge redistribution.⁴⁵ In addition, the coupling between the van der Waals stretching mode and the normal mode vibrations of HCCCN might change the bond lengths,

which induces a subsequent change of the electric field gradients, especially on the hydrogen bonded $^{14}\text{N}_1$ and H_2 nuclei. Therefore, the treatment of $\chi_{aa}(^{14}\text{N}_1)$ as a projected $\chi_0(^{14}\text{N})$ upon the a -axis of $\text{HCCCN} \cdots \text{HCCCN}$ is not as good an assumption compared with $\chi_{aa}(^{14}\text{N}_2)$ counterpart. However, without data from various dimer isotopologues, the rigid precession model is still a good starting point to provide more detailed information about $\text{HCCCN} \cdots \text{HCCCN}$. The derivations in Ref. [43] for a more rigorous treatment, but this would require additional rotational constants of multiple $(\text{HCCCN})_2$ isotopologues.

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Table 1: Observed rotational transitions of HCCCN ... HCCCN and deviations between measured and “best-fit” calculated values (Obs – Calc).

J'	F_1'	$F' - J''$	F_2''	F''	Frequency (MHz)	$Obs - Calc$ (kHz)	
2	2	2	1	2	3	1354.9850	0.0
2	2	1	1	2	1	1355.1287	-0.2
2	1	1	1	0	1	1355.5149	-0.1
2	2	3	1	2	3	1355.5947	0.2
2	1	2	1	0	1	1355.8358	0.3
2	1	0	1	0	1	1356.5387	0.1
2	2	2	1	1	1	1356.6384	0.0
2	2	2	1	1	2	1356.8212	0.3
2	3	3	1	2	2	1357.0818	0.3
2	3	2	1	2	1	1357.1683	0.0
2	3	4	1	2	3	1357.3440	0.4
2	2	3	1	1	2	1357.4306	0.3
2	2	1	1	1	0	1358.1888	0.0
2	3	2	1	2	2	1358.3920	0.0
2	1	1	1	1	1	1359.4358	-0.1
2	1	1	1	1	2	1359.6182	-0.1
2	1	2	1	1	1	1359.7564	0.1
2	1	2	1	1	2	1359.9388	0.0
2	1	0	1	1	1	1360.4594	0.0
3	3	2	2	3	2	2033.9144	0.0
3	3	4	2	3	4	2034.1470	0.2
3	2	2	2	1	2	2034.8190	0.0
3	3	3	2	2	3	2035.0074	0.1
3	2	2	2	1	1	2035.1395	0.2
3	2	1	2	1	0	2035.3394	-0.5
3	2	3	2	1	2	2035.5732	0.3
3	3	3	2	2	2	2035.6168	0.1
3	4	4	2	3	3	2035.7027	0.2
3	4	3	2	3	2	2035.7509	0.3
3	4	5	2	3	4	2035.8484	0.5
3	3	4	2	2	3	2035.8963	0.3
3	3	2	2	2	1	2035.9540	0.2
3	2	1	2	1	1	2036.3636	0.1
3	4	3	2	3	3	2037.0607	-0.3
3	2	2	2	2	3	2037.3276	0.1
3	2	2	2	2	2	2037.9367	0.0
3	2	3	2	2	3	2038.0816	0.2
3	2	3	2	2	2	2038.6908	0.0
3	2	1	2	2	2	2039.1613	0.4
4	4	3	3	4	3	2712.5814	0.2
4	4	5	3	4	5	2712.7220	0.3

4	3	3	3	2	3	2713.3147	0.2
4	4	4	3	3	4	2713.3896	0.3
4	3	3	3	2	2	2714.0688	0.3
4	3	2	3	2	1	2714.1553	0.3
4	3	4	3	2	3	2714.2705	0.8
4	4	4	3	3	3	2714.2777	-0.1
4	5	5	3	4	4	2714.3002	0.2
4	5	4	3	4	3	2714.3308	0.3
4	5	6	3	4	5	2714.3930	0.6
4	4	3	3	3	2	2714.4165	-0.7
4	4	5	3	3	4	2714.4234	0.5
4	3	2	3	2	2	2715.3795	0.3
4	5	4	3	4	4	2715.6890	0.0
4	3	3	3	3	3	2716.3885	-0.1
4	3	4	3	3	4	2716.4549	-0.1
5	5	4	4	5	4	3391.2060	0.0
5	5	6	4	5	6	3391.3002	-0.1
5	4	4	4	3	4	3391.8067	0.0
5	5	5	4	4	5	3391.8476	0.0
5	4	4	4	3	3	3392.7621	0.3
5	4	3	4	3	2	3392.8099	0.1
5	4	5	4	3	4	3392.8782	-0.5
5	6	6	4	5	5	3392.8852	-0.1
5	6	5	4	5	4	3392.9074	0.1
5	6	7	4	5	6	3392.9510	0.8
5	5	6	4	4	5	3392.9711	0.0
5	4	3	4	3	3	3394.1206	0.1
5	6	5	4	5	5	3394.2962	0.0
5	4	4	4	4	4	3394.8722	-0.3
5	4	5	4	4	5	3394.9108	-0.1
6	6	5	5	6	5	4069.8091	-0.3
6	6	7	5	6	7	4069.8769	-0.2
6	5	5	5	4	5	4070.3146	-1.0
6	6	6	5	5	6	4070.3416	-0.2
6	5	5	5	4	4	4071.3877	0.0
6	5	4	5	4	3	4071.4185	0.3
6	5	6	5	4	5	4071.4649	0.0
6	7	6	5	6	5	4071.4800	-0.1
6	7	8	5	6	7	4071.5118	0.1
6	6	7	5	5	6	4071.5272	0.3
6	5	4	5	4	4	4072.7766	-0.2
6	7	6	5	6	6	4072.8903	0.1
6	5	5	5	5	5	4073.3787	-0.3
6	5	6	5	5	6	4073.4050	0.7
7	7	6	6	7	6	4748.3983	-0.3
7	7	8	6	7	8	4748.4490	-0.5

7	6	6	6	5	6	4748.8359	0.1
7	7	7	6	6	7	4748.8533	-0.9
7	6	6	6	5	5	4749.9844	0.0
7	8	8	6	7	7	4750.0367	0.0
7	6	7	6	5	6	4750.0387	0.0
7	8	7	6	7	6	4750.0483	0.0
7	7	6	6	6	5	4750.0695	0.1
7	8	9	6	7	8	4750.0732	0.7
7	7	8	6	6	7	4750.0849	0.8
7	6	5	6	5	5	4751.3936	-0.9
7	8	7	6	7	7	4751.4734	-0.3
7	6	6	6	6	6	4751.8988	0.6
7	6	7	6	6	7	4751.9155	-0.6
8	8	7	7	8	7	5426.9767	0.0
8	8	9	7	8	9	5427.0160	-0.3
8	8	8	7	7	8	5427.3742	-1.0
8	8	9	7	7	8	5428.6401	0.8
8	7	6	7	6	6	5429.9889	-0.8
8	9	8	7	8	8	5430.0473	-0.8
8	7	7	7	7	7	5430.4227	-0.7
8	7	8	7	7	8	5430.4362	-0.7
11	11	10	10	10	9	7464.2658	-0.2
11	12	13	10	11	12	7464.2695	0.1
11	11	12	10	10	11	7464.2755	1.1
12	12	11	11	11	10	8142.7969	-0.5
12	13	14	11	12	13	8142.8007	0.0
12	12	13	11	11	12	8142.8052	0.4
13	13	12	12	12	11	8821.3195	-0.1
13	14	15	12	13	14	8821.3227	0.0
13	13	14	12	12	13	8821.3273	1.1
14	15	16	13	14	15	9499.8347	0.2
14	14	15	13	13	14	9488.8382	0.7
15	14	13	14	13	12	10178.3203	-0.9
16	15	15	15	14	14	10856.8084	-0.2
16	15	14	15	14	13	10856.8118	0.0

Table 2: The spectroscopic constants for HCCCN ... HCCCN.

Spectroscopic constants for HCCCN ... HCCCN ^{a, b}		
B_0	339.2923310(79)	MHz
D_J	32.152(82)	Hz
H	-0.00147(20)	Hz
$eqQ(^{14}\text{N}_1)^c$	-3.9902(14)	MHz
$eqQ(^{14}\text{N}_2)^d$	-4.1712(13)	MHz
# of lines / std. dev.	122 / 0.44	kHz

^a Fit using Pickett's SPFIT program package.

^b The one-standard deviation errors are given in the parentheses.

^c This can be labelled as $\chi_{aa}(^{14}\text{N}_1)$ using the rigid precession model.

^d This can be labelled as $\chi_{aa}(^{14}\text{N}_2)$ using the rigid precession model.

Table 3: A comparison of structural and hydrogen bonding parameters between for HCCCN $\cdots$ HCCCN (HCCCN)₂ and (HCN)₂.

	Rigid procession model				Linear model	$k_s(\text{N} \cdots \text{H})$	$\nu_s(\text{N} \cdots \text{H})$	$\epsilon(\text{N} \cdots \text{H})$
	$r_{c.m.} / \text{\AA}$	$\theta_1 / ^\circ$	$\theta_2 / ^\circ$	$\overline{r_0}(\text{N} \cdots \text{H}) / \text{\AA}$	$r_0(\text{N} \cdots \text{H}) / \text{\AA}$	(N/m)	(cm ⁻¹)	(cm ⁻¹)
HCCCN $\cdots$ HCCCN ^a	7.0603	13.0	8.7	2.3415	2.2489(3)	6.9	67.8	1466 ^b
HCN $\cdots$ HCN ^c	4.44735	13.7	8.7	2.2647	2.23	8.1	101	1500 ^d

^a Present work.

^b Calculated by MP2/aug-cc-PVTZ method in this work.

^c Ref. [45]. The $\overline{r_0}(\text{N} \cdots \text{H})$ was calculated based on the data and the r_s structure of HCN monomer given in Ref [45].

^d Ref. [34].

Figure 1: The observed $J' = 5 \rightarrow J'' = 4$ transition of $\text{HCCCN} \cdots \text{HCCCN}$.

* The observed frequency gap for the Doppler splitting doublets is ~ 15 kHz at 3391 MHz.

Figure 2: The simple linear model of the geometry of cyanoacetylene dimer complex^{*,†}

^{*} The r_{com} is the equilibrium center-of-mass distance between the two HCCCN subunits in HCCCN ... HCCCN

[†] The decimal numbers on top of the molecular formula are the Hirshfeld charge densities calculated by MP2/aug-cc-PVQZ method in present work. The HCCCN subunits are fixed to the r_e structure of a free HCCCN monomer in the calculation.

Figure 3: The rigid procession model of the geometry of cyanoacetylene dimer complex^{*,†,‡,§}

^{*} This diagram draws to the scale of HCCCN ... HCCCN in the rigid procession model.

[†] The angle between the a -axis and the center-of-mass axis of HCCCN ... HCCCN, α , is small enough to be ignored ($\alpha \leq 0.2^\circ$). See text and Ref. [30].

[‡] The $r_{c.m.}$ is the center-of-mass (com) distance of the two HCCCN subunits in their vibrational ground state.

[§] $\overline{r_0(N \cdots H)}$ is the distance between the two projected points of N_1 and H_2 on the a -axis of $(HCCCN)_2$.

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STRUCTURE AND QUADRUPOLE COUPLING FOR HCCCN DIMER