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The Cation, Anion, and Radical Isomers of C_4H_4N : Computational Characterization and Implications for Astrophysical and Planetary Environments

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Abstract

Nitrogen-containing ions and molecules in the gas phase have been detected in non-Earth environments such as dark molecular clouds, and more recently in the atmosphere of Saturn's moon Titan. These molecules may serve as precursors to larger heterocyclic structures that provide the foundation of complex biological molecules. On Titan, molecules of m/z 66 have been detected by the Cassini mission, and species of the empirical formula C_4H_4N may contribute to this signature. We have characterized seven isomers of C_4H_4N in anionic, neutral radical, and cationic states using density functional theory. Structures were optimized using the range-separated hybrid ω B97X-V with the cc-pVTZ and aug-cc-pVTZ basis sets. Anionic and radical C_4H_4N favor cyclic structures with aromatic and quasi-aromatic electron arrangements, respectively. Interestingly, ionization from the radical surface to the cation induces significant changes in structural stability, and the global minimum for positively charged isomers is $CH_2CCHCNH^+$, a pseudo-linear species reminiscent of cyanoallene. Select formation pathways to these structures from Titan's existing or postulated gas-phase species, reactions which are also relevant for other astrophysical environments, are discussed. By characterizing C_4H_4N isomers, we have identified energetically stable anionic, radical, and cationic structures that may be present in Titan's atmosphere and dark molecular clouds.

Introduction

The emergence of biomolecules on early Earth is an intriguing topic and the chemical origins of life have not been fully resolved. Groundbreaking experiments performed by Miller in the mid-1950's under reducing conditions showed that complex organic molecules can form from small inorganic precursors in the presence of electric discharge¹, supporting the possibility of biomolecule formation in the atmosphere of primitive Earth. Since this iconic experiment,

our understanding of chemistry in early Earth environments has continued to grow, and multiple synthetic routes leading to complex organic species have emerged²⁻¹¹.

Though these complex molecules have been shown to form without pre-existing complex organic material, the particular atmospheric conditions of our young planet are not entirely certain. Thus, it is important to consider a variety of alternative conditions supporting biomolecule origin.

Exogenous delivery of key precursors to Earth

from extraterrestrial environments is one example. Complex organic molecules have been found in many astrophysical environments including interstellar molecular clouds, protoplanetary nebulae, and primitive solar system bodies¹². Particularly, the existence of these molecules (including pristine amino acids and sugars) has been confirmed in meteoritic samples of extraterrestrial origin¹³⁻¹⁶, implying that exogenous delivery of organic molecules during or after the formation of the solar system is a viable pathway that could have precluded biomolecule formation on early Earth, and potentially contributed to the origins of life on this planet. Direct formation of these nucleobases on interstellar cold grains has been shown to occur when ices containing the appropriate precursors undergo UV irradiation¹⁷⁻²². Additionally, these compounds could be synthesized in the gas phase and condense onto cold grains for delivery to early planetary systems.

Gas-phase reactions are more likely to occur in environments such as the circumstellar envelopes of dying stars, dark molecular clouds, and select planetary atmospheres where particle densities are higher than in the diffuse interstellar medium²³⁻²⁵. As well as illuminating formation pathways to complex species that could be delivered exogenously to Earth through meteorites, some of these processes serve as useful templates when considering the atmospheric conditions of early Earth. Low temperatures typical of these environments disfavor particle growth through neutral-neutral reactions between closed-shell members, which require large activation barriers; however, reactions involving radicals and ions proceeding through small or submerged energetic barriers have been shown to produce complex nitrogen-containing molecules²⁶⁻²⁹. Ion-molecule chemistry between atomic nitrogen and cyclic precursors can generate nitrogenated polycyclic aromatic hydrocarbons (PAH)^{30,31}, and cyclization reactions of smaller nitrogenated and hydrocarbon species are also quite possible^{25,32}.

A planetary body of particularly rich nitrile chemistry is the ionosphere of Titan, Saturn's moon. Titan's dense atmosphere, composed primarily of nitrogen (94 - 98%) and methane

(1.8 - 6.0%)³³, is exposed to UV and extreme-UV radiation as well as energetic electrons from Saturn's magnetosphere³³; this particular combination favors molecular interactions involving and producing nitrogen-containing molecules. Understanding processes occurring in Titan's atmosphere that could lead to complex nitrogenated organics is important for species identification both here and in molecular clouds, and these may mimic reactions that took place in a primitive Earth environment.

The recent Cassini-Huygens mission, equipped with an ion neutral mass spectrometer (INMS), performed a fly-by of Titan and collected data on neutral, cationic, and anionic species up to several hundred daltons in size³⁴⁻³⁸. Accurate identification of new nitrogen-containing species in remote environments such as the atmosphere of Titan is experimentally difficult, and often relies on theoretical groundwork when existing molecular information is limited. Here, we explore the lower mass end of the INMS readings (<100 daltons), and specifically direct our investigation to the measured signal at m/z 66³⁹⁻⁴². There are several stoichiometries that could potentially contribute to this mass peak (e.g. C_4H_4N , $C_2N_3^-$, $C_5H_6^+$, $C_3H_2N_2$, etc.^{42,42-45}), belonging to hydrocarbons or nitriles due to the atmospheric composition. We choose to focus our attention on isomers of the empirical formula C_4H_4N due to its potential to form heterocyclic ring structures.

Similar characterizations of C_4H_5N and C_4H_3N isomers have been performed to identify energetically favorable arrangements^{46,47}. For example, C_4H_5N is by far most stable in ring form as pyrrole⁴⁷. This aromatic 5 membered ring contains 6π electrons; the apical nitrogen is sp^2 hybridized in the molecular plane, leaving its lone pair to delocalize into the aromatic system. Linear species of C_4H_3N (isomers of which have been detected in the interstellar medium⁴⁸⁻⁵⁰) have been studied by Custer et al.⁴⁶, who found that methylcyanoacetylene CH_3CCCN was the most stable isomer of those tested. The preferred structures of each chemical formula are good indicators of which isomers are most likely to be present in cold extrater-

restrial environments.

Changes in the electronic structure of these molecules influence isomer stability and reactivity. Multiple potential energy surfaces are available to C_4H_4N depending on the mechanism of formation: anionic or neutral radical species may form via deprotonation or dehydrogenation of cyclic C_4H_5N , while protonation of C_4H_3N leads to cationic $C_4H_4N^+$. In the open-shell radical or closed-shell ionic form, molecules such as C_4H_4N are especially reactive and could initiate reactions producing the larger heterocyclic structures that compose biomolecules. Reactions involving pyrrole and pyridine (the six-membered aromatic analog) have been experimentally probed in this vein^{26,27,51}.

Because chemistry in cold extraterrestrial environments is driven primarily by radical-radical and ion-radical reactions (as well as those between a closed shell species and an ion or radical), characterization of C_4H_4N in different electronic states will help us identify which species are likely to participate in pathways leading to biologically relevant molecules. Thus, we present a systematic exploration of select C_4H_4N isomers in their cationic, anionic, and radical forms. The relative stability of these structures in each electronic state is discussed, as well as select formation routes via the uni-molecular or bi-molecular reactions of available species. By characterizing C_4H_4N , we produce structures that will narrow the field of candidate molecules that may contribute to the observed mass data from Cassini INMS, and thus help guide the identification of new species. In the process, we hope to also gain a better understanding of how unique cationic, anionic, or radical isomers are formed and could contribute to the synthesis of complex organics. This will help us understand not only processes occurring in the rich atmosphere of Titan or that of early Earth, but also in cold molecular clouds where nitrogen-containing molecules may form in the gas phase and deposit onto the cold grains of meteorites for delivery to planetary bodies.

Methods

Seven isomers of C_4H_4N (see Figure 3 for optimized radical structures, which deviated the least from starting geometries) were chosen based on their presence in both the chemical physics and combustion literature^{47,52–54}. Though we recognize that these seven isomers are not fully representative of all possible configurations, the number of species was limited to likely low-energy structures to lessen computational cost and focus on adequate characterization of individual species. Full geometry optimizations were performed for structures of all seven isomers and several relevant precursors using unrestricted density functional theory (DFT), a widely used method for quantum mechanical calculations by virtue of its impressive accuracy at low computational cost. Our DFT calculations were performed on an ultra-fine integration grid of 99 radial points and 590 angular points. Optimizations of starting structures A-G were performed using the ω B97X-V functional⁵⁵. The range-separated hybrid ω B97X-V has been shown to out-perform many other existing functionals for calculations on numerous relevant systems^{56–59}. Inclusion of range-separation helps mitigate the infamous ‘self-interaction error’ inherent to DFT, which can lead to inaccuracies in energetics, especially in radical systems such as the ones studied here^{60,61}. Each structure was allowed to relax from the initial geometry on the appropriate potential energy surface: anion, neutral radical, and singlet cation. Isomers are referred to by distinguishing letter and charge symbol hereafter (e.g. A^- , A^\bullet , and A^+ for anionic, neutral radical, and cationic isomer A).

Cationic and radical isomers were optimized with ω B97X-V in the cc-pVTZ basis. Because the use of diffuse functions is generally recommended for DFT calculations involving anions, anionic structures were optimized using the larger aug-cc-pVTZ basis set. Inclusion of sufficient diffuse functions in aug-cc-pVTZ better captures the ‘tail behavior’ of atomic orbitals farther from the atom’s nucleus, a crucial feature for structures with excess electron density⁶². Natural Population Analyses⁶³ were calculated using ω B97X-V in aug-cc-pVTZ. To confirm that the equilibrium geometries of the

isomers were indeed minima and obtain zero point energies, vibrational frequency analyses were performed for cations and radicals at the ω B97X-V/cc-pVTZ level, and for anions at the ω B97X-V/aug-cc-pVTZ level. Vibrational constants and intensities are provided in the Supplemental Information. Because the accuracy of the isomer energies was crucial for the purposes of this study, single-point energies were calculated for isomers A-G of the cation, radical, and anion at the coupled cluster level, including up to triple excitations using CCSD(T)⁶⁴. In conjunction with second-order Møller-Plesset perturbation theory with the resolution of the identity approximation (RI-MP2)^{65,66} in progressively larger basis sets, energies were extrapolated to the complete basis set limit (CBS) using the following scheme:

$$E(CCSD(T)/CBS) = E(HF/cc-pV5Z) + E^{corr}(RI-MP2/CBS_{3,4,5}) + E^{corr}(CCSD(T)/cc-pVTZ) - E^{corr}(RI-MP2/cc-pVTZ) + ZPE(\omega B97X-V/cc-pVTZ)$$

Here, the $E^{corr}(RI-MP2/CBS_{3,4,5})$ term contains the complete basis extrapolation using cc-pVTZ through cc-pV5Z:

$$E^{corr}(RI-MP2/cc-pVNZ) = E^{corr}(RI-MP2/CBS_{3,4,5}) + AN^{-3}$$

The variable N corresponds to the basis set cardinal number⁶⁷, which here is 5. For anionic structures, the same scheme was followed using aug-cc-pVNZ.

In exploring potential formation pathways of the lowest-energy structures, the freezing-string method was utilized to generate a guess for transition state structures⁶⁸. Once a suitable transition state was located, its initial structure and Hessian were further improved using the partitioned-rational function optimization eigenvector following method⁶⁹. All this is done using ω B97X-V with cc-pVTZ.

All calculations were performed using the Q-Chem 5 software package⁷⁰.

Structural Results and Discussion

Anionic isomers

Figure 1 shows the energetic ordering of structures on the closed-shell anionic potential energy surface.

Isomer (Formula)	Structure	Relative Energy
A ⁻ (c-C ₄ H ₄ N)		0.00
E ⁻ (CH ₃ CCHCN)		36.01
B ⁻ (c-C _α C ₃ H ₃ NH)		36.50
D ⁻ (CH ₂ CCH ₂ CN)		45.38
C ⁻ (c-C _β C ₃ H ₃ NH)		47.28
F ⁻ (CH ₂ CCHCNH)		58.77
G ⁻ (CH ₂ CHCCHN)		88.29

Figure 1: Structures of C₄H₄N in the closed-shell anionic state. Isomer (A⁻) was found to be the energetic minimum, stabilized by a favorable 6 π aromatic electron arrangement. Energetic differences are calculated with respect to (A⁻) in kcal/mol.

The energetic differences of the anionic isomers were computed with respect to cyclic iso-

mer (A^-), which was found to be the most stable structure (energetic minimum). Electronically, (A^-) is isoelectronic to pyrrole. Pyrrole and $C_4H_4N^-$ are aromatic heterocycles, each with a total of 6π electrons; four π electrons are contributed by carbon atoms in the conjugated 5-member ring, and the remaining two are donated from the nitrogen’s lone pair.

In neutral pyrrole, the nitrogen atom has an in-plane trigonal configuration, bonding to the surrounding α carbons and a single hydrogen; the remaining lone electron pair occupies $2p_z$ out-of-plane, contributing to the 6π aromatic ring system⁷¹. Deprotonation of pyrrole occurs at the apical nitrogen, as the electronegativity difference between N and H makes this proton the most acidic. In the anionic C_4H_4N (structure (A^-)), the aromatic configuration is retained. Due to this favorable electronic arrangement, isomer (A^-) is by far the favored structure on the anionic surface - the second lowest energy structure (E^-) lies 36 kcal/mol above (A^-) in energy and is quasi-linear, stabilized by several resonance structures. Most of the negative charge in (E^-) is localized on the carbon at which the molecule sharply bends; because of (E^-)’s shape, electron density centered on this carbon is spatially separated from the lone electron pair on nitrogen, decreasing steric interactions between the respective electron clouds. To the point, cyclic (B^-) (deprotonated at the α carbon) is slightly destabilized by comparison; steric interactions between electrons on the alpha carbon and the adjacent nitrogen are comparatively unfavorable.



Figure 2: Bond lengths (**I.**) and Natural charges (**II.**) for anionic (A^-) calculated in ω B97X-V/aug-cc-pVTZ. Charges indicated on carbon atoms are a sum of the C-H moiety. The aromatic nature of the ring leads to a planar structure with lengthened $C_\alpha=C_\beta$ and slightly shortened $C_\beta-C_\beta$ and $C_\alpha-N$ (compared to pyrrole).

Figure 2 shows bond lengths (**I.**) and Natural charges (**II.**) in anionic isomer (A^-), the global minimum for this set. The 6π aromatic conjugation of the structure results in a shortened 1.416 Å $C_\beta-C_\beta$ (vs 1.424 Å), a lengthened 1.397 Å $C_\alpha=C_\beta$ (vs 1.371 Å), and shortened 1.357 Å $C_\alpha-N$ (vs 1.370 Å) bond (compared to those in neutral pyrrole), culminating in a planar structure with C_{2v} symmetry. These slight deviations from parent pyrrole (optimized at the same level of theory) are due largely to the extra electron density of the anionic lone pair atop the apical nitrogen, which also drives the 109.7° $C_\alpha-N-C_\alpha$ angle in pyrrole to a more acute 105.0° in deprotonated (A^-). Natural charges reflect the spread of electron density across the ring, with negative charge centered mostly at nitrogen as expected, but also distributed in a good proportion to the β carbons.

Structural stability depends highly on the deprotonation site in the anionic C_4H_4N cyclic isomers. Deprotonation of the heteroatom to form (A^-) is clearly the most favorable process - as discussed previously, the distinct difference in electronegativity along the N-H bond makes this proton highly acidic. Deprotonation at an α or β carbon in the ring is comparatively more difficult, despite the similarities in N-H and C-H bond enthalpies (both 338 kJ/mol⁷²). Structures (B^-) and (C^-) (with C-H bond cleavage at α and β sites, respectively) lie over 36 kcal/mol higher in energy than (A^-). Deprotonation at the α carbon in (B^-) is preferred over a similar process at the

β site in (C^-), with the latter relatively destabilized by just over 11 kcal/mol. In general, electrophilic substitutions to five-member heterocyclic rings favor attack at the α carbon. Compared to the β site, substitution at the α carbon leads to a greater number of intermediate resonance structures, allowing for more facile charge delocalization and a more stabilized product⁷³. Due to this effect and the proximity of the electron-withdrawing heteroatom, the hydrogen atom at the α carbon is more acidic than that at the β carbon, favoring α deprotonation of the cycle. These effects stabilize (B^-) relative to (C^-).

Radical isomers

For the radical electronic configuration, (A^\bullet) is once again found to be the global minimum as shown in Figure 3. Interestingly, quasi-linear isomer (E^\bullet) is quite close in energy to cyclic radical isomers (B^\bullet) and (C^\bullet); these isomers all lie ~ 23 - 26 kcal/mol above (A^\bullet) in energy. The relative energetics of isomers (B^\bullet) and (C^\bullet) with respect to (A^\bullet) indicate that the location of the radical electron influences heterocycle stability. Other linear and semi-linear isomers of C_4H_4N are found to be subsequently higher in energy than their cyclic counterparts on the radical PES, though with energetic differences less dramatic than in the anionic case.

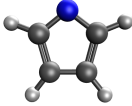
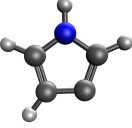
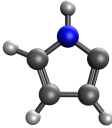
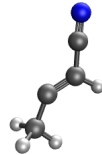
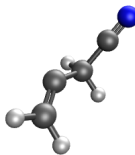
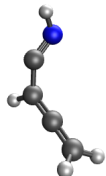
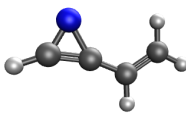
Isomer (Formula)	Structure	Relative Energy
A^\bullet (c- C_4H_4N)		0.00
C^\bullet (c- $C_\beta C_3H_3NH$)		23.55
B^\bullet (c- $C_\alpha C_3H_3NH$)		24.22
E^\bullet (CH_3CCHCN)		26.65
D^\bullet (CH_2CCH_2CN)		30.67
F^\bullet ($CH_2CCHCNH$)		46.73
G^\bullet ($CH_2CHCCHN$)		56.42

Figure 3: Structures of C_4H_4N in the radical configuration; relative energies are calculated with respect to (A^\bullet) in kcal/mol. Similar to the anionic state, (A^\bullet) is the lowest energy structure. Though electron removal has resulted in loss of complete aromaticity, (A^\bullet) still benefits from some delocalization of the remaining 5π electrons over the ring.

Recent calculations performed by Sah et al. on a variety of five-membered heterocyclic species found that radicals centered at the heteroatom were favored over those located on nearby α or β carbon atoms - unpaired electrons on heteroatoms can delocalize across the π orbitals of the ring more easily⁵². For dehydrogenated pyrrole species (C_4H_4N), these authors optimized heteroatom, α carbon, and β

carbon centered radicals (corresponding to our (A \cdot), (B \cdot), and (C \cdot)) at several levels of theory, and our computed energetic differences are in good agreement.

The particular stability of (A \cdot) can be rationalized in a way similar to the anionic analog. Recall the nature of the apical nitrogen - in both pyrrole and the aforementioned anionic counterpart, N is sp^2 hybridized and maintains a trigonal configuration within the molecular plane. In anionic (A $^-$), nitrogen has two electron pairs. One occupies the $2p_y$ orbitals to maintain the sp^2 arrangement, and the other resides in $2p_z$ out of the molecular plane, contributing to the aromatic ring system. (A $^-$) is isoelectronic to cyclopentadienyl anion, which has degenerate π molecular orbitals due to the D_{5h} symmetry of the molecule⁷⁴. However, inclusion of a nitrogen atom in the ring reduces the overall symmetry to C_{2v} in pyrrole and (A $^-$), and the π orbitals are no longer energetically degenerate⁷⁵. Due to their hybridization and non-participation in the π system, nitrogen's $2p_y$ orbitals lie lower in energy than the $2p_z$ orbitals. Because of this, electron removal from (A $^-$) to form the radical (A \cdot) occurs from $2p_z$ - this disturbs the aromaticity of the cycle, but the radical electron can still delocalize over the ring, resulting in a pseudo-aromatic 5π arrangement. Considering the stabilization of $2p_y$ and the observation that (A \cdot) suffers no distortion from the x-y plane, it is reasonable to assert that the unpaired electron of the radical occupies $2p_z$ and the lone pair of $2p_y$ remains intact.

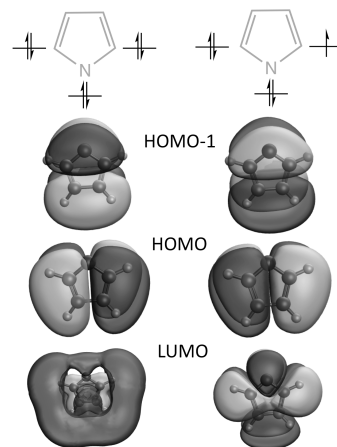


Figure 4: Comparison of molecular orbitals and electron configuration between (A $^-$) (left) and (A \cdot) (right). The HOMO of anionic (A $^-$) is similar to the SOMO of the corresponding radical species, indicating electron removal from the anionic occurs from $2p_z$ orbitals on nitrogen that contribute to the π system. The $2p_y$ orbitals are largely undisturbed and contribute to the planarity of (A \cdot).

The orbitals shown in Figure 4 support this picture. The highest occupied molecular orbital (HOMO) of anionic (A $^-$) and singly occupied molecular orbital (SOMO) of radical (A \cdot) show similar shapes, indicating a similar contribution from the atomic orbitals.

The molecular orbitals of these heterocycles and their occupations have been previously appraised; Gianola et al. investigated the electronic structure of pyrrolide anion and its corresponding radical in detail, noting the clear bonding character between α and β carbons⁷⁵. In our systems, this interaction is particularly strong in the anion, and removal of an electron to form the radical reduces bonding character. This manifests as a slight lengthening of the central $C_\alpha=C_\beta$ bonds highlighted in Figure 5. Though these structural changes occur due to the loss of aromaticity in radical (A \cdot), decreased interaction between α and β carbons does not completely destabilize the ring.

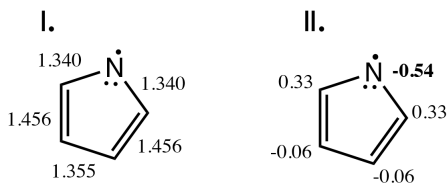


Figure 5: Bond lengths (**I.**) and Natural charges (**II.**) for radical (A^\bullet) calculated in ω B97X-V/cc-pVTZ. Charges indicated on carbon atoms are a sum of the C–H moiety. Electron removal from anionic (A^-) has disrupted the aromaticity of the heterocycle, inducing small structural changes in the radical and reflecting the depletion of bonding character between α and β carbons.

Figure 5 shows the bond lengths (**I.**) and Natural charges (**II.**) of isomer (A^\bullet) in the radical configuration. Though (A^\bullet) is pseudo-aromatic and stabilized on the radical surface, the loss of complete aromaticity is reflected in the bond lengths and charge distribution.

Stretching and shortening of bonds in radical (A^\bullet) reflects fluctuations of electron density. Compared to anionic (A^-), there is a slight lengthening of the 5-member heterocycle, as the $C_\alpha=C_\beta$ bonds stretch by 0.059 \AA while $C_\alpha-N$ and $C_\beta-C_\beta$ shorten by 0.017 and 0.061 \AA respectively.

While the loss of bonding character between α and β carbons manifests in $C_\alpha=C_\beta$ lengthening, the apical $C_\alpha-N-C_\alpha$ angle remains nearly unaltered from the aromatic anion ring at 104.6° , indicating that the position of the lone pair atop N remains undisturbed and providing further support for the proposed 5π electronic arrangement.

As shown in Figure 5 **II.**, charge differences between ring atoms have become more pronounced than in the anionic case of (A^-). These changes in charge distribution go hand-in-hand with the altered bond lengths. Stretching of $C_\alpha=C_\beta$ in (A^\bullet) brings the p orbitals of the α carbons closer to nitrogen, donating some of their electron density to the more electronegative atom. As a consequence, α carbons have taken on a noticeable positive charge, and are quite charge separated from their neighboring nitrogen.

The β carbons of (A^\bullet) pull closer together at

a distance nearing that of a carbon-carbon double bond. Like the α carbons, β carbons have become more positive than nitrogen (by 0.48 charge units, versus their 0.36 charge unit difference in (A^-)). Though the effect is less drastic, α and β carbons themselves are charge separated to a greater degree as bonding character between them decreases.

Additionally, spin density delocalization contributes to the stability of (A^\bullet) and helps explain the relative stabilities of cyclic isomers (B^\bullet) and (C^\bullet). As shown in Figure 3, there is a ~ 24 kcal/mol difference in energy between (A^\bullet) and the other cyclic isomers, though (B^\bullet) and (C^\bullet) less than 1 kcal/mol apart. This is in contrast to anionic (B^-) and (C^-) isomers, which were energetically separated by about 11 kcal/mol (with relative stabilization of (B^-)).

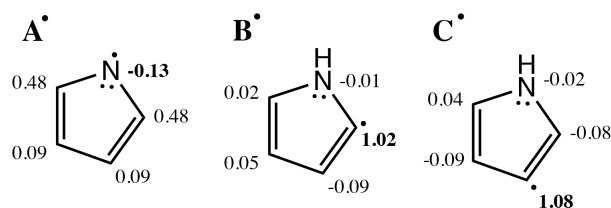


Figure 6: Spin densities calculated for isomers (A^\bullet), (B^\bullet), and (C^\bullet). Electron spin is relatively delocalized in (A^\bullet), while it is highly localized for (B^\bullet) and (C^\bullet).

For dehydrogenation reactions of pyrrole to form the radical, acidity of the departing hydrogen is less predictive of the preferred reaction site than it is for deprotonation reactions; since isomers (A^\bullet), (B^\bullet), and (C^\bullet) are carrying a radical electron, spin densities help explain some of the observed stability trends, shown in Figure 6. Highly localized electron spin results in a very reactive species, while delocalized spin conversely stabilizes a structure⁵². Figure 6 shows the distribution of spin between the two α carbons in (A^\bullet), contributing to the stability of the structure. Conversely, (B^\bullet) and (C^\bullet) show highly localized spin densities at their respective dehydrogenation sites, and spin is localized to the same degree in each, so α dehydrogenation is not particularly favored over the β site, and vice versa.

Cationic isomers

Removal of another electron from the C_4H_4N radical surface results in the singlet cationic electronic configuration. Ionization is accompanied by more major shifts in the stability ordering of these isomers shown in Figure 7.

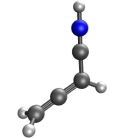
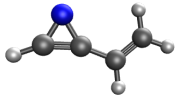
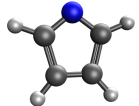
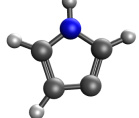
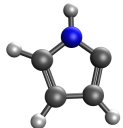
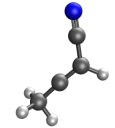
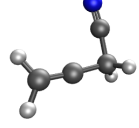
Isomer (Formula)	Structure	Relative Energy
F^+ ($CH_2CCHCNH$)		0.00
G^+ ($CH_2CHCCHN$)		23.91
A^+ ($c-C_4H_4N$)		25.83
C^+ ($c-C_\beta C_3H_3NH$)		32.95
B^+ ($c-C_\alpha C_3H_3NH$)		34.81
E^+ (CH_3CCHCN)		40.25
D^+ (CH_2CCH_2CN)		40.62

Figure 7: Structures of C_4H_4N in the cationic state; relative energies are expressed in kcal/mol. Heterocyclic (A), the global minimum on both anionic and radical potential energy surfaces, is now reduced to an anti-aromatic arrangement with 4π electrons in the ring, destabilizing the structure. The global minimum for the cationic surface was found to be (F^+), a linear structure reminiscent of cyanoallene.

Previously, cyclic (A) was found to be the global minimum on the radical and anionic potential energy surfaces; however, in the cationic

case, (G^+) and (F^+) are found to be lower in energy. Similar to the anion/radical transition, transition from radical (A^\bullet) to the cation can occur via electron removal from either the $2p_y$ or $2p_z$ of nitrogen, and once again this removal occurs from the higher energy $2p_z$ orbitals. Nitrogen's lone pair continues to occupy $2p_y$ and planarity is retained; however, (A^+) is now left relatively higher in energy due to its anti-aromatic 4π electron arrangement.

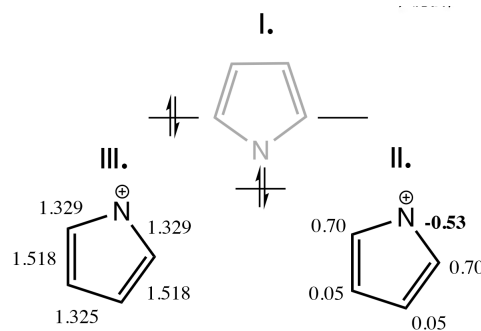


Figure 8: Electronic configuration (**I.**), Natural charges (**II.**), and bond lengths (**III.**) for cationic (A^+). Charges indicated on carbon atoms are a sum of the C–H moiety. Half-filled orbitals contribute to the destabilization of this structure.

In response, the $C_\alpha=C_\beta$ bonds elongate to 1.518 Å, close to a typical C–C single bond.

Cationic (A^+) was found to be a transition state structure, and the now half-filled molecular orbitals (Fig. 8 **I.**) contribute to structural distortion that lowers the overall energy of the molecule. Despite its stretched and strained structure, the singlet cation was found to be lower in energy than the triplet configuration, though the singlet-triplet gap is small (~ 5.2 kcal/mol).

As shown in Figure 8 **III.**, the $C_\alpha=C_\beta$ bonds have lengthened significantly compared to aromatic pyrrole or anionic (A^-), approaching the length one would expect from a C–C single bond. Since (A^+) is now antiaromatic, the bonding character between α and β carbons established for anionic and radical species⁷⁵ is disrupted completely. Similar phenomena have been discussed in detail for the isoelectronic cyclopentadienyl cation^{74,76}, another planar C_{2v} ring with modes of distortion leading

to lower symmetry (more energetically stable) structures⁷⁷.

The stabilization of (G^+) compared to (A^+) is slightly surprising - however, structural strain within the three-membered ring is mitigated by electron delocalization, as the ring is aromatic by the $4n+2$ rule, where here $n=0$. In isoelectronic 3-membered carbocations such as cyclopropenyl, structures are stabilized by delocalization of the 2π electrons residing in the ring system, which can spread into empty $2p$ orbitals of the positively charged carbon atoms^{78,79}. Azirinyli cation, a three-membered ring with an apical nitrogen atom, has recently been investigated in the interstellar context and was found to be the most stable structural isomer of the formula $C_2H_2N^+$ ⁸⁰.

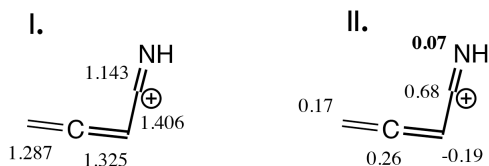


Figure 9: Bond lengths (**I.**) and Natural charges (**II.**) for cationic (F^+). Charges indicated on carbon atoms are a sum of the $C-H$ moiety. This carbocation is of C_s symmetry, and is stabilized by electronic donation from the neighboring nitrogen and $C-H$ σ bond to vacant p orbitals of the positively charged carbon.

The global minimum on the singlet cationic surface was found to be (F^+), a highly conjugated quasi-linear isomer with C_s symmetry. As shown in Figure 9, the unsaturated carbon participating in the $C=N$ double bond (C_2) carries most of the positive charge. Hyperconjugation and resonance contribute to the stability of this carbocation. The empty p orbital on C_2 can accept electron density from the nearby $C-H$ σ bond; this stabilizing interaction results in a lower-energy electron occupancy versus the isolated positively charged p orbital. Structurally, this manifests as the slight shortening of the C_2-C_3 single bond. Similarly, a non-negligible amount of electron density from the lone pair on nitrogen interacts with the C_2 empty p orbital, again stabilizing the positively charged carbon

atom and shortening the $C=N$ double bond to a length approaching that of a $C\equiv N$ triple bond.

Ionization energies and electron affinities

Table 1 shows the adiabatic electron affinities and ionization energies of all isomers studied here as compared to the radical form in units of eV. Unsurprisingly, electron attachment to radical (A^\bullet) forming anionic (A^-) is quite favorable, as this leads to 6π electrons in the ring. Energetic stabilization through anion formation decreases with structural stability of the anionic isomer. Electron affinity for isomer (F^\bullet) was not included in this table due to the significant structural rearrangement that occurs upon electron gain (See Figures 1 and 3 for comparison between the structures).

Table 1: Adiabatic electron affinities and ionization energies (eV) relative to the radical species for all isomers. Single point energies were calculated for the $\omega B97X-V/cc-pVTZ$ optimized geometries using (CCSD(T)/CBS) for all isomers. All species (except perhaps G) are stabilized by electron gain. Ionization of radical (A^\bullet) requires significant energy, while ionization of radical (F^\bullet) is markedly more feasible.

Isomer	EA	IE
A	2.21	9.20
B	1.68	8.54
C	1.18	8.48
D	1.57	8.51
E	1.80	8.67
F	—	6.05
G	0.83	6.67

An interesting trend has emerged regarding ionization states of isomer (F). On the anionic surface, previously linear (F) rearranges to adopt a central 3-membered ring, promoting delocalization of negative charge. These structural adaptations require significant energy. In contrast, ionization to the cationic state supports the original linear arrangement.

Astrochemistry Implications

In the previous sections, we calculated low-energy structures of cationic, radical, and anionic isomers, providing a structural starting point for further identification of species that may be present in Titan’s atmosphere and elsewhere. Providing highly accurate rotational data using theoretical methods for use in conclusive species identification is a challenging prospect^{81,82}. Though our goal in this work was not to provide such data, our accurate structures in conjunction with their vibrational frequencies and IR intensities may still be used for species identification in interstellar measurements. As an example, the SOFIA EXES instrument gathers spectra in the 4.5–28.3 μm wavelength range⁸³; for applications such as these, *ab initio* quantum mechanics would produce reliable data to match signals to molecules^{84–86}. Because calculated vibrational frequencies and IR intensities in addition to molecular structures are thus useful to provide astronomers with a solid foundation for deconvoluting measurable ro-vibrational data for small molecules, we provide vibrational frequencies and intensities for the energetic minima of each $\text{C}_4\text{H}_4\text{N}$ state in the SI.

Small nitrogen-containing molecules such as $\text{C}_4\text{H}_4\text{N}$ may be found in molecular clouds or in the ionospheres of planetary bodies such as Titan, and perhaps even existed in the young atmosphere of our own Earth long ago. In Titan’s nitrogen-rich atmosphere, many energy sources are available to initiate the formation of radicals and ions, including short wavelength ultraviolet (UV) radiation, extreme ultraviolet radiation (EUV) and an energetic flux of electrons from Saturn’s magnetosphere³³. Nitriles produced in the upper atmosphere through photochemistry involving N_2 and CH_4 ^{87–89} presumably combine through ion-neutral or radical chemistry to form more complex species, contributing to the organic haze surrounding this planetary moon⁹⁰.

Here, we investigate several relevant formation pathways leading to ions of $\text{C}_4\text{H}_4\text{N}$ and their preferred structures.

Anion species

The Cassini-Huygens mission identified a number of nitrogen-containing anionic species in Titan’s atmosphere, including anions of this molecular weight ($m/z = 66$)⁴². Though cyclic species such as isomers (A), (B), and (C) have yet to be unambiguously observed in the gas phase, precursors such as pyrrole and other N-heterocycles have been detected as products in plasma-discharge, H-NMR, and other experiments performed in Titan-like conditions or on tholin mixtures^{91,92}.

With these observations in mind, the presence of pyrrole ($\text{C}_4\text{H}_5\text{N}$) in Titan’s haze (or elsewhere in the interstellar medium) cannot be discounted, and we thus consider the direct formation of anionic (A^-) from this hydrogenated five member ring to be a viable possibility.

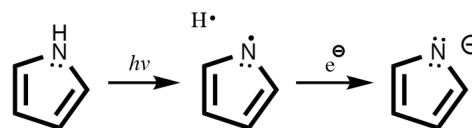


Figure 10: Formation of anionic (A^-) from pyrrole via photodissociation. Dehydrogenation of the apical N follows excitation via energetic UV radiation, and electron attachment yields the stable anionic isomer.

Figure 10 depicts the formation of anionic (A^-) through photodissociation of pyrrole and subsequent electron attachment. The photofragmentation and dynamics of excited state pyrrole have been extensively studied^{93–104}(and references therein). Irradiation of ground state pyrrole (S_0 ($^1\text{A}_1$)) at wavelengths from 238–250 nm (corresponding to photons of energy >4.8 eV) excites the molecule into the $^1\pi\sigma^*$ ($^1\text{A}_2$) excited state from which hydrogen atoms are ejected quickly with high kinetic energy, yielding the ground state radical (A^\bullet)^{93,100,101}; though this is formally electric-dipole forbidden, this mode intensifies by borrowing vibrational energy from higher energy states^{100,103}. At shorter excitation wavelengths, ejection can also occur after direct excitation to the $^1\pi\pi^*$ state ($^1\text{B}_2$), which accesses the $^1\pi\sigma^*$ ($^1\text{A}_2$) energetic state via a conical intersec-

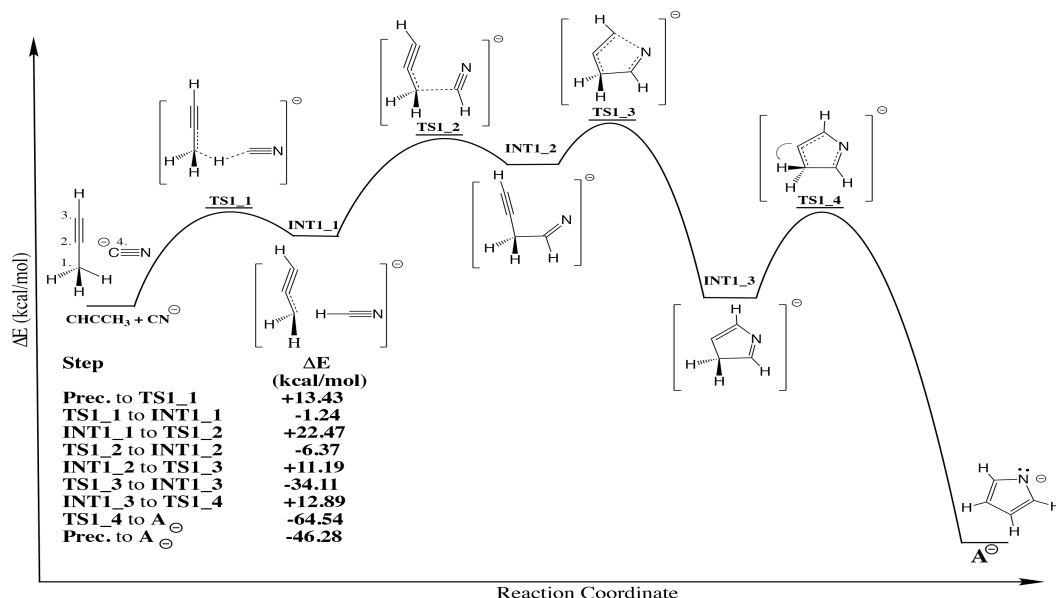


Figure 11: Schematic reaction path to anionic (A^-) via CN^- and CH_3CCH . Both propyne and cyano anion have been detected in Titan's ionosphere, and could react to produce anionic (A^-). However, the high energetic barriers to cyclization through this path are likely insurmountable without outside energetic input.

tion^{100,102}. Slower hydrogen ejection can occur from a "vibrationally hot" pyrrole ground state S_0 , where additional energy is dispersed to the many vibrational modes of the heterocycle^{100,101,103}. In Titan's atmosphere, long wave UV radiation (>155 nm) pierces down to intermediate altitudes (nearing 500 km), providing an adequate energy source for the photodissociation of pyrrole.

After formation of the ground state radical (A^\bullet), the high electron affinity of this species (see Table 1) makes it a good candidate for thermal electron attachment. Processes such as radiative electron attachment (REA) have been investigated as a viable pathway to anion formation in Titan's atmosphere¹⁰⁵. With many vibrational modes to disperse excess energy, (A^\bullet) could efficiently form (A^-) through this process, depicted in the second step of Figure 10. Additionally, the atmosphere is dense enough³⁹ to support third body interactions that may assist in diffusing the newly formed molecule's energy.

Alternatively, formation of anionic (A^-) is possible through recombination of smaller species, such as CN^- and propyne ($CHCCH_3$). Both precursors have been detected in molec-

ular clouds^{106,107} and more recently in Titan's atmosphere: the signatures of various negative ions including CN^- were observed by Cassini-Huygens^{35,36}, and several models calculate cyanide anion to be ubiquitous¹⁰⁵. Heavier hydrocarbons including propyne have been detected at lower altitudes¹⁰⁸.

Despite the availability of both of these species and the possibility of their reaction, our calculations have shown that the feasibility of this pathway is questionable; Figure 11 show that the reaction between CN^- and $CHCCH_3$ passes through high barriers and would require significant energetic driving force. In this pathway, hydrogen shift from C1 of propyne to the C atom of CN^- (C4) and complexation of the two species requires >30 kcal/mol in energy to proceed, even with the slight stabilization of INT1.1 after the hydrogen shift. Following this high entrance barrier to TS1.2, N attacks C3 in TS1.3 to form the cycle, and one more hydrogen shift from C1 to C2 (passing through a moderate barrier of ~ 13 kcal/mol following stabilization of INT1.3) finally leads to the highly stabilized product, (A^-). Despite the fact that anionic (A^-) is stabilized by ~ 46 kcal/mol compared to the reactants alone, cy-

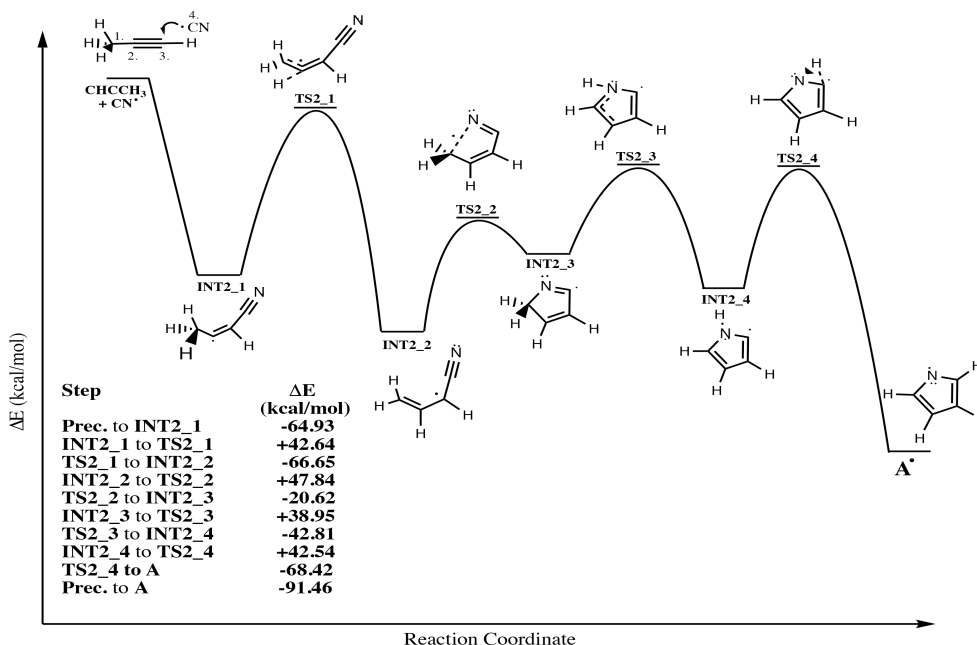


Figure 12: Schematic pathway to radical (A^*) via CN^* and CH_3CCH . The presence of CN^* in Titan's ionosphere is predicted by several models to be significant. Cyclization of this radical and propyne proceeds barrierlessly to (A^*), and thermal electron attachment to an intermediate or the product could result in (A^-).

clization between CN^- and $CHCCH_3$ appears to be difficult beginning from ground state reactants. To overcome the intermediate transition states, these two molecules would need to collide with a considerable amount of energy (which seems unlikely), or receive outside stimulation from photon absorption, as discussed for the process depicted in Figure 10.

Formation of anions such as (A^-) through electron attachment to radical species is also possible. Reactions of radicals proceed rapidly through small or negligible barriers²⁸, which is crucial in the cold environment of Titan's atmosphere or dense molecular clouds. Reactions of CN^* with propyne and other small hydrocarbons have been characterized experimentally and theoretically¹⁰⁹, though heterocycle formation is not discussed in these works. In Figure 12, we have expanded the $CN^*/CHCCH_3$ to include the possibility of cyclization.

Initial attack of $CHCCH_3$ by CN^* leads to the highly stabilized intermediate INT2_1, which has been previously characterized¹⁰⁹ and lies ~ 65 kcal/mol below the initial reactants. Hydrogen shift from C1 to C2 to form INT2_2 via

TS2_1 passes through a seemingly tall barrier, but one that is still submerged below reactants by ~ 22 kcal/mol. From INT2_2, cyclization following N attack of C1 proceeds through TS2_2, and the resulting structure (INT2_3) is briefly stabilized before a subsequent hydrogen shift to form INT2_4 (recognizable as (B^*)). Just one more adjacent shift of this hydrogen results in (A^*), the global minimum on the radical surface, which is stabilized relative to reactants by ~ 91 kcal/mol. Notably, unlike the reaction between $CHCCH_3$ and CN^- forming the anionic (A^*) (Fig. 11), energetic barriers encountered in the cyclization reaction involving CN^* are all submerged, making this formation pathway to (A^*) feasible without outside stimulation. To move to the anionic surface, thermal electron attachment to an intermediate in the reaction pathway or the final product (A^*) could lead to (A^-) under appropriate conditions.

Cationic species

Positively charged ions are also ubiquitous on Titan and in other extraterrestrial environ-

ments. The aforementioned energy sources (solar radiation and energetic electrons from Saturn’s magnetosphere) ionize N_2 and CH_4 , the main constituents composing the upper atmosphere. These ions react with neutrals to create a variety of charged hydrocarbon species.

Molecular mass data obtained during the fly-by of Titan includes traces linked to cations^{39–41} - the mass peak appearing at m/z 66 has been investigated by several models^{90,110}, and is assigned by some to be $CH_2CCHCNH^+$, our isomer (F^+). Because we found (F^+) to be the global minimum cationic structure in our calculations, we propose that isomer (F^+) is quite likely to contribute to this signal.

Cationic isomers of C_4H_4N such as (F^+) could be interesting precursors to larger structures. As shown by values in Table 1, ionization to the cationic state requires significant energy, but sources of radiation are plentiful in this environment and ions are readily formed from their parent neutrals. Several potential reaction pathways have been included in models for cationic C_4H_4N .^{90,110}

One likely formation route to (F^+) is through protonation of allenyl cyanide (cyanoallene, CH_2C_2HCN), which has been detected in the interstellar medium⁴⁸ and is predicted in Titan’s ionosphere. Isomers of the empirical formula C_3H_3N are most stable as methylcyanoacetylene (CH_3CCCN), but cyanoallene (CH_2C_2HCN , direct precursor to (F^+)) only lies about 2.4 kcal/mol higher in energy⁴⁶. This species has also been detected extraterrestrially near the Taurus Molecular Cloud (TMC-1)^{49,50}.

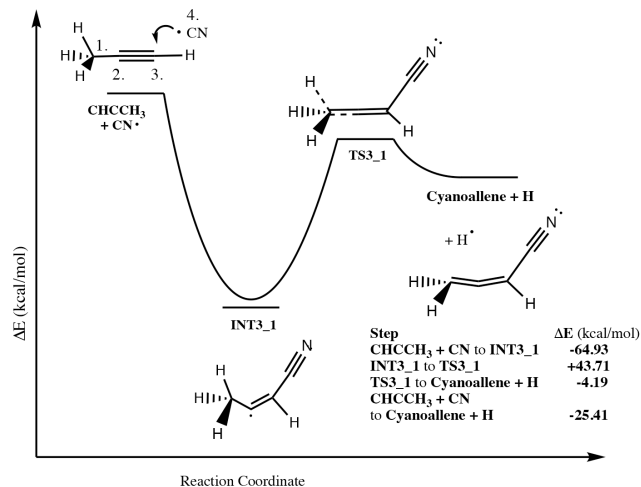


Figure 13: Schematic representation of cyanoallene formation via the reaction of propyne (CH_3CCH) and cyano radical (CN^\bullet). The relevant transition state has been characterized by Balucani et al. and occurs through a submerged energetic barrier. This reaction is exothermic by about 25 kcal/mol.

The formation of cyanoallene may occur through reactions between precursors discussed above, namely propyne (CH_3CCH) and cyano radical (CN^\bullet). The reaction of cyano radical with propyne has been investigated experimentally and theoretically¹¹¹. Balucani et al. used a combination of crossed beam experiments and *ab initio* calculations to characterize products and transition states. Reaction of cyano radical with CH_3CCH to form products including CH_2CCHCN (cyanoallene) is barrierless and exothermic overall¹¹¹. When examined at the $\omega B97X-V/cc-pVTZ$ level of theory, the geometries and energetics of key structures along this reaction path (shown in Figure 13) are in good agreement with Balucani’s calculations.

Because the reaction depicted in Figure 13 is barrierless, it could feasibly occur in the cold environments of Titan’s atmosphere or molecular clouds. Formation of isomer (F^+) ($CH_2CCHCNH^+$) from cyanoallene would simply require protonation of the neutral species. Due to their high proton affinities, nitriles are good acceptors for H^+ ¹¹⁰.

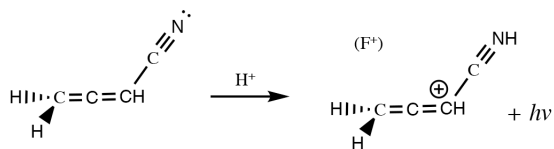


Figure 14: Protonation of cyanoallene to form isomer (F^+). The excess energy may be emitted as a photon, or dispersed via collisions with a third body in the dense atmosphere of Titan. Structures were here optimized at the ω B97X-V/aug-cc-pVTZ level of theory.

Figure 14 shows the protonation of cyanoallene to form isomer (F^+). Cyanoallene has a high proton affinity (over 8eV). Excess energy resulting from this process could be emitted as a photon from isomer (F^+), or be dispersed through third body interactions in the dense atmosphere of Titan.

Conclusions

In this work, we have investigated isomers of C_4H_4N in cationic, neutral radical, and anionic states to determine the structures of C_4H_4N that could be present in Titan’s atmosphere or in molecular clouds. We found the energetic ordering of isomers to change with electronic state; that is, the most stable structures for anionic isomers were different from those same configurations on the cationic PES. For anionic species, the global minimum was found to be (A^-). This cyclic isomer, analogous in structure to deprotonated pyrrole, is an aromatic ring containing six π electrons. Negative charge is well distributed between the electronegative nitrogen atom and β carbons of the ring. On the radical PES, (A^\bullet) remains the most stable isomer, preserving a quasi-aromatic five π arrangement after electron removal from the anion. Lengthening of the central $C_\alpha=C_\beta$ bonds occurs as bonding character between α and β carbons decreases. Electron density again centers on the apical nitrogen and β carbons, though charge discrepancy between ring members is more pronounced.

Upon ionization to the cationic state, structural trends in stability present for anionic and radical isomers change notably. Previously

stable (A) now has only four π electrons in the cationic ring, creating an unfavorable anti-aromatic arrangement. In contrast to the anionic and radical species, linear isomer (F^+) was found to be the global minimum on the cationic surface. Hyperconjugation contributes to the stability of this structure, and the terminal nitrogen can donate electron density into empty p orbitals of the carbocation.

(A), the most stable C_4H_4N isomer of those studied here for anions and radicals, could form through numerous feasible mechanisms. Though the presence of N-heterocycles such as pyrrole is unconfirmed in Titan’s atmosphere or the interstellar medium, photoexcitation of pyrrole leads to homolytic dehydrogenation of the apical nitrogen, leaving the ground state radical (A^\bullet). Radiative electron attachment to this species, which has a high electron affinity, would result in the aromatic (A^-).

Other pathways, such as cyclization reactions between CN and propyne, could similarly lead to (A^-) or (A^\bullet). We found that one such pathway involving CN^- was not particularly feasible, as it passed through high energy transition states and intermediates over the course of cyclization. However, a similar reaction involving *radical* CN^\bullet was not hindered in this way. All barriers were submerged beneath the energy of reactants for the radical pathway leading to (A^\bullet), indicating that formation of this heterocycle could occur without outside energetic input in cold extraterrestrial environments.

(F^+), the minimum-energy isomer of C_4H_4N on the cationic PES, could similarly form via many routes. Ion-neutral chemistry between carbocations and small nitrogen-containing species are viable production pathways to (F^+), as is proton attachment to allenyl cyanide.

By characterizing C_4H_4N in anionic, radical, and cationic states, we identified lowest-energy structures of each respective type that could be present in non-Earth environments. We have found that anionic (A^-) and cationic (F^+) isomers are global minima on their respective potential energy surfaces. Either of these species can form from reactions between smaller molecules that are readily available in some interstellar environments such as dense molecu-

lar clouds. Our work indicates that these ionic isomers of C_4H_4N may be synthesized in Titan’s atmosphere and contribute to the molecular mass data collected by the Cassini INMS. Given the reactivity of ionic species in this environment, molecules such as anionic (A^-) and cationic (F^+) could go on to participate in the formation of complex organics. These accurate structures, along with their ro-vibrational data (provided in the SI) may also be useful for deconvoluting extraterrestrial spectra of nitrogen-containing molecules.

Additionally, we’ve highlighted that the formation of these molecules through reactions involving radicals can pass through submerged barriers, and are thus quite feasible in cold, energy deficient environments. Radical (A), potentially formed via the radical-neutral pathway shown in Fig. 12 could have similar reactivity to its precursors and is a very interesting candidate to explore when contemplating the formation mechanisms of nitrogenated PAH.

Our results are a contribution towards better understanding species present and chemistry occurring in the atmosphere of Titan (and perhaps that of early Earth), dense molecular clouds, or other extraterrestrial sources. Further studies interrogating C_4H_4N and other nitrogen-containing ions are needed to continue to probe the composition and chemistry of Titan’s atmosphere and beyond.

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Supplementary Information

Molecular geometries for all molecules mentioned here are available in the SI document online. As indicated in the text, the SI also contains vibrational constants and IR intensities, as well as a comparison between CCSD(T)/CBS and DFT (using $\omega B97X-V/aug-cc-pVTZ$) for calculated isomer energetics.

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