NCCN and NCCCCN Formation in Titan's Atmosphere: 1. Competing Reactions of Precursor HCCN ($^3A''$) with H (^2S) and CH_3 ($^2A'$)

Yoshihiro Osamura*,† and Simon Petrie*,‡

Department of Chemistry, Rikkyo University, 3-34-1 Nishi-ikebukuro Tokyo 171-8501, Japan, and Department of Chemistry, the Faculties, Australian National University, Canberra ACT 0200 Australia

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Quantum chemical calculations, at the CCSD(T)/aug-cc-PVTZ//B3-LYP/6-311G** level of theory, have been used to characterize stationary points on the C_2H_2N and C_3H_4N potential energy surfaces. Reactions which occur on these surfaces include the processes H (^2S) + HCCN ($^3A''$) and CH_3 ($^2A'$) + HCCN ($^3A''$), which are previously unconsidered but very important potential loss processes for the proposed key intermediate, HCCN ($^3A''$), implicated in the formation of NCCN and NCCCCN within the upper atmosphere of the Saturnian satellite Titan. We find that both H (^2S) + HCCN ($^3A''$) and CH_3 ($^2A'$) + HCCN ($^3A''$) have exothermic product channels lacking positive activation energy barriers, and thus should occur with high efficiency at the low temperatures (∼200 K) characteristic of Titan's atmosphere. We suggest that the occurrence of these competing reactions poses severe problems for the viability of existing mechanisms of Titanian NCCN and NCCCCN formation.

Introduction

The dicyanopolyynes N≡C−C≡N and N≡C−C≡C−C≡N, detected respectively as gas-phase and solid-phase trace constituents of the large Saturnian moon Titan,[1−4] are presumed to arise via the rich photochemistry resulting from upper-atmospheric photolysis of the N_2 and CH_4 molecules that dominate Titan's cold and dense atmosphere. Following the detection of NCCCCN (which remains one of the largest molecules yet seen within any planetary atmosphere outside Earth's), the preferred principal route to both NCCN and NCCCCN has involved formation of the ground-state triplet carbenoid species, cyanomethylene (HCCN ($^3A''$)) as a precursor:[5]

$$\mathrm{N}\ (^2\mathrm{D}) + \mathrm{C_2H_2} \rightarrow \mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \quad (1)$$

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{N}\ (^4\mathrm{S}) \rightarrow \mathrm{NCCN} + \mathrm{H}\ (^2\mathrm{S}) \quad (2)$$

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{HCCN}\ (^3\mathrm{A}'') \rightarrow \mathrm{NCCCCN} + \mathrm{H_2} \quad (3)$$

Incorporation of these reactions, with estimated rate coefficients of $k_1 = 1.0 \times 10^{-11}$, $k_2 = 1.0 \times 10^{-12}$, and $k_3 = 5.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1},[5] was deemed sufficient to account for the observed abundances of both NCCN and NCCCCN.

A common problem in kinetic modeling networks, particularly relevant to the chemistry of intermediate species that exist only as transient species in laboratory studies, is that of sparseness of the reaction set. In the present context, wherein we might expect the diradical HCCN ($^3A''$) to be of high intrinsic reactivity, the dicyanopolyyne-forming reactions 2 and 3 are the *only* HCCN loss processes in the models of Toublanc et al.[6] and Lara et al.,[7] implying perfect conversion of triplet cyanomethylene into NCCN and NCCCCN. In the only other recent Titanian atmospheric model, by Lebonnois et al.,[8] reactions 1−3 are surprisingly omitted; NCCCCN does not feature in this model, which produces NCCN only by a largely discredited pathway[5,9−12]

$$\mathrm{HCN} + \mathrm{CN}\ (X\ ^2\Sigma^+) \rightarrow \mathrm{NCCN} + \mathrm{H}\ (^2\mathrm{S}) \quad (4)$$

Experimental[9−12] and theoretical[11,13] studies of this process have established that at low temperatures it is quite inefficient, with the most recent measurement[12] indicating a rate coefficient of only $k_4 = 4.6 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 200 K. Lebonnois et al.[8] acknowledge the inadequacy of reaction 4 by noting that NCCN formation is badly underestimated.

A fresh assessment of dicyanopolyyne formation seems required to address the problems evident in the various Titanian atmospheric models. While the exhaustive inclusion of all possible reactions can make kinetic models unworkably inefficient, it nevertheless seems that the modeled chemistry of HCCN, as outlined above, is unreasonably oversimplified. A striking indication may be its reaction with CH_3:

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{CH_3}\ (^2\mathrm{A}') \rightarrow \text{products} \quad (5)$$

As a radical−radical recombination process, reaction 5 may feasibly be expected to have a rate coefficient close to the collisional value of $\sim 2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Since CH_3 is modeled to have much higher abundance than N at Titanian altitudes above 800 km,[6−8,14] where NCCN formation by reaction 2 is held to be most efficient,[5] the inclusion of the methyl radical reaction (5) conceivably has the potential to reduce the NCCN production rate due to reaction 2 by several orders of magnitude. The impact on reaction 3, as the apparent route to NCCCCN, is potentially even greater: efficient occurrence of reaction 5 would effectively “wipe out” reaction 3 as a viable process because of the dramatic reduction in the HCCN lifetime, implying a vanishingly small probability of an encounter between two surviving cyanomethylene diradicals. A further possible process,

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* E-mail: osamura@rikkyo.jp; simon.petrie@anu.edu.au.
† Rikkyo University.
‡ Australian National University.

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$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \rightarrow \text{products} \qquad (6)$$

involving another abundant high-altitude radical (H), possesses additional potential to impact adversely on the proposed "cyanomethylene route" to NCCN and NCCCCN.

In the present work, we report the results of quantum chemical calculations, at the CCSD(T)/aug-cc-pVTZ//B3-LYP/6-311G** levels of theory, on the [C_2H_2N] and [C_3H_4N] potential energy surfaces. These calculations provide critical information on the viability of reactions 5 and 6, thereby illuminating their possible impact on models of Titanian atmospheric chemistry.

Theoretical Methods

Stationary points on the various potential energy surfaces were obtained by geometry optimization (supplemented by vibrational frequency calculation) at the B3-LYP/6-311G** level of theory, where B3-LYP denotes the hybrid density functional method combining Becke's three-parameter exchange functional[15] with the correlation functional of Lee, Yang, and Parr,[16] used here in conjuction with the triple-split-valence 6-311G** basis set.[17] Single-point total energy calculations on the optimized B3-LYP geometries were performed at the CCSD(T)/aug-cc-pVTZ level of theory, where CCSD(T) denotes coupled-cluster calculations with single, double, and perturbative triple excitations[18,19] and aug-cc-pVTZ is the augmented correlation-consistent polarized valence triple-ζ basis set of Dunning and co-workers.[20]

All calculations were performed using the GAUSSIAN98 program suite.[21]

Results and Discussion

1. The C_2H_2N Potential Energy Surface. Figure 1 shows the schematic potential energy surface of C_2H_2N. Reaction 6 occurs on this surface and may involve either a doublet or a quartet overall spin multiplicity for this combination of reactants. It appears that reaction 6 has not been subjected to previous experimental or theoretical study, although the reactions of N (^{2}D) and N (^{4}S) with C_2H_2, which occur elsewhere on this surface, have been extensively investigated by other workers.[22−28]

The doublet PES, which has direct relevance also to the occurrence of reaction 6, features an exothermic channel to H_2 + CCN (X $^2\Pi$), which can potentially occur by H-atom abstraction

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \rightarrow \mathrm{H_2} + \mathrm{CCN}\ (X\ ^2\Pi) \qquad (7)$$

However, our exploration of the doublet PES does not reveal any apparent direct H-atom abstraction pathway. Instead, reaction 7 proceeds via addition of H, yielding the doublet mutliplicity intermediate H_2CCN ($^2B_1$), followed by H_2 loss from this intermediate (see Figure 2). There is no entrance channel barrier to this process at the B3-LYP/6-311G** level of theory. The tendency for B3-LYP to underestimate barrier heights[29] leaves scope for the existence of a small entrance barrier not detected by this computational method, although as a straightforward attractive bond-forming/electron-pairing interaction between radicals, it is expected that the absence of an entrance barrier is genuine. Rigorous testing of this notion would require the use of multiconfigurational quantum techniques which we have not pursued here. The exit channel barrier, in our CCSD(T)/aug-cc-pVTZ//B3-LYP/6-311G** calculations, is 14 kJ mol^{-1} below the energy of reactants H (^{2}S) + HCCN (^{3}A″), while the exothermicity of H_2 + CCN (X $^2\Pi$) is 19 kJ mol^{-1}. The submerged exit barrier implies that this addition−elimination mechanism should proceed efficiently even at low temperature, and thus reaction 7 can be identified as a probable major loss process for cyanomethylene within Titan's atmosphere.

The relative energy value found for H_2CCN ($^2B_1$) versus dissociation to H (^{2}S) + HCCN (^{3}A″) indicates a bond dissociation energy (BDE) (at zero K) of D_0(H−C(H)CN) = 427.8 kJ mol^{-1}. This value shows excellent agreement with the (298 K) experimental BDE determinations of 435 ± 8 kJ mol^{-1} and 449 ± 27 kJ mol^{-1} resulting, respectively, from mass-spectrometric flow tube studies of the proton-transfer reactions of various neutrals with HCCN$^-$ [30] and of the collision-induced dissociation of a series of protonated nitriles.[31] An earlier theoretical determination of 440.6 kJ mol^{-1} for this quantity, at the projected MP4/cc-pVTZ level of theory, has also been reported.[26]

The H_2 + CCN (X $^2\Pi$) product channel is also expected to be accessible from other regions on the C_2H_2N PES. This consideration is particularly relevant to the reaction of N (^{2}D) with C_2H_2 (reaction 1), held to be the route to Titanian HCCN (^{3}A″) production.[5] A crossed-beam study[28] of reaction 1 has reported time-of-flight mass-spectrometric detection of CCN as a product accompanying quasilinear HCCN formation, although in that study[28] the generation of CCN (detected as CCN$^+$, m/z = 38 amu) was attributed to dissociative ionization of HCCN within the mass-spectrometric detector, with the possibility of H_2 + CCN formation dismissed as a four-center H_2 elimination process for which a very high exit channel barrier would be expected. The H_2 loss channel has also not been explored within existing theoretical studies of reaction 1.[26,27] Consequently, it remains unclear to what extent the H_2 + CCN (X $^2\Pi$) product channel, which is apparently the most exothermic channel overall but which requires an indirect route from reactant N (^{2}D) + C_2H_2, is able to compete with HCCN (^{3}A″) + H (^{2}S) production.

Other product channels, exothermic from N (^{2}D) + C_2H_2 but endothermic from HCCN (^{3}A″) + H (^{2}S), have been explored in earlier studies on the doublet surface and are not investigated here. Such product channels include CH (X $^2\Pi$) + HCN, which is endothermic by 18.8 kJ mol^{-1} according to our calculations. Laboratory studies suggest that this reaction occurs with an activation energy not exceeding the reaction's endothermicity, since the reverse process

$$\mathrm{CH}\ (X\ ^2\Pi) + \mathrm{HCN} \rightarrow \mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \qquad (8)$$

is seen to proceed efficiently and with a negative temperature dependence, $k_8 = 5 \times 10^{-11}\ e^{500/T}$ cm^3 molecule^{-1} s^{-1}.[32]

The quartet PES has been studied to assess the feasibility of the processes

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \rightarrow \mathrm{CH}\ (^4\Sigma^-) + \mathrm{HCN} \qquad (9a)$$

and

$$\mathrm{HCCN}\ (^3\mathrm{A}'') + \mathrm{H}\ (^2\mathrm{S}) \rightarrow \mathrm{N}\ (^4\mathrm{S}) + \mathrm{HCCH} \qquad (9b)$$

which would appear to be the lowest-energy product channels on this surface. According to established ΔH_f° values for reactants and products,[33] acetylene production is approximately thermoneutral while the channel leading to quartet-state methylidyne and hydrogen cyanide is signficantly endothermic. Our B3-LYP/6-311G** investigation of the quartet PES (Figure 1; see also Figure 3) reveals that the entrance channel (to formation of an intermediate HCC(H)N, for which the interconversion barrier between cis and trans isomers lies signficantly below the total energy of reactants) is not impeded by any barrier.

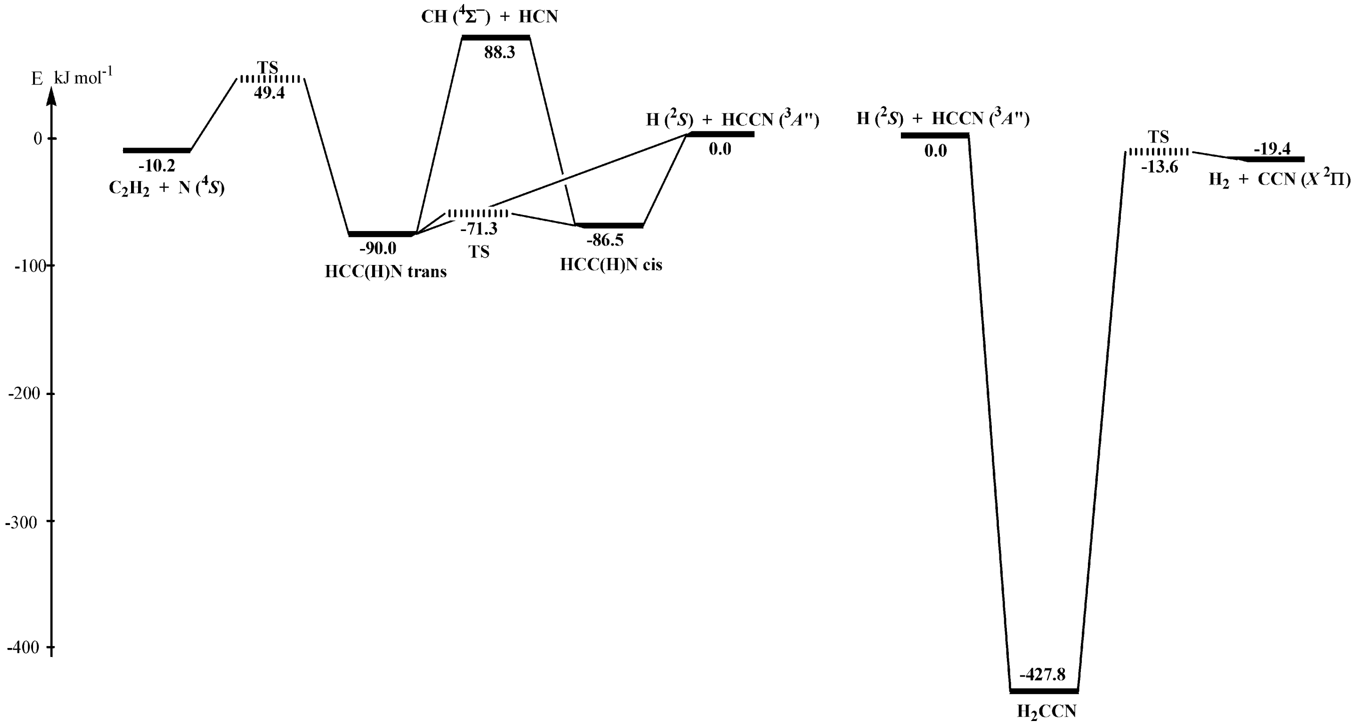

Figure 1. Pathways between stationary points on the quartet-multiplicity (left) and doublet-multiplicity (right) C_2H_2N potential energy surfaces, at the CCSD(T)/aug-cc-pVTZ//B3-LYP/6-311G** level of theory.

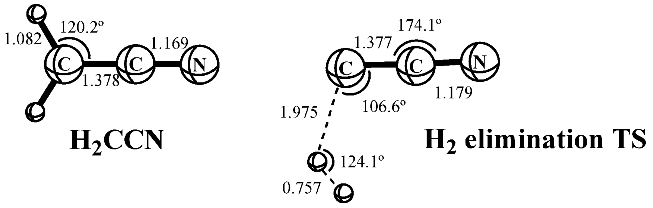

Figure 2. Geometries of the key stationary points (respectively, the H_2CCN intermediate and the transition state to H_2 loss) obtained on the doublet-multiplicity C_2H_2N potential energy surface, at the B3-LYP/6-311G** level of theory. Bond lengths are shown in Å with bond angles in degrees.

Dissociation to CH ($^4\Sigma^-$) + HCN is also free of any intervening transition states, although the substantial endothermicity of this product channel (88 kJ mol^{-1} at the CCSD(T)/aug-cc-pVTZ level of theory) rules it out of consideration at low temperatures. Formation of C_2H_2 + N (^{4}S) is 10 kJ mol^{-1} exothermic according to our CCSD(T) calculations, a margin which is close to the ascribed uncertainty for this method, but in any event the barrier height of 49 kJ mol^{-1} calculated for the transition state to dissociation also effectively discounts the viability of reaction 9 as a loss process for HCCN under conditions appropriate to Titan's upper atmosphere.

When the transition state energy is expressed relative to the total energy of C_2H_2 + N (^{4}S), E_{rel} (TS) = 59 kJ mol^{-1}, it reveals a discrepancy with the value of 86 kJ mol^{-1} obtained from spin-projected MP4/cc-pVTZ calculations;[28] nevertheless, this disagreement does not exceed the ascribed uncertainty of the MP4 calculations.[28] Moreover, we would generally expect the present CCSD(T) calculations with a larger basis set to be somewhat more accurate than MP4 calculations, particularly with regard to species for which the issue of spin contamination is not negligible (our TS expectation value of $<S^2> = 4.09$ is significantly higher than the value of 3.75 expected for a pure quartet state). The magnitude of this barrier also indicates that, while the conversion of ground-state N (^{4}S) and C_2H_2 to the putative dicyanopolyyne precursor HCCN (^{3}A″) + H (^{2}S) may be essentially thermoneutral (within the precision of our calculations), it is inhibited by a barrier of sufficient magnitude to prevent its occurrence at a measurable rate, in accord with previous experimental studies.[22,23,25]

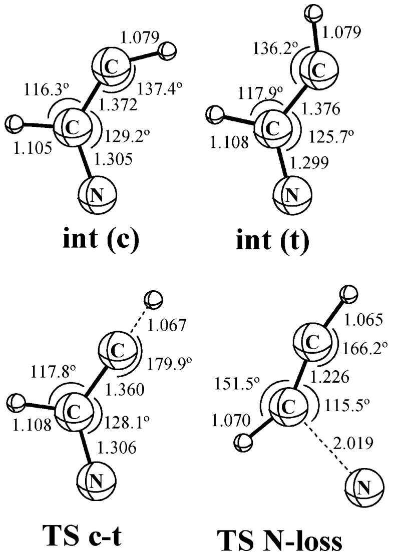

Figure 3. Geometries of the key stationary points obtained on the quartet-multiplicity C_2H_2N potential energy surface, at the B3-LYP/6-311G** level of theory. Bond lengths are shown in Å with bond angles in degrees.

2. The C_3H_4N Potential Energy Surface. No previous explorations of reaction 5, between CH_3 and HCCN, have been reported. As with reaction 6, the combination of reactants may occur on a doublet or quartet surface. Examination of literature thermochemical values suggests that the most readily apparent possible quartet-state product combinations (e.g., N (^{4}S) + CH_3-CCH, CH ($^4\Sigma^-$) + CH_3CN, and CH_2 (X $^3B_1$) + H_2CCN ($^2B_1$)) all correspond to significantly endothermic processes which are not, therefore, expected to be accessible under low-temperature conditions. Accordingly, we have restricted the current inves-

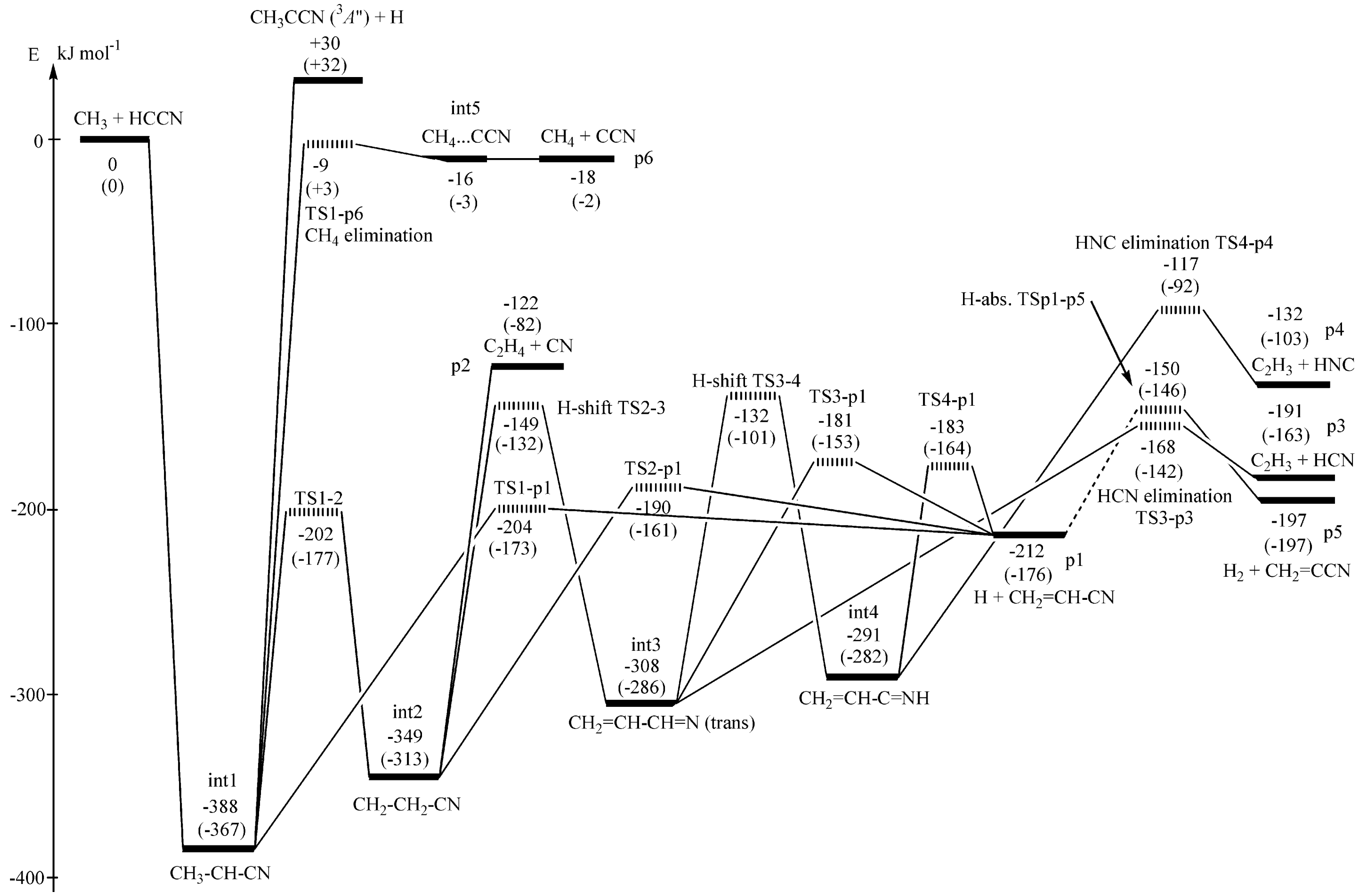

Figure 4. Pathways between stationary points on the (doublet multiplicity) C_3H_4N potential energy surface, at the CCSD(T)/aug-cc-pVTZ//B3-LYP/6-311G** level of theory. Relative energies, according to our CCSD(T) calculations and including B3-LYP zero-point vibrational energy corrections, are shown in kJ mol^{-1} (with B3-LYP/6-311G** relative energy values in parentheses). For clarity, this diagram does not include the higher-energy 'cis' isomer of int3, viz. CH_2CHCHN (cis), nor the transition state to interconversion of cis and trans structures. Our calculations on the latter species provide relative energies of −297 (−276) kJ mol^{-1} for the cis isomer and −291 (−263) kJ mol^{-1} for the transition state.

tigation to the doublet PES as is shown in Figure 4. Optimized geometries for these species, when not previously reported,[37] are shown in Figure 5. On this PES, other regions encompassing the reactions

$$\mathrm{CN}\ (\mathrm{X}\ ^2\Sigma^+) + \mathrm{C_2H_4} \rightarrow \text{products} \qquad (10)$$

$$\mathrm{C_2H_3}\ (^2\mathrm{A}') + \mathrm{HCN} \rightarrow \text{products} \qquad (11)$$

and

$$\mathrm{C_2H_3}\ (^2\mathrm{A}') + \mathrm{HNC} \rightarrow \text{products} \qquad (12)$$

have been previously investigated using high-level quantum chemical methods;[37,38] the first two of these reactions have also been quite widely subjected to experimental measurements,[37,39−45] while reaction 10 has also been studied using RRKM theory.[37,46]

The reaction of CH_3 (^{2}A′) with HCCN (^{3}A″) initially proceeds through formation (without any apparent barrier at the B3-LYP/6-311G** level) of the radical CH_3CHCN, which appears to be the global minimum upon the potential energy surface. The CH_3CHCN intermediate, here labeled 'int1',[47] has been previously characterized at the B3-LYP/6-311G** level of theory by Balucani et al.[37] in their study of the CN (X $^2\Sigma^+$) + C_2H_4 reaction mechanism. From int1, two deeply submerged transition states TS1-p1 and TS1-2 lead respectively to product H (^{2}S) + CH_2CHCN or to CH_2CH_2CN (here 'int2'); the latter intermediate, also previously characterized using B3-LYP/6-311G**,[47] can dissociate to CN (X $^2\Sigma^+$) + C_2H_4 in a barrierless fashion or can alternatively also produce H (^{2}S) + CH_2CHCN via a barrier lying at much lower energy than reactant CH_3 + HCCN (^{3}A″).

The production of H (^{2}S) + CH_2CHCN via either the more direct

$$\text{int1} \rightarrow \text{TS1-p1} \rightarrow \mathrm{H} + \mathrm{CH_2CHCN}\ (\text{'p1'})$$

or the less direct route

$$\text{int1} \rightarrow \text{TS1-2} \rightarrow \text{int2} \rightarrow \text{TS2-p1} \rightarrow \text{p1}$$

occurs with all stationary points lying at least 190 kJ mol^{-1} below the total energy of reactants. No other product channels are accessible over such a consistently deeply submerged stretch of the C_3H_4N potential energy surface, and thus it appears probable that H (^{2}S) + CH_2CHCN is the dominant product channel for reaction 5 under low-pressure conditions. For good measure, two further routes to H + CH_2CHCN can also be identified:

$$\text{int1} \rightarrow \text{TS1-2} \rightarrow \text{int2} \rightarrow \text{TS2-3} \rightarrow \mathrm{CH_2CHCHN}\ (\text{'int3'}) \rightarrow \text{TS3-p1} \rightarrow \text{p1}$$

and

$$\text{int1} \rightarrow \text{TS1-2} \rightarrow \text{int2} \rightarrow \text{TS2-3} \rightarrow \text{int3} \rightarrow \text{TS3-4} \rightarrow \mathrm{CH_2CHCNH}\ (\text{'int4'}) \rightarrow \text{TS4-p1} \rightarrow \text{p1}$$

although in these two cases both the number and the relative

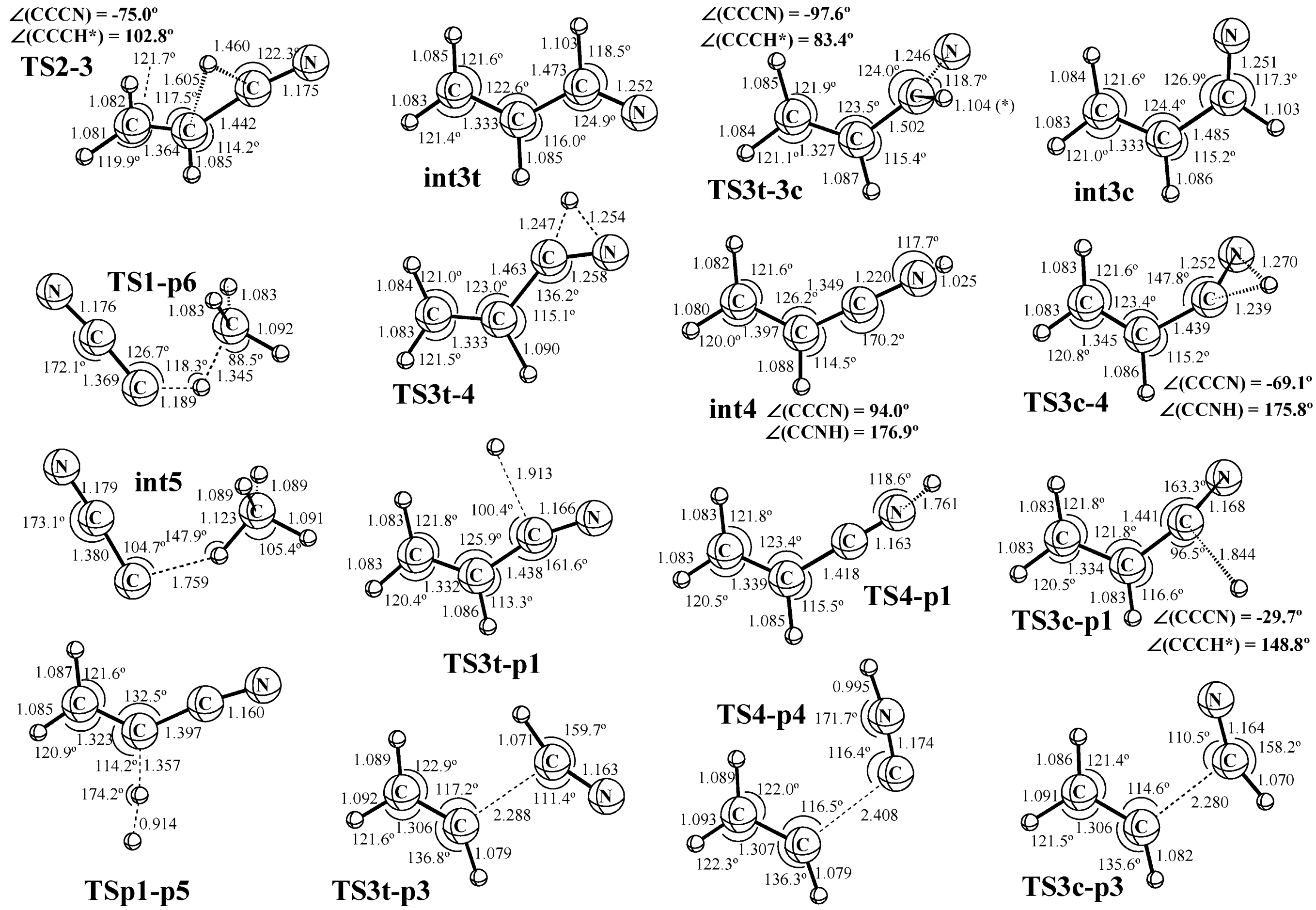

Figure 5. Geometries of stationary points obtained on the C_3H_4N potential energy surface, at the B3-LYP/6-311G** level of theory. Bond lengths are shown in Å, while bond angles (in degrees) are only shown when they do not exceed 175°. Important dihedral angles are shown only when there is significant deviation from planarity. This figure shows only those structures which have not previously been reported (in ref 36).

energies of the transition states would appear to disfavor these routes somewhat in competition with the less convoluted pathways noted above.

Other feasible product channels are CN + C_2H_4, as noted above; C_2H_3 + HCN; C_2H_3 + HNC; H_2 + CH_2CCN; and CH_4 + CCN. However, the C_2H_3 + HCN product channel is most obviously accessible via the process

$$\text{int1} \rightarrow \text{TS1-2} \rightarrow \text{int2} \rightarrow \text{TS2-3} \rightarrow \text{int3} \rightarrow \text{TS3-p3} \rightarrow C_2H_3 + \text{HCN ('p3')}$$

requiring the negotiation of three successive transition states. The final encountered TS3-p3 is in direct competition with TS3-p1 (which is the final step on an expected *minor* pathway to H + CH_2CHCN), and it is probable that TS3-p1 wins out by virtue of its lower energy relative to reactants as well as via the shorter (vibrational) time scale of C−H versus C−C fragmentation. We suggest that C_2H_3 + HCN formation by this route, though accessible, is likely only a minor product channel at best. Similar comments relate also to production of C_2H_3 + HNC, which requires at least four successive transition states

$$\text{int1} \rightarrow \text{TS1-2} \rightarrow \text{int2} \rightarrow \text{TS2-3} \rightarrow \text{int3} \rightarrow \text{TS3-4} \rightarrow \text{int4} \rightarrow \text{TS4-p4} \rightarrow C_2H_3 + \text{HNC ('p4')}$$

with the final encountered TS4-p4 having a relative energy 87 kJ mol^{-1} above that of the sole TS impeding the most direct route to H + CH_2CHCN.

An alternative path to both C_2H_3 + HCN and C_2H_3 + HNC has also been identified. This variant of C_2H_3 + HCN production involves the sequence

$$\text{int1} \rightarrow \text{TS1-p1} \rightarrow \text{H} + CH_2CHCN \text{ ('p1')} \rightarrow \text{TS3-p1} \rightarrow \text{int3} \rightarrow \text{TS3-p3} \rightarrow \text{p3}$$

with an analogous route

$$\text{int1} \rightarrow \text{TS1-p1} \rightarrow \text{p1} \rightarrow \text{TS4-p1} \rightarrow \text{int4} \rightarrow \text{TS4-p4} \rightarrow \text{p4}$$

capable of C_2H_3 + HNC production. For HCN formation, the highest traversed barrier here is rather more deeply submerged than from int2. However, for both of these putative pathways, the identified product channels here require that the nominally separate products H and CH_2CHCN recombine to traverse additional barriers and form product channels which are overall less exothermic than the more direct process of H + CH_2CHCN formation. We conclude that formation of C_2H_3 and either HCN or HNC is feasible in principle but unlikely to be a major product channel of reaction 5.

Similar arguments apply also to occurrence of the process

$$\text{int1} \rightarrow \text{TS1-p1} \rightarrow \text{H} + CH_2CHCN \text{ ('p1')} \rightarrow \text{TSp1-p5} \rightarrow H_2 + CH_2CCN$$

for which alternative pathways exist, but invariably also pass through 'product' H + CH_2CHCN as a necessary intermediate.

The final exothermic product channel displayed in Figure 2, to $CH_4 + CCN$, is possible in principle by a reasonably direct mechanism

$$\text{int1} \rightarrow \text{TS1-p6} \rightarrow CH_4{\cdots}CCN\ (\text{‘int5’}) \rightarrow CH_4 + CCN\ (\text{‘p6’})$$

but as a near-thermoneutral process occurring in competition with highly exothermic direct processes this H abstraction process is significantly disfavored. The van der Waals complex $CH_4{\cdots}CCN$ (int5), located here as a local minimum at the B3-LYP/6-311G** level of theory, may well be an artifact since in our CCSD(T)/aug-cc-pVTZ single-point calculations it possesses a higher relative energy than the separated products. The reaction profile for this process, featuring a very deep initial well followed by a slightly submerged barrier leading to mildly exothermic products, is very similar to the analogous process leading to $H_2 + CCN$, which is the only product channel accessible in the reaction of H (^2S) with HCCN ($^3A''$) as described in the previous section.

A further product channel, to CH_3CCN ($^3A''$) + H (^2S), is entirely free of any activation energy barriers leading to or from int1; however, since this “switching” process is 30 kJ mol^{-1} endothermic it cannot occur measurably at the temperatures relevant to Titanian atmospheric processes.

Another endothermic product channel, $CH_3CN + CH$ (X $^2\Pi$) ($\Delta H° > 45$ kJ mol^{-1} according to literature thermochemical values) is accessible in principle by methyl radical addition to the cyano C atom. In view of the obvious thermochemical obstacle to this pathway, which is apparently the least endothermic of several channels that may involve methyl attack of the CN group, we have not performed a detailed evaluation of this section of the PES.

Much of the surface discussed in the paragraphs above has been earlier explored at the B3-LYP/6-311G** level, in relation to the CN (X $^2\Sigma^+$) + C_2H_4 reaction,[37] while some overlap exists also with the exploration of the reactivity of C_2H_3 ($^2A'$) + HNC.[38] Agreement between the B3-LYP/6-311G** and CCSD(T)/aug-cc-pVTZ relative energies of the stationary points previously examined by Balucani and co-workers[37] is excellent when the “reference energy” value employed is that for CN (X $^2\Sigma^+$) + C_2H_4, but when reactant CH_3 ($^2A'$) + HCCN ($^3A''$) is instead employed as the energy reference for relative energy determinations, much of the surface is 25−40 kJ mol^{-1} lower (in relative energy terms) at the CCSD(T)/aug-cc-pVTZ level than at B3-LYP/6-311G**. The qualitative features of the surface are largely unaffected by this tendency. Opportunities for comparison with the CBS−RAD study concerning the reaction of C_2H_3 ($^2A'$) + HNC[38] are rather more limited, but our CCSD(T)/aug-cc-pVTZ calculations show generally good agreement with CBS−RAD over the duplicated portion of the PES.

3. Comparison with Related Potential Energy Surfaces. The reactions of H or hydrocarbon radicals with cyanomethylene have not received any previous laboratory or theoretical attention. The sole previous study of HCCN ($^3A''$) reactivity,[48] motivated by an interest in the combustion chemistry of this species (which has been identified as a likely major thermal decomposition product of constituents of coal-derived-liquid (CDL) used as an industrial fuel),[49] has established that HCCN reacts with NO and with O_2 (with 298 K rate coefficients of respectively 3.5×10^{-11} and 1.8×10^{-12} cm^3 molecule^{-1} s^{-1}) but is apparently inert toward CH_4, C_2H_2, C_2H_4, CO_2, CO, and H_2 at room temperature. Our present theoretical study supports the suggestion, from the existing experimental record, that HCCN ($^3A''$) is generally reactive with open-shell species. There is also indirect experimental support for substantial intramolecular rearrangement within the reactive intermediates resulting from radical−radical collisions of HCCN, by analogy with the proposed formation of, for example, C_2H_3 + HCN from CH_3 + HCCN. The NO + HCCN product channels are seen to include HCN, while the products detected from the reaction of O_2 include CO_2 and HNC.[48]

The reaction chemistry of methylene, which shares with cyanomethylene a triplet ground state, provides another relevant point of reference. The reaction of CH_2 (X $^3B_1$) with H (^2S) has been widely studied, both experimentally[50−56] and theoretically.[57−59] It has been found to occur with high efficiency, $k \sim 2.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, at room temperature and below,[50,53] with addition followed by H_2 elimination as the sole observed product channel:

$$CH_2\ (X\ ^3B_1) + H\ (^2S) \rightarrow CH + H_2 \tag{13}$$

Our investigation of the cyanomethylene/H atom reaction yields a comparable result, in that addition/dihydrogen elimination appears to be the only viable process at low temperatures.

Several experimental and theoretical studies of CH_2 (X $^3B_1$) + CH_3 ($^2A'$) have also been reported.[51,52,60−63] Here the product channel seen is C=C double bond formation with loss of H from the methyl reactant carbon atom

$$CH_2\ (X\ ^3B_1) + CH_3\ (^2A') \rightarrow C_2H_4 + H\ (^2S) \tag{14}$$

again exhibiting very strong similarity to the analogous reaction of cyanomethylene for which we find the direct C=C bond-forming channel, yielding CH_2CHCN + H, to be the most readily accessible of several feasible product channels. Although the established literature value for the k_{14} rate coefficient, 7×10^{-11} cm^3 molecule^{-1} s^{-1},[51,52] is somewhat below the expected collision rate coefficient for a radical/neutral reaction, this value does not appear to derive from a direct measurement of the reaction rate, and a recent direct measurement[63] has yielded a significantly larger value, $k_{14} = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The close similarity in reaction mechanisms for the CH_2 (X $^3B_1$) and HCCN ($^3A''$) radicals, and the rapid reaction rates evident for reactions 13 and 14, further strengthen the probability that the reactions of triplet cyanomethylene with H and with CH_3 will occur with near-collisional efficiency.

4. Implications of These Results for Existing Models of Titanian Chemistry. Formation of NCCN and NCCCCN by the “cyanomethylene route” necessitates, first, the efficient production of HCCN in reaction 1 and, second, the occurrence of the dicyanopolyyne-forming reactions 2 and 3 in the absence of significant competing reactions. While several experimental and theoretical studies[24,26−28] provide strong evidence that reaction 1 does indeed yield HCCN, perhaps with a larger rate coefficient[26] than the value of $k_1 = 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} originally postulated by Yung,[5] the question of NCCN formation from reaction 2 now appears substantially more vexatious. This reaction has received no experimental attention beyond an indirect determination[64] of a lower limit to the overall rate coefficient, $k_2 > 6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, and an estimation, in the same work,[64] of a probable value of $k_2 \sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. It is the latter value that has been adopted in the dicyanopolyyne-forming mechanism of Yung[5] and which continues to be implemented in Titanian atmospheric models,[6,7] yet there is still no direct experimental or theoretical validation for reaction 2. The viability of this reaction (if indeed it occurs) as a source of Titanian NCCN depends crucially on the absence of competing effective sinks for HCCN. In the

TABLE 1: Loss Processes for HCCN ($^3A''$) within Titan's Upper Atmosphere

		[X]/10^3 molecule cm^{-3} [a]					%loss[d]		
intermediate	reactant X	$z = 800$	1000	1200	k_{200}[b]	products[c]	$z = 800$	1000	1200
HCCN ($^3A''$)	N (^4S)	1.3	8	10	1.0×10^{-12} [e]	NCCN + H (^2S)	3E(−5)	0.001	0.007
	HCCN ($^3A''$)	≪ (25	200	20)[f]	5.0×10^{-11} [e]	NCCCCN + H_2	≪ (0.03	1.2	0.7)
	H (^2S)	7.5E(4)	8000	800	3.0×10^{-11} [g]	CCN (X $^2\Pi$) + H_2	54	28	17
	CH_3 ($^2A'$)	6.5E(4)	2E(4)	4000	3.0×10^{-11} [g]	CH_3CN + H (^2S)	46	71	83

[a] Reactant concentrations in molecule cm^{-3}, at altitudes of 800, 1000, and 1200 km, were obtained by graphical interpolation of data presented in the modeling studies of Banaszkiewicz et al. (ref 14: H, CH_3, N) and Toublanc et al. (ref 6: HCCN). [b] Rate coefficients in cm^3 molecule^{-1} s^{-1}, at $T = 200$ K. [c] Expected major product channel of the indicated combination of reactants. [d] Efficiency of the indicated HCCN removal mechanism, expressed as a percentage of the total removal rate due to the processes listed here, at the indicated altitude. [e] Values recommended in ref 5 and adopted in the subsequent Titanian models (refs 6, 7, and 14). [f] Literature value (ref 6), considered to be a severe overestimate. See text for discussion. [g] Ascribed rate coefficient for an exothermic radical/unsaturated neutral reaction lacking an activation barrier.

present work, our elucidation of exothermic and freely accessible product channels in the reactions of HCCN ($^3A''$) with H (^2S) and with CH_3 ($^2A'$) are a grave impediment to cyanomethylene-mediated synthesis of NCCN, since both H and CH_3 are generally expected to exist in much higher concentrations than N over the entire altitude range throughout which NCCN is thought to be produced. A representation of the comparative importance of the various loss processes for HCCN is given in Table 1, which deals with the altitude range (800−1200 km) at which modeled NCCN production is greatest.[5,6] Perusal of this table suggests that the H and CH_3 reactions are HCCN removal processes with time scales at least 4 orders of magnitude shorter than the reaction of HCCN with N. Furthermore, without adjusting [HCCN], the H and CH_3 reactions clearly outstrip the HCCN + HCCN reaction by more than 2 orders of magnitude. It is therefore likely that the modeled HCCN concentration is *at least* 2 orders of magnitude too high. It follows, also, that if the reactions of HCCN with H and with CH_3 are as efficient as our quantum chemical calculations indicate, NCCN and NCCCCN can be viewed as only minor products, at best, of the Titanian atmospheric chemistry of HCCN. Instead, the dominant initial products from cyanomethylene, at the low pressures applicable to Titan's upper atmosphere, would appear to be CH_2CHCN from reaction 5 and CCN from reaction 6. Acrylonitrile, CH_2CHCN has not been detected within Titan's atmosphere to date, although it has been identified as a strong candidate for discovery (perhaps by the ESA *Huygens* mission of 2004) due to the reaction of CN with C_2H_4.[37,43,65] The CCN radical, also unseen to date, is presumed principally to act as a minor reservoir for CN in existing models.[8] It is not clear, at this point, whether production by HCCN significantly enhances the expected abundances of either of the CH_2CHCN or CCN daughter species, and among other points raised in the present work, this is a feature for which further study, involving detailed kinetic modeling, is recommended.

The reactivity of HCCN with H and with CH_3 is also pertinent to other remote gaseous environments, insofar as cyanomethylene has been detected within the outflowing circumstellar envelope of the carbon-rich mass-losing star IRC+10216.[66] Within this environment, atomic hydrogen is expected to be one of the principal neutral reactants. The addition−elimination reaction of H (^2S) with HCCN ($^3A''$) yields CCN (X $^2\Pi$); our examination of the potential energy surface suggests that this reaction should have high efficiency even at the low temperature ($T \sim 30$ K) appropriate to the outer envelope of IRC +10216. Such a process provides an alternative path to CCN, which Mebel and Kaiser[67] have suggested as a likely product of the reaction of C (^3P) with HCN and, therefore, as a feasible trace component of circumstellar envelopes such as IRC +10216. Note, however, that production of CCN (X $^2\Pi$) + H (^2S) from C (^3P) + HCN is substantially endothermic ($\Delta H° = 59$ kJ mol^{-1})[67] and is thus capable of occurrence only within the hottest inner regions of a circumstellar envelope, while the reaction of H (^2S) + HCCN ($^3A''$) does not have this thermochemical disadvantage. The mechanism of formation of circumstellar HCCN itself is not currently known but may involve reaction 8 or perhaps the direct radiative association reaction of C (^3P) + HCN (shown, in the study on putative circumstellar CCN formation,[67] to be substantially exothermic and accessible at low temperature).

Conclusions

Our high-level quantum chemical study of the C_2H_2N potential energy surface demonstrates the absence of an absolute activation energy barrier to exothermic addition/dihydrogen elimination in the reaction of H (^2S) with HCCN ($^3A''$), while several exothermic product channels on the C_3H_4N surface are shown to be accessible, and free of barriers, in the reaction of CH_3 ($^2A'$) + HCCN ($^3A''$). The apparently efficient reactions of HCCN with these two highly abundant radicals may invalidate the long-accepted hypothesis that, within Titan's atmosphere, HCCN is the key precursor to both NCCN and NCCCCN. Consequently, alternative routes to these dicyanopolyynes within Titan's atmosphere are necessary. The exploration of some such alternative pathways forms the basis of the following paper.[68]

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