

Gas-phase formation and spectroscopic characterization of the disubstituted cyclopropenylenes $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ *

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ABSTRACT

Aims. The detection of $c\text{-C}_3\text{HC}_2\text{H}$ and possible future detection of $c\text{-C}_3\text{HCN}$ provide new molecules for reaction chemistry in the dense interstellar medium (ISM) where $\text{R-C}_2\text{H}$ and R-CN species are prevalent. Determination of chemically viable $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$ derivatives and their prominent spectral features can accelerate potential astrophysical detection of this chemical family. This work characterizes three such derivatives: $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$.

Methods. Interstellar reaction pathways of small carbonaceous species are well replicated through quantum chemical means. Highly accurate cc-pVXZ-F12/CCSD(T)-F12 ($X = \text{D}, \text{T}$) calculations generate the energetics of chemical formation pathways as well as the basis for quartic force field and second-order vibrational perturbation theory rovibrational analysis of the vibrational frequencies and rotational constants of the molecules under study.

Results. The formation of $c\text{-C}_3(\text{C}_2\text{H})_2$ is as thermodynamically and, likely, as stepwise favorable as the formation of $c\text{-C}_3\text{HC}_2\text{H}$, rendering its detectability to be mostly dependent on the concentrations of the reactants. Both $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ will be detectable through radioastronomical observation with large dipole moments of 2.84 D and 4.26 D, respectively, while $c\text{-C}_3(\text{CN})_2$ has an exceedingly small and likely unobservable dipole moment of 0.08 D. The most intense frequency for $c\text{-C}_3(\text{C}_2\text{H})_2$ is ν_2 at 3316.9 cm^{-1} ($3.01\text{ }\mu\text{m}$), with an intensity of 140 km mol^{-1} . The mixed-substituent molecule $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ has one frequency with a large intensity, ν_1 , at 3321.0 cm^{-1} ($3.01\text{ }\mu\text{m}$), with an intensity of 82 km mol^{-1} . The molecule $c\text{-C}_3(\text{CN})_2$ lacks intense vibrational frequencies within the range that current instrumentation can readily observe.

Conclusions. Both $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ are viable candidates for astrophysical observation, with favorable reaction profiles and spectral data produced herein, but $c\text{-C}_3(\text{CN})_2$ will not be directly observable through any currently available remote sensing means, even if it forms in large abundances.

Key words. astrochemistry – ISM: molecules – infrared: ISM – molecular processes

1. Introduction

The detection of ethynyl cyclopropenyldiene ($c\text{-C}_3\text{HC}_2\text{H}$), the first substituent-functionalized cyclopropenyldiene derivative to be observed in space (Cernicharo et al. 2021), has sparked renewed interest in its parent molecule, $c\text{-C}_3\text{H}_2$. A proposed mechanism for the formation of $c\text{-C}_3\text{HC}_2\text{H}$ from the abundant $c\text{-C}_3\text{H}_2$ molecule and ethynyl radical ($\cdot\text{C}_2\text{H}$) suggests that $c\text{-C}_3\text{HC}_2\text{H}$ can be produced through rapid substituent addition followed by hydrogen dissociation (Fortenberry 2021). This reaction represents one of the few known cosmic chemical pathways utilizing $c\text{-C}_3\text{H}_2$. The existence of $c\text{-C}_3\text{HC}_2\text{H}$ questions the idea that $c\text{-C}_3\text{H}_2$ is a carbonaceous “dead end” (Lin et al. 2016) in space. In TMC-1, the column density of $c\text{-C}_3\text{HC}_2\text{H}$ is calculated to be $3.1(8) \times 10^{11}\text{ cm}^{-2}$, giving a relative abundance to H_2 of 3.1×10^{-11} . In comparison to $c\text{-C}_3\text{H}_2$, $c\text{-C}_3\text{HC}_2\text{H}$ has an abundance of 5.3×10^{-3} (Cernicharo et al. 2021). While present in relatively low densities, the overall available concentrations may make the detection of other $c\text{-C}_3\text{H}_2$ derivatives, as well as derivatives of $c\text{-C}_3\text{HC}_2\text{H}$ itself, possible.

* Additional data obtained from spectroscopic analysis alongside structural information for all molecules can be found at https://egrove.olemiss.edu/chem_facpubs/33

Given that reaction between $c\text{-C}_3\text{H}_2$ and $\cdot\text{C}_2\text{H}$ is shown to be energetically allowed at the low temperatures of the interstellar medium (ISM; Fortenberry 2021), the detection and abundances of $c\text{-C}_3\text{HC}_2\text{H}$ are far from surprising, as its precursors are some of the most abundant carbonaceous species in space. Both $c\text{-C}_3\text{H}_2$ and its ^2D and ^{13}C isotopologues are found in a myriad of cosmic environments (Thaddeus et al. 1981, 1985; Matthews & Irvine 1985; Seaquist & Bell 1986; Cox et al. 1987; Vrtilek et al. 1987; Madden et al. 1989; Lucas & Liszt 2000; Oike et al. 2004; Teyssier et al. 2004; Qi et al. 2013; Nixon et al. 2020; Bell et al. 1986; Majumdar et al. 2017; Gomez Gonzalez et al. 1986; Madden et al. 1986; Spezzano et al. 2013). Its abundances rival those of CH_3OH in cold regions, such as the Magellanic Clouds (Heikkilä et al. 1999), and have been used as a standard for the calculation of hydrogen abundances in Sagittarius B2 (Corby et al. 2018). Likewise, $\cdot\text{C}_2\text{H}$ is ubiquitous in space (Tucker & Kutner 1978; Tucker et al. 1974; Huggins et al. 1984; Henkel et al. 1988), having been one of the first interstellar molecules detected, along with its isotopologues (Combes et al. 1985; Vrtilek et al. 1985; Saleck et al. 1994).

Similarly, the large presence of the $\cdot\text{CN}$ radical in various cosmic environments (Adams 1941; Jefferts et al. 1970; Henkel et al. 1988; McKellar 1940; Turner & Gammon 1975;

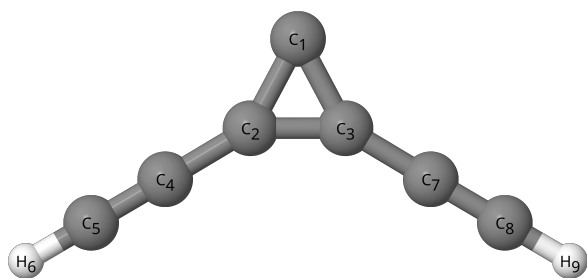


Fig. 1. Molecular structure of $c\text{-C}_3(\text{C}_2\text{H})_2$.

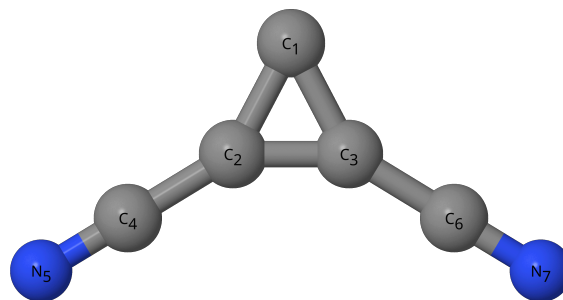


Fig. 2. Molecular structure of $c\text{-C}_3(\text{CN})_2$.

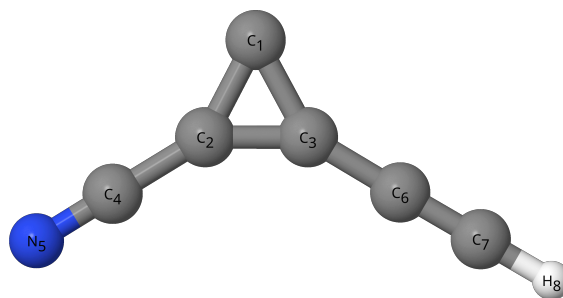


Fig. 3. Molecular structure of $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$.

Paron et al. 2021) makes a $c\text{-C}_3\text{H}_2$ nitrile derivative possible as well. While the search for $c\text{-C}_3\text{HCN}$ is still ongoing (Cernicharo et al. 2021), its energetically viable formation mechanism most strongly resembles the formation mechanism of $c\text{-C}_3\text{HC}_2\text{H}$, both in reaction coordinate structures and in exothermicity (Flint & Fortenberry 2022). This mechanism, combined with high reactant concentrations in several molecular clouds, suggests its detection to be the next most probable out of any currently proposed substituted cyclopropenylidene. The likelihood that $c\text{-C}_3\text{HCN}$ also exists in the ISM means that a potential derivative of it, too, must be further considered.

The common occurrence of the cyano and ethynyl substituents within astrophysical discussions is not only a result of radical abundances. Cyano-functionalized hydrocarbons comprise a large fraction of the astrochemical detections within the last five years (Lee et al. 2021b,a; McGuire et al. 2018, 2020, 2021; Cernicharo et al. 2020; Loomis et al. 2021; Xue et al. 2020) as a result of the enhanced dipole moment of such molecules compared to the pure hydrocarbon parent molecule. Likewise, ethynyl groups and other $\text{C}\equiv\text{C}$ linkages are common in both observed chemical species as well as in the reaction pathways that produce them. Hydrocarbons are among the most frequently detected molecules in interstellar environments, and the vast majority of them have at least one degree of unsaturation (McGuire et al. 2021). Such unsaturated molecules appear to be the driving force of interstellar chemistry, and they may play a key role in the synthesis of polycyclic aromatic hydrocarbons (PAHs), species thought to be responsible for the unidentified infrared bands (Tielens 2008). As such, the R-CN and $\text{R-C}_2\text{H}$ functional groups are key to the continued study of interstellar astrochemistry as it currently is understood.

Following its laboratory detection by McCarthy et al. (1997), $c\text{-C}_3\text{HC}_4\text{H}$, a monosubstituted $c\text{-C}_3\text{H}_2$ derivative with an elongated substituent chain, compared to that of $c\text{-C}_3\text{HC}_2\text{H}$, has been hypothesized in the literature as a possible candidate for interstellar detection (Chandra et al. 2005). However, its disubstituted isomer $c\text{-C}_3(\text{C}_2\text{H})_2$ (shown in Fig. 1) has eluded even laboratory detection, despite being one of the most stable isomers of C_7H_2 , as determined quantum chemically (Thaddeus et al. 1998; Dua et al. 2000). Though $c\text{-C}_3(\text{C}_2\text{H})_2$ has been considered previously using ab initio methods, the results are limited to optimized geometries, harmonic frequencies, and IR intensities (Thimmakondur & Karton 2017). Moreover, these results identify $c\text{-C}_3(\text{C}_2\text{H})_2$ as having a large dipole moment of 3.77 D, bringing it into the realm of detectability through radioastronomical observation. Additionally, the C-H antisymmetric stretch ($\omega = 3450$, $\lambda = 2.899 \mu\text{m}$) of $c\text{-C}_3(\text{C}_2\text{H})_2$ was shown to have an intensity of 122 km mol^{-1} , making it ripe for infrared detection as well. Similar ring-containing C_5N_2 structures have received even less attention, with only one mention of $c\text{-C}_3(\text{CN})_2$, shown in Fig. 2, in the literature to date (Jiang et al. 2004). The linear

and bent isomers of C_5N_2 , as well as its anionic form, have been discussed in prior studies (Singh & Chaturvedi 1989; Belbruno et al. 2001; Yang et al. 2011). The general lack of information regarding this molecule is possibly linked to the lower intrinsic stability of linear $\text{C}_{2n+1}\text{N}_2$ compounds (Belbruno et al. 2001; Jiang et al. 2004). Laboratory studies have been successful in forming the linear isomer of C_5N_2 (Smith et al. 1994), as verified by Tittle et al. (1999). However, $c\text{-C}_3(\text{CN})_2$, like $c\text{-C}_3(\text{C}_2\text{H})_2$, has seemingly also eluded laboratory observation.

With such complex ring-chain molecules brought into the realm of possibility for astrophysical observation by the detection and formation mechanisms of their monosubstituted relatives, the gap between the potential for these species and the lack of information in the literature concerning them must be bridged. This work presents the results of highly accurate quantum chemical calculations for the purpose of spectroscopically characterizing $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$ as well as the mixed-substituent derivative $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$, shown in Fig. 3. The rovibrational data reported could lend support to future experimental work as well as NASA projects, such as the *James Webb* Space Telescope (JWST). Thermodynamics of reaction were calculated for the formation of $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ to create a basis for their existence in astrophysical environments. Reaction pathways for $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$ are proposed in order to provide additional astrochemical motivation for this spectroscopic search. Such formation mechanisms build upon existing cyclopropenylidene chemistry, bringing the field of astrochemistry closer to making the fullest use of this ubiquitous family of molecules. These cyclopropenylidene derivatives in particular may be necessary for explaining the formation and growth of larger unsaturated hydrocarbon systems and soot grains.

2. Computational details

2.1. Reactions in the ISM

The regions of space where these substitution reactions are expected to take place lack a significant photon flux.

Consequently, processes that occur in the cold ISM cannot benefit from photon collisions and the subsequent influx of energy to propel their chemistry. The only energy available to the reaction pathway is the energy that is inherent to it via the reactants (Puzzarini 2022). This places constraints on the chemical mechanisms such that any energetically disallowed reaction pathways – ones that contain thermodynamic or kinetic barriers – are filtered out. The combined energy of the reacting species must represent a maximum on the reaction coordinate. The association of the species for bimolecular reactions, like the ones proposed within this work, must be initially barrierless to fulfill this requirement (Puzzarini 2022; Grosselin & Fortenberry 2022). The net reaction must also be exothermic.

Bimolecular associations that occur within the ISM, as a consequence of being exothermic in nature, often result in the creation of a submerged intermediate structure that contains an excess of energy with respect to the reactants. This excess energy must be dissipated, which is assumed to occur via exit of a leaving group that carries away the energy in the form of kinetic energy. The dissipation of energy through radiative means is assumed to be infeasible for the submerged intermediates on the $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$ reaction coordinates without destruction of the complex (Puzzarini 2022). Radiative association becomes slowed compared to other processes, such as the removal of a leaving group, as the relative velocity of the reactants decreases. In the coldest regions of the ISM, such as TMC-1 and other areas where neutral-neutral reactions are plentiful, radiative association would therefore be hindered (Herbst 2021). As a result, the rate of hydrogen dissociation is assumed to control the final step(s) of the reaction pathway.

Exit from the pathway from a more shallow potential well (i.e., a decrease in $E_{\text{Products}} - E_{\text{Intermediate}}$) for a barrierless exit is assumed to be faster than the same process for a deeper potential well (Tielens 2005). Additionally, despite the assumption that radiative dissipation will not occur for any submerged intermediates, exit from shallower wells on the reaction coordinate would decrease the opportunity for radiative dissipation of energy to compete with dissociation of a leaving group (Herbst 2001, 2021).

2.2. Mechanisms

Geometry optimization and harmonic frequency calculations of the starting materials and products of the $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$ formation pathways are based on coupled cluster theory at the singles, doubles, and perturbative triples level [CCSD(T)] (Raghavachari et al. 1989; Hampel et al. 1992; Knowles et al. 1993; Shavitt & Bartlett 2009; Crawford & Schaefer III 2000) in conjunction with the explicitly correlated F12b formalism [CCSDT-F12b] (Adler et al. 2007) and the cc-pVXZ-F12 basis set (Peterson et al. 2008; Yousaf & Peterson 2008; Knizia et al. 2009). This combination is referred to as F12-TZ. Optimization and harmonic frequency calculations for all intermediates on the pathways were performed with the B3LYP functional (Yang et al. 1986; Becke 1993; Lee et al. 1988; Stephens et al. 1994; Vosko et al. 1980) and the aug-cc-pVTZ basis set (Dunning 1989; Kendall et al. 1992; Woon & Dunning 1993). The single-point energies of the optimized intermediate geometries were computed with F12-TZ (Ramal-Olmedo et al. 2021), which were corrected with the B3LYP/aug-cc-pVTZ zero-point vibrational energies (ZPEs). All calculations of reaction coordinate minima made use of the MOLPRO2022.2 (Werner et al. 2012, 2022, 2020) quantum chemical software package. Locatable transition states on the reaction pathway were optimized

at the B3LYP/aug-cc-pVTZ level of theory with GAUSSIAN16 (Frisch et al. 2016). The F12-TZ single-point energy at this geometry was computed and corrected with the B3LYP/aug-cc-pVTZ ZPE, and the same was done for the intermediates. Gabedit (Allouche 2010, 2017) was used to visualize the motion corresponding to the vector of the imaginary frequency of the geometry in order to confirm the connection between two minima. When necessary for mechanistic analysis, the molecular orbitals (MOs) of a geometry were computed in GAUSSIAN16 with ROHF/aug-cc-pVTZ, as this is the reference for the F12-TZ energies, (Roothaan 1951; Brinkley et al. 1974; Watts et al. 1993) and visualized with Gabedit. Natural bond orbitals (NBOs; Foster & Weinhold 1980; Reed & Weinhold 1983; Reed et al. 1985; Reed & Weinhold 1985; Carpenter 1987; Carpenter & Weinhold 1988; Weinhold & Carpenter 1988; Reed et al. 1988) were computed with UHF/cc-pVTZ for specified minima in GAUSSIAN16 in order to extract additional information about the MOs, including which orbitals are participating in bonding-to-antibonding delocalization. Analyses of these orbital calculations provide a guide for the electronic basis on which the reaction coordinate proceeds.

The radical character of the reaction pathways within this work required that single-reference methods such as CCSD(T)-F12 be used carefully, as such species are commonly prone to influence from multireference effects during computation. For calculations performed via F12-TZ, Lee & Taylor (1989) define the T1 diagnostic that provides a measure of how greatly the system is affected by static correlation. For T1 diagnostic values below 0.02, the system is generally accepted as well behaved under a single-reference frame. The T1 diagnostics for all molecules on both reaction pathways were evaluated to ensure that static correlation would not significantly contaminate the calculated results.

Previous studies on $c\text{-C}_3\text{H}_2$ substitution (Fortenberry 2021; Flint & Fortenberry 2022) show that in every case where a substitution reaction of this type is permitted thermodynamically, no barrier to association to form the initial submerged well is present. Removal of the leaving group upon exit of a submerged well, in every case, either crosses no exit barrier or crosses a barrier that is kinetically accessible to the reaction. When subjected to a second substitution, $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$ are expected to also lack hindering entrance and exit barriers, and thus barrierless associations were assumed for all reaction pathways calculated in this work. This follows experimental data (Smith 2006, 2011) that show a decrease in reaction rate between a radical and a neutral unsaturated species in the gas phase as the temperature decreases.

Despite the assumption that no barriers to hydrogen dissociation are present, the dissociation itself can be impacted by other factors, such as the nature of the intermediates and dissociation complexes. Where deemed necessary for analyzing how these dissociations occur, relaxed potential energy scans (PESs) generated the single-point energies of a series of geometries along a specified reaction coordinate at step sizes of 0.01 Å. The reaction coordinate variable was defined as an internuclear distance, and at fixed variable values, the remainder of the geometry was optimized. The PES calculations were performed at the F12-TZ/B3LYP/aug-cc-pVTZ combined level of theory in order to remain consistent with the reaction pathway.

2.3. Spectroscopic methods

In order to provide a means of detecting the products of the examined reaction mechanisms, the theoretical spectroscopic

data in this work were computed by quartic force fields (QFFs), which are fourth-order Taylor series expansions of the potential energy portion of the internuclear Watson Hamiltonian (Fortenberry & Lee 2019). The QFFs utilized in this work are also based on coupled cluster theory at the singles, doubles, and perturbative triples level [CCSD(T)] (Raghavachari et al. 1989; Shavitt & Bartlett 2009; Crawford & Schaefer III 2000) in conjunction with the explicitly correlated F12b formalism [CCSD(T)-F12b] (Adler et al. 2007).

In this work, QFFs were computed for $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ with three different levels of theory, which all utilize the CCSD(T)-F12b method. Two QFFs employed the cc-pVXZ-F12 basis set (Peterson et al. 2008; Yousaf & Peterson 2008; Knizia et al. 2009), where X is D or Z. These combinations are referred to hereafter as F12-DZ and F12-TZ, respectively. The other QFF employed the cc-pCVDZ-F12 basis set (Hill & Peterson 2010) with additional corrections for scalar relativity utilizing canonical CCSD(T) with the cc-pVTZ-DK basis set (Douglas & Kroll 1974; Jansen & Hess 1989). This combination is referred to hereafter as F12-DZ-cCR (Watrous et al. 2021). The F12-DZ combination is the only level of theory at which QFFs are computed for $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ due to the increase in computational cost of the other two levels of theory utilized in this work.

The QFFs for $c\text{-C}_3(\text{CN})_2$ have a symmetry-internal coordinate (SIC) system of 10325 points with atom labels corresponding to Fig. 2 defined below:

$$S_1(a_1) = \frac{1}{\sqrt{2}}[r(\text{C}_1 - \text{C}_2) + r(\text{C}_1 - \text{C}_3)], \quad (1)$$

$$S_2(a_1) = \frac{1}{\sqrt{2}}[r(\text{C}_2 - \text{C}_4) + r(\text{C}_3 - \text{N}_6)], \quad (2)$$

$$S_3(a_1) = \frac{1}{\sqrt{2}}[r(\text{C}_2 - \text{C}_5) + r(\text{C}_3 - \text{N}_7)], \quad (3)$$

$$S_4(a_1) = \frac{1}{\sqrt{2}}[\angle(\text{C}_1 - \text{C}_2 - \text{C}_5) + \angle(\text{C}_1 - \text{C}_3 - \text{N}_7)], \quad (4)$$

$$S_5(a_1) = \frac{1}{\sqrt{2}}[\angle(\text{C}_1 - \text{C}_2 - \text{C}_4) + \angle(\text{C}_1 - \text{C}_3 - \text{N}_6)], \quad (5)$$

$$S_6(a_1) = \angle(\text{C}_2 - \text{C}_1 - \text{C}_3), \quad (6)$$

$$S_7(b_2) = \frac{1}{\sqrt{2}}[r(\text{C}_1 - \text{C}_2) - r(\text{C}_1 - \text{C}_3)], \quad (7)$$

$$S_8(b_2) = \frac{1}{\sqrt{2}}[r(\text{C}_2 - \text{C}_4) - r(\text{C}_3 - \text{N}_6)], \quad (8)$$

$$S_9(b_2) = \frac{1}{\sqrt{2}}[r(\text{C}_2 - \text{C}_5) - r(\text{C}_3 - \text{N}_7)], \quad (9)$$

$$S_{10}(b_2) = \frac{1}{\sqrt{2}}[\angle(\text{C}_1 - \text{C}_2 - \text{C}_5) - \angle(\text{C}_1 - \text{C}_3 - \text{N}_7)], \quad (10)$$

$$S_{11}(b_2) = \frac{1}{\sqrt{2}}[\angle(\text{C}_1 - \text{C}_2 - \text{C}_4) - \angle(\text{C}_1 - \text{C}_3 - \text{N}_6)], \quad (11)$$

$$S_{12}(b_1) = \frac{1}{\sqrt{2}}[\tau(\text{C}_5 - \text{C}_2 - \text{C}_1 - \text{C}_3) - \tau(\text{N}_7 - \text{C}_3 - \text{C}_1 - \text{C}_2)], \quad (12)$$

$$S_{13}(b_1) = \frac{1}{\sqrt{2}}[\tau(\text{C}_4 - \text{C}_2 - \text{C}_1 - \text{C}_3) - \tau(\text{N}_6 - \text{C}_3 - \text{C}_1 - \text{C}_2)], \quad (13)$$

$$S_{14}(a_2) = \frac{1}{\sqrt{2}}[\tau(\text{C}_5 - \text{C}_2 - \text{C}_1 - \text{C}_3) + \tau(\text{N}_7 - \text{C}_3 - \text{C}_1 - \text{C}_2)], \quad (14)$$

$$S_{15}(a_2) = \frac{1}{\sqrt{2}}[\tau(\text{C}_4 - \text{C}_2 - \text{C}_1 - \text{C}_3) + \tau(\text{N}_6 - \text{C}_3 - \text{C}_1 - \text{C}_2)]. \quad (15)$$

The QFFs for $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ were run directly in Cartesian coordinates and are composed of 115 746 points and 145 824 points, respectively.

Table 1. Thermodynamics of reaction for formation of $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$.

Product	$\cdot\text{X}$	ΔE_{rxn}
$c\text{-C}_3(\text{C}_2\text{H})_2$	$\cdot\text{C}_2\text{H}$	−26.84
$c\text{-C}_3(\text{CN})_2$	$\cdot\text{CN}$	−13.16
$c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$	$\cdot\text{C}_2\text{H}$	−26.52
	$\cdot\text{CN}$	−15.85

Notes. Elements in the $\cdot\text{X}$ column denote the radical used as the starting material to achieve the final result. All energies reported in kcal mol^{−1}.

The SIC QFFs begin with the optimization of the geometry at each level of theory. The geometry was then displaced by 0.005 Å or 0.005 radians to form the QFF. Single-point energies were computed at each displacement. These single-point energies were then refit by a least-squares procedure to yield the equilibrium geometry. A refit to the function minimum zeroed the gradients and yielded the force constants and the new equilibrium geometry. The force constants were converted from SICs to Cartesian coordinates utilizing the INTDER program (Allen 2005). For the Cartesian QFFs, each geometry was first optimized at the F12-DZ level of theory. The optimized geometry was then displaced along the x , y , and z axes by 0.005 Å to form the QFF (Westbrook et al. 2021).

For all of the QFFs, the rovibrational spectroscopic data was computed utilizing the Cartesian force constants in second order vibrational perturbation theory (Watson 1977; Papoušek & Aliev 1982; Franke et al. 2021) in the SPECTRO software package (Gaw et al. 1996). To further increase the accuracy of the data, type-1 and type-2 Fermi resonances, Fermi resonance polyads (Martin & Taylor 1997), Coriolis resonances, and Darling-Dennison resonances were taken into account (Martin & Taylor 1997; Martin et al. 1995).

The dipole moment for $c\text{-C}_3(\text{CN})_2$ was computed at the F12-TZ level of theory, and the dipole moments for $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ were computed at the F12-DZ level of theory. The intensities were computed at the B3LYP/aug-cc-pVTZ (Yang et al. 1986; Lee et al. 1988; Becke 1993; Dunning 1989) level of theory using GAUSSIAN16 (Frisch et al. 2016). The geometry optimizations, harmonic frequencies, single-point energies, and dipole moments were computed with the MOLPRO 2022.2 software package (Werner et al. 2022).

3. Results and discussion

3.1. Reaction mechanisms

Figure 4 displays the reaction pathway for the formation of $c\text{-C}_3(\text{C}_2\text{H})_2$ from $c\text{-C}_3\text{HC}_2\text{H}$ and $\cdot\text{C}_2\text{H}$. Analogously, Fig. 5 shows the mechanism for the formation of $c\text{-C}_3(\text{CN})_2$ from $c\text{-C}_3\text{HCN}$ and $\cdot\text{CN}$. The relative ZPE-corrected electronic energies of all points on the pathways are summarized in Tables 1 and 2. Exothermicities for the single substitutions (Fortenberry 2021; Flint & Fortenberry 2022) show that a second substitution onto the cyclopropenylidene moiety to create $c\text{-C}_3(\text{C}_2\text{H})_2$ is as thermodynamically favorable as the first. However, the formation of $c\text{-C}_3(\text{CN})_2$ was less exothermic than the formation of $c\text{-C}_3\text{HCN}$ by 2.94 kcal mol^{−1}.

Table 2 also lists the amount of energy needed to exit the reaction pathway from a given intermediate, titled ΔE_{exit} .

Table 2. Intermediate and transition state energies relative to starting materials for second substitution of $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$ to form $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$.

Product	$E_{\text{rel}}, \text{I1 (C}_s\text{)}$	$E_{\text{rel}}, \text{I1 (C}_1\text{)}$	$E_{\text{rel}}, \text{I2 (C}_s\text{)}$	$E_{\text{rel}}, \text{I2 (C}_{2v}\text{)}$	$E_{\text{rel}}, \text{TS}_{\text{I1}}$	$E_{\text{rel}}, \text{TS}_{\text{I2}}$
$c\text{-C}_3(\text{C}_2\text{H})_2$	-67.53	-70.61	-80.85	-85.27	-39.92	-80.31
$c\text{-C}_3(\text{CN})_2$	-61.40	-62.25	-71.07	-77.67	-22.43	-70.75
	$\Delta E_{\text{exit}}, \text{I1 (C}_s\text{)}$	$\Delta E_{\text{exit}}, \text{I1 (C}_1\text{)}$	$\Delta E_{\text{exit}}, \text{I2 (C}_s\text{)}$	$\Delta E_{\text{exit}}, \text{I2 (C}_{2v}\text{)}$		
$c\text{-C}_3(\text{C}_2\text{H})_2$	40.69	43.77	54.01	58.43		
$c\text{-C}_3(\text{CN})_2$	48.25	49.10	57.91	64.51		

Notes. All energies reported in kcal mol^{-1} .

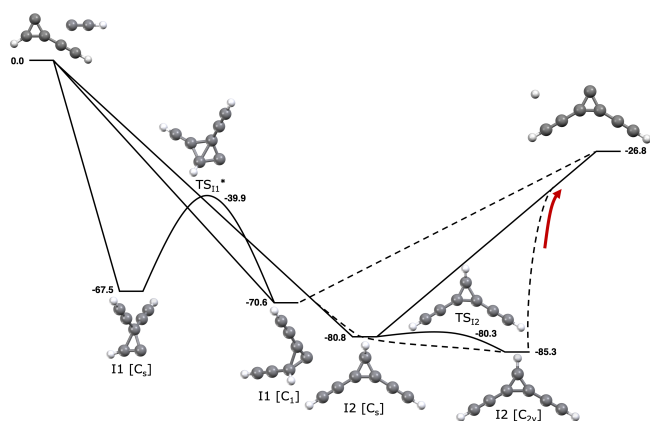


Fig. 4. Reaction pathway for formation of $c\text{-C}_3(\text{C}_2\text{H})_2$ from $c\text{-C}_3\text{HC}_2\text{H}$ and $\cdot\text{C}_2\text{H}$. I1 and I2 refer to intermediates 1 and 2, respectively. TS refers to a transition state, and the intermediate type involved in the transition is noted as a subscript. Dashed lines indicate procession across electronic states. All associations are assumed to require intersystem crossing to proceed but are indicated with solid lines for clarity. Relative energies in kcal mol^{-1} .

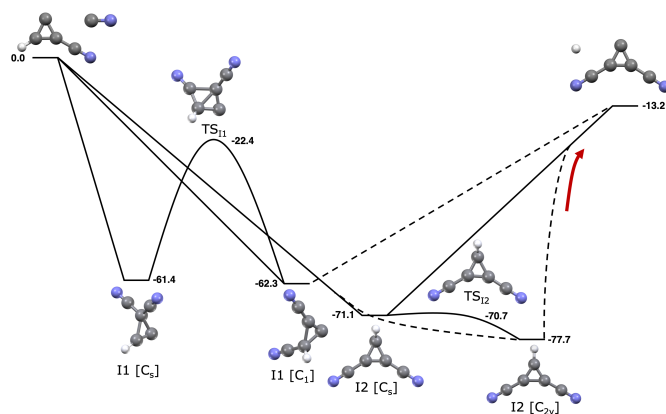


Fig. 5. Reaction pathway for formation of $c\text{-C}_3(\text{CN})_2$ from $c\text{-C}_3\text{HCN}$ and $\cdot\text{CN}$. I1 and I2 refer to intermediates 1 and 2, respectively. TS refers to a transition state, and the intermediate type involved in the transition is noted as a subscript. Dashed lines indicate procession across electronic states. All associations are assumed to require intersystem crossing to proceed but are indicated with solid lines for clarity. Relative energies in kcal mol^{-1} .

As shown previously for the monosubstituted derivatives (Fortenberry 2021; Flint & Fortenberry 2022), less of the potential energy gained by creation of the submerged well was required to be given up upon exit from the pathway by the

diethynyl derivative at every point within the mechanism. Formation of $c\text{-C}_3(\text{C}_2\text{H})_2$ is less likely to be impeded by a competing radiative stabilization process.

Evaluation of the T1 diagnostics of all reactants, products, and intermediates showed negligible influence from static correlation effects. Several transition states gave a T1 diagnostic greater than 0.02, indicating possible multireference effects. Given the nature of these molecules and that the largest of the T1 diagnostic values for the transition states is 0.031, the impact of static correlation on these structures was neglected.

The disubstitution mechanisms are close analogues of the monosubstitution mechanisms for $\cdot\text{C}_2\text{H}$ and $\cdot\text{CN}$ in most regards. However, some structures on the reaction coordinate differ slightly from previous iterations of this mechanism type. An I1 variant with C_s symmetry is able to form due to chemically nonequivalent sites of radical addition to $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$. This symmetric intermediate cannot lead to product formation on its own and must pass through a transition state to form the C_1 isomer of I1 if formed as a result of the initial collision. For the $c\text{-C}_3(\text{C}_2\text{H})_2$ pathway, the TS_{I1} structure proved difficult to locate. An approximate upper-bound energy and structure were given for this transition state resulting from a coordinate scan, as the failure of the structure to converge to the correct molecular motion may be a consequence of the level of theory used and not the potential surface as a whole. An I2 structure with C_1 symmetry arising from displacement of a substituent group out of the plane was not able to form on these potential surfaces, unlike for the formation of $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$. As a result, transition from the C_s I1 structure to an I2 structure could not occur. A hydride shift from the C_1 I1 isomer to an I2 structure was also not locatable for these surfaces at this level of theory. Due to the nature of the available transition states, the reaction pathways were essentially stratified by the submerged well type.

The pathways also present a new planar reaction intermediate with C_{2v} symmetry that is not seen within the monosubstitution mechanisms. Such planar structures, as is in the case of the $c\text{-C}_3\text{H}_3$ radical (Hoffmann et al. 1984), usually experience Jahn-Teller distortions that force one group out of the plane of the molecule, giving rise to a pseudoplanar geometry for the remainder of the structure. Such planar intermediates were avoided in all cases for the monosubstituted pathways (Flint & Fortenberry 2022), which were optimized purely at the F12-TZ level of theory. To ensure that planar geometries for the disubstituted variants were not produced as artifacts of optimization at the B3LYP/aug-cc-pVTZ level of theory, planar structures were generated and optimized at B3LYP/aug-cc-pVTZ for $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3\text{HCN}$. Harmonic frequency analysis showed an imaginary frequency that forces the substituent group out of the plane

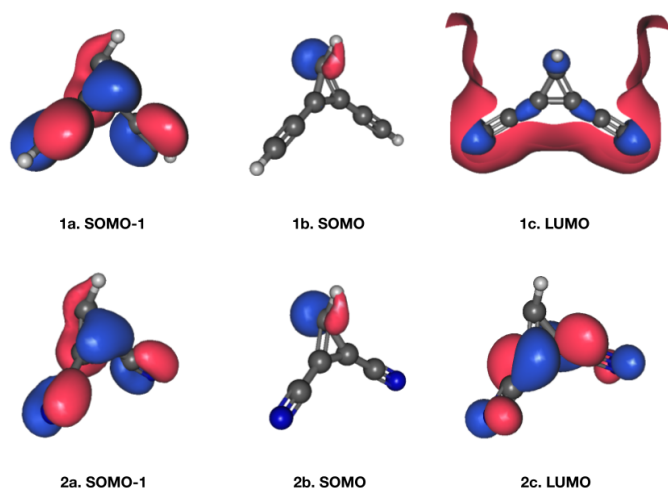


Fig. 6. Two highest-occupied and lowest-occupied MOs for C_s isomer of I2.

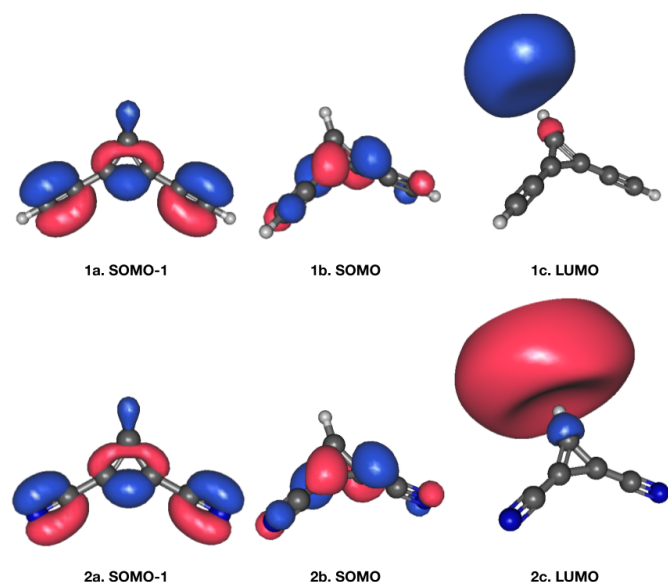


Fig. 7. Two highest-occupied and lowest-occupied MOs for C_{2v} isomer of I2.

of the molecule. The planarity of one of the intermediates for the disubstituted pathways was thus deemed to be a consequence of the potential surface and not largely attributed to the level of theory at which the calculations were performed.

Figures 6 and 7 show the frontier MOs of both I2 isomers for the two reaction pathways. Most interestingly, the lowest-occupied molecular orbital (LUMO) of the C_{2v} isomers of both pathways shows strong C-H antibonding character. The NBO analysis of these structures showed that the electronic occupation of the C-H σ^* orbital for the C_s isomer was reduced by a factor of over 2.5 compared to that of the C_{2v} isomer for both pathways. Additionally, the frontier MOs of the products (Fig. 8) replicated those of the C_{2v} I2 isomer. Upon hydrogen dissociation, the hydrogen atom harbored the new singly occupied molecular orbital (SOMO) of the system. The former I2 SOMO, having released its electron density to the leaving group, became the LUMO of the product, while the SOMO-1 became the highest-occupied molecular orbital (HOMO) of the product. We note that the C_{2v} I2 SOMO does not become the LUMO of $c\text{-C}_3(\text{C}_2\text{H})_2$

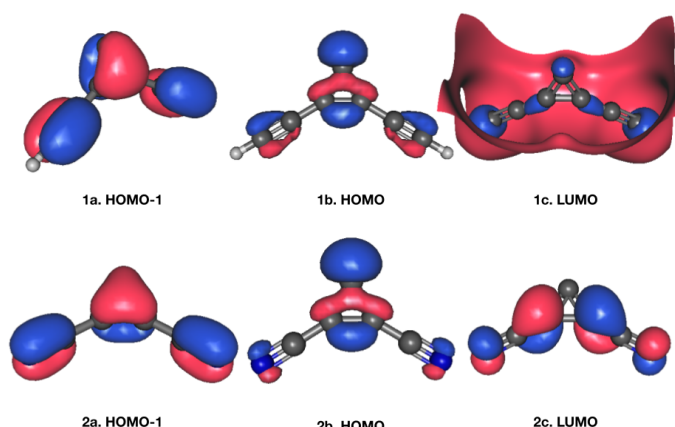


Fig. 8. Two highest-occupied and lowest-occupied MOs for $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$.

– this orbital is instead displaced to the LUMO+2, as the antibonding orbitals along the ethynyl groups comprising the LUMO and LUMO+1 are slightly lower in energy. An overall MO analysis of these complexes set up the planar I2 isomer for more facile product formation from this intermediate. Despite this, the C_s I2 isomer remained in control of product formation. Since an a_2 electronic excitation is required to fully populate both C_{2v} I2 LUMOs, this transition requires excess energy (Pople & Sidman 1957), rendering it unlikely to occur. A relaxed scan of the labile C-H coordinate for both I2 symmetries showed that the geometry and orbitals of the dissociating complex resemble that of the C_{2v} isomer until the approximate bond-breaking distance of C-H = 1.55 Å, where continued dissociation results in a large spike in the electronic energy. As the C-H interatomic distance begins to surpass the bond-breaking distance, the geometry of the complex must distort to the lower C_s symmetry. At these C-H distances, the MOs of the C_s isomer closely resemble those in Fig. 7 and the predicted shifts in orbital occupation upon dissociation discussed previously. The C_{2v} I2 isomer may provide a greater electronic incentive for product formation while the leaving group remains bound, but dissociation from either isomer is possible, as they merge toward the same complex as dissociation occurs in order to remain in the lowest energy orbital occupation. This phenomenon is expected to take place for the association to form either intermediate I2 for the $c\text{-C}_3(\text{C}_2\text{H})_2$ and to form the $c\text{-C}_3(\text{CN})_2$ pathways as well.

Given that the exothermicities of reaction for the formation of $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3(\text{C}_2\text{H})_2$ are nearly equal, the thermodynamic incentive for reaction is the same, provided that the primary formation pathway for both molecules involves the addition of $\cdot\text{C}_2\text{H}$. The available densities of $c\text{-C}_3\text{HC}_2\text{H}$ for reaction likely dictate the ability of this pathway to occur and therefore also control the expected concentrations of $c\text{-C}_3(\text{C}_2\text{H})_2$. Approximating the $c\text{-C}_3\text{HC}_2\text{H}/c\text{-C}_3\text{H}_2$ density ratio to be equal to that of $c\text{-C}_3(\text{C}_2\text{H})_2/c\text{-C}_3\text{HC}_2\text{H}$, observations may find a column density for $c\text{-C}_3(\text{C}_2\text{H})_2$ of roughly 1.6×10^9 or a relative density to H_2 of 1.6×10^{-14} in TMC-1.

3.2. Quartic force field spectra

Of the three molecules, $c\text{-C}_3(\text{C}_2\text{H})_2$, $c\text{-C}_3(\text{CN})_2$, and $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$, for which rovibrational data was computed, the $c\text{-C}_3(\text{C}_2\text{H})_2$ molecule has the largest anharmonic frequency intensities. The largest intensity for $c\text{-C}_3(\text{C}_2\text{H})_2$, as shown in Table 3, is ν_2 at 3316.9 cm^{-1} ($3.01 \text{ }\mu\text{m}$), with an intensity

Table 3. Harmonic and fundamental vibrational frequencies (in cm^{-1}) and B3LYP/TZ intensities (in km mol^{-1}) of $c\text{-C}_3(\text{C}_2\text{H})_2$.

Mode	Description	F12-DZ	f	Freq. ^(a)	$f^{(a)}$
$\omega_1 (a_1)$	Symmetric C-H stretch	3453.6	42	3455	32
$\omega_2 (b_2)$	Antisymmetric C-H stretch	3453.1	157	3450	122
$\omega_3 (a_1)$	C_7, C_4 symmetric motion	2170.4	1	2169	4
$\omega_4 (b_2)$	C_7, C_4 antisymmetric motion	2162.5	9	2159	26
$\omega_5 (a_1)$	$\text{C}_2\text{-C}_3$ stretch	1771.6	1	1768	0
$\omega_6 (a_1)$	$\text{C}_1\text{-C}_2 + \text{C}_1\text{-C}_3$ stretch	1245.2	30	1237	33
$\omega_7 (b_2)$	$\text{C}_1\text{-C}_2 - \text{C}_1\text{-C}_3$ stretch	1231.1	38	1224	36
$\omega_8 (b_2)$	$\text{C}_1\text{-C}_2\text{-C}_4 - \text{C}_1\text{-C}_3\text{-C}_7$ bend	781.7	3	777	5
$\omega_9 (a_2)$	$\text{C}_4\text{-C}_5\text{-H}_6 - \text{C}_7\text{-C}_8\text{-H}_9$ out-of-plane bend	707.3	–	703	–
$\omega_{10} (b_1)$	$\text{C}_4\text{-C}_5\text{-H}_6 + \text{C}_7\text{-C}_8\text{-H}_9$ out-of-plane bend	705.3	58	704	60
$\omega_{11} (a_1)$	$\text{C}_4\text{-C}_2 + \text{C}_3 + \text{C}_7$ stretch	679.0	4	678	7
$\omega_{12} (a_2)$	$\text{C}_2 \text{ C}_3$ out-of-plane motion	627.5	–	633	–
$\omega_{13} (b_2)$	Antisymmetric in-plane H bend	611.5	28	607	24
$\omega_{14} (a_1)$	Symmetric in-plane H bend	609.8	70	606	66
$\omega_{15} (b_2)$	$\text{C}_1\text{-C}_3\text{-C}_7 - \text{C}_1\text{-C}_2\text{-C}_4$ bend	546.5	8	540	2
$\omega_{16} (b_1)$	$\text{C}_4 \text{ C}_7$ out-of-plane symmetric bend	439.9	23	461	18
$\omega_{17} (a_1)$	$\text{C}_2\text{-C}_4\text{-C}_5 + \text{C}_2\text{-C}_7\text{-C}_8$ bend	417.0	8	418	3
$\omega_{18} (b_2)$	$\text{C}_2\text{-C}_4\text{-C}_5 - \text{C}_2\text{-C}_7\text{-C}_8$ bend	220.9	1	227	0
$\omega_{19} (a_2)$	$\text{C}_2\text{-C}_4\text{-C}_5 - \text{C}_2\text{-C}_7\text{-C}_8$ out-of-plane bend	218.9	–	230	–
$\omega_{20} (b_1)$	$\text{C}_2\text{-C}_4\text{-C}_5 + \text{C}_2\text{-C}_7\text{-C}_8$ out-of-plane bend	170.7	1	179	1
$\omega_{21} (a_1)$	$\text{C}_4\text{-C}_5\text{-H}_6 + \text{C}_7\text{-C}_8\text{-H}_9$ bend	94.0	2	96	2
$\nu_1 (a_1)$	Symmetric C-H stretch	3315.9	37		
$\nu_2 (b_2)$	Antisymmetric C-H stretch	3316.9	140		
$\nu_3 (a_1)$	C_7, C_4 symmetric motion	2128.2	1		
$\nu_4 (b_2)$	C_7, C_4 antisymmetric motion	2122.6	6		
$\nu_5 (a_1)$	$\text{C}_2\text{-C}_3$ stretch	1716.8	1		
$\nu_6 (a_1)$	$\text{C}_1\text{-C}_2 + \text{C}_1\text{-C}_3$ stretch	1211.9	19		
$\nu_7 (b_2)$	$\text{C}_1\text{-C}_2 - \text{C}_1\text{-C}_3$ stretch	1209.9	55		
$\nu_8 (b_2)$	$\text{C}_1\text{-C}_2\text{-C}_4 - \text{C}_1\text{-C}_3\text{-C}_7$ bend	770.2	–		
$\nu_9 (a_2)$	$\text{C}_4\text{-C}_5\text{-H}_6 - \text{C}_7\text{-C}_8\text{-H}_9$ out-of-plane bend	688.4	59		
$\nu_{10} (b_1)$	$\text{C}_4\text{-C}_5\text{-H}_6 + \text{C}_7\text{-C}_8\text{-H}_9$ out-of-plane bend	685.5	3		
$\nu_{11} (a_1)$	$\text{C}_4\text{-C}_2 + \text{C}_3 + \text{C}_7$ stretch	674.8	–		
$\nu_{12} (a_2)$	$\text{C}_2 \text{ C}_3$ out-of-plane motion	649.9	–		
$\nu_{13} (b_2)$	Antisymmetric in-plane H bend	583.2	28		
$\nu_{14} (a_1)$	Symmetric in-plane H bend	592.8	71		
$\nu_{15} (b_2)$	$\text{C}_1\text{-C}_3\text{-C}_7 - \text{C}_1\text{-C}_2\text{-C}_4$ bend	546.4	7		
$\nu_{16} (b_1)$	$\text{C}_4 \text{ C}_7$ out-of-plane symmetric bnd	504.5	23		
$\nu_{17} (a_1)$	$\text{C}_2\text{-C}_4\text{-C}_5 + \text{C}_2\text{-C}_7\text{-C}_8$ bend	413.1	8		
$\nu_{18} (b_2)$	$\text{C}_2\text{-C}_4\text{-C}_5 - \text{C}_2\text{-C}_7\text{-C}_8$ bend	218.8	1		
$\nu_{19} (a_2)$	$\text{C}_2\text{-C}_4\text{-C}_5 - \text{C}_2\text{-C}_7\text{-C}_8$ out-of-plane bend	238.6	–		
$\nu_{20} (b_1)$	$\text{C}_2\text{-C}_4\text{-C}_5 + \text{C}_2\text{-C}_7\text{-C}_8$ out-of-plane bend	152.9	1		
$\nu_{21} (a_1)$	$\text{C}_4\text{-C}_5\text{-H}_6 + \text{C}_7\text{-C}_8\text{-H}_9$ bend	97.1	2		

Notes. ^(a)Previous theory from Thimmakondur & Karton (2017) at the CCSD(T)/cc-pVTZ level of theory.

of 140 km mol^{-1} , and the second largest intensity is ν_{14} at 592.8 cm^{-1} ($16.9 \mu\text{m}$), with an intensity of 71 km mol^{-1} . Both of these intensities are on the same magnitude or larger of the antisymmetric stretch of water, which is about 70 km mol^{-1} . The two intense frequencies for $c\text{-C}_3(\text{C}_2\text{H})_2$ fall within the range of the Near Infrared Spectrograph (NIRSpec) instrument on JWST, which has high resolution and could aid in detection. These two frequencies should be intense enough to be observed with JWST if the abundances as estimated above are true. The harmonic vibrational frequencies and intensities have been previously computed at the CCSD(T)/cc-pVTZ level of theory (Thimmakondur & Karton 2017). Between the previous level of theory and the F12-DZ computed in this work, a majority of

the harmonic frequencies agree within 5 cm^{-1} . The biggest differences come from the symmetric and antisymmetric stretches of carbon in the ring and the out-of-plane bends. While the two levels of theory for the harmonic intensities differ quantitatively from each other, they agree qualitatively in the relative intensities of the frequencies.

Shown in Table 4, $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ has one intense peak: ν_1 at 3321.0 cm^{-1} ($3.01 \mu\text{m}$), with an intensity of 82 km mol^{-1} . This intense frequency corresponds to the C-H stretch of the ethynyl group and is nearly the same as the ν_2 stretch in $c\text{-C}_3(\text{C}_2\text{H})_2$. This one intense peak for $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ falls within the range of the NIRSpec instrument on JWST. However, $c\text{-C}_3(\text{CN})_2$ does not have any intensities of around 70 km mol^{-1}

Table 4. Harmonic and fundamental vibrational frequencies (in cm^{-1}) and intensities (in km mol^{-1}) of $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$.

Mode	Description	F12-DZ	f
$\omega_1 (a')$	C-H stretch	3449.9	95
$\omega_2 (a')$	C-N stretch	2277.7	4
$\omega_3 (a')$	C ₆ shuttle	2169.4	31
$\omega_4 (a')$	C ₂ -C ₃ stretch	1783.7	14
$\omega_5 (a')$	C ₁ -C ₂ stretch	1254.6	43
$\omega_6 (a')$	C ₁ -C ₃ stretch	1219.1	17
$\omega_7 (a')$	C ₁ -C ₂ -C ₄ bend	776.8	3
$\omega_8 (a'')$	C ₆ -C ₇ -H ₈ out-of-plane bend	721.0	26
$\omega_9 (a')$	C ₂ -C ₄ stretch	671.0	4
$\omega_{10} (a'')$	C ₂ C ₃ out-of-plane antisymmetric bend	637.1	2
$\omega_{11} (a')$	C ₆ -C ₇ -H ₈ in-plane bend	620.6	46
$\omega_{12} (a')$	C ₂ -C ₄ -C ₅ bend	552.5	4
$\omega_{13} (a'')$	Out-of-plane C ₂ C ₃ symmetric motion	453.9	5
$\omega_{14} (a')$	C ₃ -C ₆ -C ₇ + C ₂ -C ₄ -N ₅ in-plane bend	434.7	2
$\omega_{15} (a')$	C ₃ -C ₆ -C ₇ - C ₂ -C ₄ -N ₅ in-plane bend	231.0	10
$\omega_{16} (a'')$	C ₃ -C ₆ -C ₇ - C ₂ -C ₄ -N ₅ out-of-plane bend	231.0	17
$\omega_{17} (a'')$	C ₃ -C ₆ -C ₇ + C ₂ -C ₄ -N ₅ out-of-plane bend	173.6	9
$\omega_{18} (a')$	C ₆ -C ₇ -C ₇ +N ₅ in-plane bend	95.8	2
$\nu_1 (a')$	C-H stretch	3321.0	82
$\nu_2 (a')$	C-N stretch	2238.7	3
$\nu_3 (a')$	C ₆ shuttle	2126.3	25
$\nu_4 (a')$	C ₂ -C ₃ stretch	1755.1	8
$\nu_5 (a')$	C ₁ -C ₂ stretch	1225.3	7
$\nu_6 (a')$	C ₁ -C ₃ stretch	1194.2	10
$\nu_7 (a')$	C ₁ -C ₂ -C ₄ bend	761.9	1
$\nu_8 (a'')$	C ₆ -C ₇ -H ₈ out-of-plane bend	693.2	27
$\nu_9 (a')$	C ₂ -C ₄ stretch	664.4	1
$\nu_{10} (a'')$	C ₂ C ₃ Out-of-plane antisymmetric bend	628.9	2
$\nu_{11} (a')$	C ₆ -C ₇ -H ₈ in-plane bend	593.4	49
$\nu_{12} (a')$	C ₂ -C ₄ -C ₅ bend	544.0	4
$\nu_{13} (a'')$	Out-of-plane C ₂ C ₃ symmetric motion	452.0	5
$\nu_{14} (a')$	C ₃ -C ₆ -C ₇ + C ₂ -C ₄ -N ₅ in-plane bend	429.5	2
$\nu_{15} (a')$	C ₃ -C ₆ -C ₇ - C ₂ -C ₄ -N ₅ in-plane bend	226.7	9
$\nu_{16} (a'')$	C ₃ -C ₆ -C ₇ - C ₂ -C ₄ -N ₅ out-of-plane bend	225.7	15
$\nu_{17} (a'')$	C ₃ -C ₆ -C ₇ + C ₂ -C ₄ -N ₅ out-of-plane bend	172.5	9
$\nu_{18} (a')$	C ₆ -C ₇ -C ₇ +N ₅ in-plane bend	71.4	2

or greater (see Table 5), which could increase the difficulty of the vibrational detection for $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$. Additionally, the NIRSpect and Mid-Infrared Instrument (MIRI) can only capture spectra to about 333 cm^{-1} , which makes ν_4 at 1218.3 cm^{-1} ($8.21 \mu\text{m}$), with an intensity of 37 km mol^{-1} , the frequency with the highest intensity that could be detected by the JWST. Between the levels of theory in the harmonic vibrational frequencies, F12-DZ and F12-TZ agree within 3 cm^{-1} . Though F12-DZ-cCR differs more in the harmonic vibrational frequencies, this is expected when considering F12-DZ-cCR also includes core correlation and relativistic corrections that are not included in F12-DZ and F12-TZ. There is more variation in the anharmonic vibrational frequencies between the levels of theory, but many of the frequencies have little to no intensity or fall below the high resolution capabilities of the aforementioned instruments on JWST.

Though $c\text{-C}_3(\text{CN})_2$ has not been reported experimentally, the studies of Smith et al. (1994) and Tittle et al. (1999) show that while NC_4N discharges in Ar matrices successfully produce the linear isomer of $c\text{-C}_3(\text{CN})_2$, there are unidentified infrared

features in the experimental spectrum of Smith et al. (1994) that were not computationally reproduced by Tittle et al. (1999). Upon examination of these “leftover” vibrational frequencies, $c\text{-C}_3(\text{CN})_2$ was found not to be responsible for the excess features. For this to be the case, the bright $\nu_4 (a_1)$ vibrational mode of $c\text{-C}_3(\text{CN})_2$ would be expected to be prominent due to the experimental methods of Smith et al. (1994) filtering out most vibrational features that do not belong to the totally symmetric, irreducible representation (Tittle et al. 1999). Therefore, $c\text{-C}_3(\text{CN})_2$ may not have yet been produced in a laboratory environment or may have only been produced in environments in which it immediately undergoes isomerization or some other chemical process. As such, additional and unknown chemistry of this molecule persists even though $c\text{-C}_3(\text{CN})_2$ appears to form easily. These aspects will be explored in future work.

Of the three molecules, $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ has the largest dipole moment, 4.26 D, shown in Table 6. The molecule $c\text{-C}_3(\text{C}_2\text{H})_2$ has the next largest dipole moment, 3.84 D, as shown in Table 7, which is slightly larger than the dipole moment for the known interstellar molecule $c\text{-C}_3\text{HC}_2\text{H}$, which

Table 5. Harmonic and fundamental vibrational frequencies (in cm^{-1}) and intensities (in km mol^{-1}) of $c\text{-C}_3(\text{CN})_2$.

Mode	Description	F12-DZ	F12-DZ-cCR	F12-TZ	B3LYP/TZ
ω_1 (a_1)	Symmetric C-N stretch	2282.4	2289.0	2284.3	1
ω_2 (b_2)	Antisymmetric C-N stretch	2278.7	2285.4	2280.6	2
ω_3 (a_1)	$\text{C}_3\text{-C}_2$ stretch	1800.6	1807.1	1802.6	1
ω_4 (a_1)	$\text{C}_1\text{-C}_2 + \text{C}_1\text{-C}_3$	1248.3	1253.6	1250.4	41
ω_5 (b_2)	$\text{C}_1\text{-C}_2 - \text{C}_1\text{-C}_3$	1220.1	1225.5	1223.6	12
ω_6 (b_2)	In-plane antisymmetric $\text{C}_2\text{-C}_1\text{-C}_3$ bend	770.1	773.7	772.1	2
ω_7 (a_1)	In-plane symmetric bend	662.3	664.5	663.9	2
ω_8 (a_2)	C_2 and C_3 Out-of-plane antisymmetric bend	640.8	642.5	643.7	–
ω_9 (b_2)	$\text{C}_1\text{-C}_2\text{-N}_6 - \text{C}_1\text{-C}_3\text{-N}_7$ bend	552.6	556.0	555.3	1
ω_{10} (b_1)	C_4 and C_6 out-of-plane motion	465.3	465.3	467.8	1
ω_{11} (a_1)	$\text{C}_1\text{-C}_2\text{-N}_6 + \text{C}_1\text{-C}_3\text{-N}_7$ bend	451.0	452.3	453.5	2
ω_{12} (b_2)	C_4 and C_5 antisymmetric in-plane bend	242.6	243.5	243.7	11
ω_{13} (a_2)	$\text{C}_2\text{-C}_4\text{-N}_6 + \text{C}_3\text{-C}_5\text{-N}_7$ out-of-plane bend	240.0	240.0	240.6	–
ω_{14} (b_1)	$\text{C}_2\text{-C}_4\text{-N}_6 - \text{C}_3\text{-C}_5\text{-N}_7$ in-plane symmetric bend	180.2	180.4	180.3	39
ω_{15} (a_1)	$\text{C}_2\text{-C}_4\text{-N}_6 - \text{C}_3\text{-C}_5\text{-N}_7$ out-of-plane bend	99.0	99.4	99.0	6
ν_1 (a_1)	Symmetric C-N stretch	2241.9	2249.1	2243.2	1
ν_2 (b_2)	Antisymmetric C-N stretch	2240.5	2241.2	2238.5	2
ν_3 (a_1)	$\text{C}_3\text{-C}_2$ Stretch	1771.6	1773.8	1771.7	1
ν_4 (a_1)	$\text{C}_1\text{-C}_2 + \text{C}_1\text{-C}_3$	1205.2	1216.4	1218.3	37
ν_5 (b_2)	$\text{C}_1\text{-C}_2 - \text{C}_1\text{-C}_3$	1177.7	1154.8	1172.5	10
ν_6 (b_2)	In-plane antisymmetric $\text{C}_2\text{-C}_1\text{-C}_3$ bend	755.5	741.3	748.8	1
ν_7 (a_1)	In-plane symmetric motion	648.9	654.8	654.0	1
ν_8 (a_2)	C_2 and C_3 out-of-plane antisymmetric bBend	359.9	690.5	540.7	–
ν_9 (b_2)	$\text{C}_1\text{-C}_2\text{-N}_6 - \text{C}_1\text{-C}_3\text{-N}_7$ bend	539.6	518.4	529.9	1
ν_{10} (b_1)	C_4 and C_6 out-of-plane motion	440.5	476.6	389.8	1
ν_{11} (a_1)	$\text{C}_1\text{-C}_2\text{-N}_6 + \text{C}_1\text{-C}_3\text{-N}_7$ bend	446.4	447.6	440.1	2
ν_{12} (b_2)	C_4 and C_5 antisymmetric in-plane bend	234.6	214.9	221.3	11
ν_{13} (a_2)	$\text{C}_2\text{-C}_4\text{-N}_6 + \text{C}_3\text{-C}_5\text{-N}_7$ out-of-plane bend	200.5	264.8	197.4	–
ν_{14} (b_1)	$\text{C}_2\text{-C}_4\text{-N}_6 - \text{C}_3\text{-C}_5\text{-N}_7$ in-plane symmetric bend	141.6	261.2	69.4	38
ν_{15} (a_1)	$\text{C}_2\text{-C}_4\text{-N}_6 - \text{C}_3\text{-C}_5\text{-N}_7$ out-of-plane bend	92.7	98.1	101.7	6

Table 6. Rotational constants of $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$.

Const.	Units	F12-DZ
A_e	MHz	7863.9
B_e	MHz	1551.1
C_e	MHz	1295.7
A_0	MHz	7866.6
B_0	MHz	1550.6
C_0	MHz	1293.6
Δ_J	Hz	417.244
Δ_K	kHz	114.390
Δ_{JK}	kHz	–11.700
δ_J	Hz	150.528
δ_K	Hz	860.046
Φ_J	kHz	1.088
Φ_K	MHz	4.845
Φ_{JK}	kHz	–14.831
Φ_{KJ}	kHz	–275.182
ϕ_j	Hz	499.839
ϕ_{jk}	kHz	1.878
ϕ_k	kHz	428.547
Dipole	D	4.26

is computed to be 3.59 D via F12-TZ (Watrous et al. 2022; Flint & Fortenberry 2022). The molecule $c\text{-C}_3(\text{CN})_2$ has a small dipole moment, 0.08 D, which is much smaller than the dipole moment of $c\text{-C}_3\text{HCN}$, computed to be 3.06 D at the F12-TZ level of theory (Flint & Fortenberry 2022). There are currently no reported experimental equilibrium (e) or vibrationally averaged (0) rotational constants or distortion constants in the literature for these molecules. There are, however, theoretical values for the equilibrium rotational constants and quartic distortion constants for $c\text{-C}_3(\text{C}_2\text{H})_2$. The equilibrium rotational constants differ the most in the A_e constant (1.6%) but have agreement within 0.3% for B_e and C_e , implying that our current results are in line with those of previous studies but should be more accurate due to the anharmonic corrections and the higher level of theory employed. The distortion constants still compare well but have a larger disagreement. For $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$, the only method utilized in this paper is F12-DZ, and it has previously been shown to be accurate within 0.57% of the experiment (Watrous et al. 2021). Between the three different levels of theory utilized for calculating the rotation and distortion constants for $c\text{-C}_3(\text{CN})_2$, as shown in Table 8, there is a strong agreement between the levels of theory with the largest difference in A_0 , which has a 0.63% difference between F12-DZ and F12-DZ-cCR. Of the three levels of theory, F12-DZ-cCR has been shown to be the most accurate, with a mean absolute difference of 0.26% (Watrous et al. 2021). As

Table 7. Rotational constants of $c\text{-C}_3(\text{C}_2\text{H})_2$.

Constant	Units	F12-DZ	Previous theory ^(a)
A_e	MHz	7845.3	7716.69
B_e	MHz	1539.4	1539.34
C_e	MHz	1287.0	1283.34
A_0	MHz	7823.0	
B_0	MHz	1540.8	
C_0	MHz	1285.6	
Δ_J	Hz	404.959	398.5
Δ_K	kHz	119.284	109.249
Δ_{JK}	GHz	-11.774	-11.16
δ_J	Hz	147.856	145.5
δ_K	Hz	827.098	805.15
Φ_J	mHz	1.139	
Φ_K	Hz	4.981	
Φ_{JK}	mHz	-17.750	
Φ_{KJ}	mHz	-241.466	
ϕ_j	uHz	524.768	
ϕ_{jk}	mHz	2.063	
ϕ_k	mHz	463.676	
Dipole	D	3.84	3.774

Notes. ^(a)Previous theory from Thimmakonda & Karton (2017) at the CCSD(T)/cc-pVTZ level of theory.

Table 8. Rotational constants of $c\text{-C}_3(\text{CN})_2$.

Constant	Units	F12-DZ	F12-DZ-cCR	F12-TZ
A_e	MHz	7907.6	7957.4	7913.6
B_e	MHz	1558.9	1564.6	1560.7
C_e	MHz	1302.3	1307.4	1303.8
A_0	MHz	7917.1	7967.3	7923.0
B_0	MHz	1558.0	1563.5	1559.8
C_0	MHz	1300.2	1305.4	1301.6
Δ_J	Hz	415.914	416.018	417.561
Δ_{JK}	kHz	-11.325	-11.384	-11.367
Δ_K	kHz	108.179	109.330	108.401
δ_J	Hz	147.856	147.786	148.466
δ_K	Hz	873.535	876.629	875.637
Φ_J	mHz	1.119	1.117	1.126
Φ_K	Hz	4.108	4.169	4.122
Φ_{JK}	mHz	-16.530	-16.586	-16.589
Φ_{KJ}	mHz	-212.244	-214.214	-213.595
ϕ_j	μHz	510.191	509.199	513.219
ϕ_{jk}	mHz	2.165	2.173	2.176
ϕ_k	mHz	406.415	410.122	407.972
Dipole	D			0.08

such, these results should be taken as the ones to reference for any future experimental or theoretical comparison.

4. Conclusions

This work proposes synthetic pathways consistent with the cold chemistry of the ISM for the formation of two disubstituted $c\text{-C}_3\text{H}_2$ derivatives, $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$, along with

promising thermodynamics for $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$. A second substitution of a radical species onto the ring moiety of $c\text{-C}_3\text{HC}_2\text{H}$ or $c\text{-C}_3\text{HCN}$ is generally found to be as energetically favorable as the initial substitution mechanism. In particular, values for ΔE_{rxn} are nearly equal for the formations of $c\text{-C}_3\text{HC}_2\text{H}$ and $c\text{-C}_3(\text{C}_2\text{H})_2$. As a result, column densities of $c\text{-C}_3(\text{C}_2\text{H})_2$ in TMC-1 are hypothesized to depend mostly on $c\text{-C}_3\text{HC}_2\text{H}$ concentrations, which leads to a potential column density of $c\text{-C}_3(\text{C}_2\text{H})_2$ within the range of current observational capabilities.

In order to aid observation of these molecules that are predicted to form, QFF calculations provide chemically accurate spectroscopic data for the astrochemically viable $c\text{-C}_3(\text{C}_2\text{H})_2$ and $c\text{-C}_3(\text{CN})_2$ as well as for a mixed-substituent molecule, $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$. The intense ν_2 frequency of $c\text{-C}_3(\text{C}_2\text{H})_2$, corresponding to the C-H antisymmetric stretch, coupled with the large dipole moment of 3.84 D allow for its facile astrophysical detection. The strong agreement of these more advanced (and likely more accurate) QFF results with previous theory further validates the spectroscopic methodology used to compute them. Through all current means of astrophysical observation, $c\text{-C}_3(\text{CN})_2$ is likely undetectable due to its near-zero dipole moment as well as its low intensity and low frequency for most of its vibrational motions. In contrast, the considerable dipole moment of $c\text{-C}_3(\text{C}_2\text{H})(\text{CN})$ when taken into account alongside the reasonably intense ν_1 C-H stretch and favorable thermodynamics of formation through either synthetic route may allow for interstellar detection of this molecule. Collectively, these data have the potential to add a new pure hydrocarbon, as well as a new nitrile, to the molecular ranks of the ISM. These molecules may be the key to unlocking hidden chemical pathways to more complex molecules, such as PAHs, as well as formation routes to soot grains and other essential astrophysical building blocks.

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