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Low-Temperature Mechanisms for the Formation of Substituted Azanaphthalenes through Consecutive CN and C_2H Additions to Styrene and *N*-Methylenebenzenamine: A Theoretical Study

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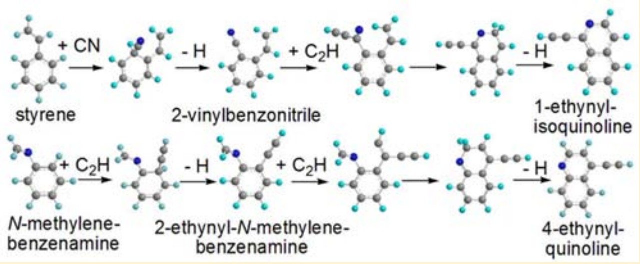
Supporting Information



ABSTRACT: Ab initio G3(MP2,CC)/B3LYP/6-311G** calculations of potential energy surfaces (PESs) for the reactions of cyano and ethynyl radicals with styrene and *N*-methylenebenzenamine have been performed to investigate a possible formation mechanism of the prototype nitrogen-containing polycyclic aromatic compounds: (substituted) 1- and 2-azanaphthalenes. The computed PESs and molecular parameters have been used for RRKM and RRKM-Master Equation calculations of reaction rate constants and product branching ratios under single-collision conditions and at pressures from 3 to 10^{-6} mbar and temperatures of 90−200 K relevant to the organic aerosol formation regions in the stratosphere of a Saturn's moon Titan. The results show that ethynyl-substituted 1- and 2-azanaphthalenes can be produced by consecutive CN and C_2H additions to styrene or by two C_2H additions to *N*-methylenebenzenamine. All CN and C_2H radical addition complexes are formed in the entrance channels without barriers, and the reactions are computed to be exothermic, with all intermediates and transition states along the favorable pathways residing lower in energy than the respective initial reactants. The reactions are completed by dissociation of chemically activated radical intermediates via H losses, so that collisional stabilization of the intermediates is not required to form the final products. These features make the proposed mechanism viable even at very low temperatures and under single-collision conditions and especially significant for astrochemical environments. In Titan's stratosphere, collisional stabilization of the initial CN + styrene reaction adducts may be significant, but substantial amounts of 2-vinylbenzonitrile and 2-ethynyl-*N*-methylenebenzenamine can still be produced and then react with C_2H to form substituted azanaphthalenes.

■ INTRODUCTION

Titan, one of Saturn's moons, has attracted significant attention over the past decades, largely due to its supposed similarity to the prebiotic Earth.[1] Like Earth, Titan's atmosphere is predominantly composed of nitrogen, mixed with a few percent of hydrocarbons but with almost no oxygen. Also like Earth, the atmosphere is dense, with the surface pressure measured to be approximately 1.4 bar. For these reasons, Titan is often dubbed as a natural chemical laboratory for the investigation of chemical processes on the prebiotic Earth, though at a frozen stage, because the surface temperature on Titan is only ~90 K.[1] By studying Titan's atmosphere, it is hoped that some insight can be gained as to how small, simple molecules react to form increasingly larger and more complex organic molecules at cold temperatures in the gas phase, which is also important for understanding chemical evolution in other reducing planetary atmospheres and in the interstellar medium (ISM). Two particularly interesting classes of such molecules include polycyclic aromatic hydrocarbons (PAH) and their nitrogen-containing analogues (N-containing polycyclic aromatic compounds, N-PACs), which may represent building blocks to biologically relevant molecules. N-PACs in particular are considered as important prebiotic molecules, as some of them constitute the central fragment of nucleobases (pyrimidine, purine), and as a link between other prebiotic molecules, such as PAHs and nitriles abundant in the ISM. It is believed that both PAHs and N-PACs may be present and contribute to the formation of aerosols in the brownish-red organic haze layers of Titan's atmosphere,[2] but individual polycyclic aromatic species have yet to be positively identified to date.

To understand chemical processes in Titan's atmosphere and the formation of the organic haze layers, the research community has turned toward laboratory atmospheric models, in addition to astronomical observations and measurements by the Cassini−Huygens mission. The studies of tholins, laboratory analogues of Titan's haze, support the hypothesis that neutral PAHs and their cations as well as N-PACs may constitute the fundamental building blocks of aerosol particles in Titan's hazes.[3,4] N-PACs and PAHs have been detected in tholins by Khare et al.,[5] Sagan et al.,[6] and Ehrenfreund et al.[7] More recently, Khare and co-workers measured time-depend-

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ent infrared spectra of a simulated Titan's tholin synthesized in their laboratory and found that one of the earliest spectral features to emerge was a very strong absorption band at ~1351 cm^{-1} ascribed to skeletal ring vibrations[8] between members of C and N rings, perhaps arranged in relatively dehydrogenated, positively charged heterocyclic ring structures reminiscent of graphitic structures.[9] The spectra indicated an upper mass limit of 6% for benzenes, heterocyclics, and PAHs with more than four rings.[9] Quirico et al.[10] generated powdered carbon−nitrogen-hydrogen tholins to mimic Titan's atmosphere aerosols under levitation conditions and studied them using various spectroscopic techniques. The observed first-order UV Raman bands at 690 and 980 cm^{-1} suggested the presence of C_3N_3 rings inserted in the macromolecular network. Moreover, tholin's IR spectra measured by Carrasco et al.[11] contained intense absorption bands at ~1560 and 1630−1650 cm^{-1}, which can be attributed to C═N groups and/or to N-bearing heteroaromatic or heterocyclic groups. Imanaka et al.[9] have studied tholins produced in an inductively coupled plasma from a nitrogen−methane gas mixture at various pressures of 13−2300 Pa and concluded, based on a spectroscopic structural analysis, that tholins formed at low pressures include clusters of N-PACs in a matrix of carbon and nitrogen branched chain networks, which are tightly connected through hydrogen bonding of N−H bonds. Nitrogen was found to be incorporated into aromatic rings of tholin more efficiently at lower deposition pressures, showing an increase in the N:C ratio as pressure is decreased,[9] whereas at high pressures, N atoms are mainly incorporated into terminal positions of polymers. Imanaka et al. suggested[9] that the tholins formed at low pressures of 13 and 26 Pa may better represent Titan's hazes than those formed at high pressures, and hence the N-PACs found in tholin formed at low pressure may be characteristic for Titan's organic aerosols. Also, in 2012 He et al. reported a ^{15}N, ^{13}C, and ^{1}H NMR study of tholins and identified various nitrogen functional groups, with N-heteroaromatics being one of them.[12] The aromatic macromolecules might have a significant influence over the thermal structure and complex organic chemistry in Titan's atmosphere, because they efficiently absorb UV radiation and are effective charge exchange intermediaries.[12]

The successful identification of benzene during the Cassini−Huygens mission[13] provided further support for the existence of polycyclic aromatic species in Titan's organic hazes, as benzene is considered to be a critical precursor for PAH formation in combustion flames and the formation of the first aromatic ring is generally believed to be a bottleneck for the PAH growth. In the combustion realm, the growth of PAHs starting from benzene has been largely attributed to the hydrogen-abstraction−C_2H_2-addition (HACA) mechanism,[14] involving H abstraction from benzene by a radical-forming phenyl, followed by additions of two C_2H_2 molecules and closure of a second C_6 ring. However, the barriers involved in the HACA mechanism make it an unlikely path for the PAH growth in cold temperature environments typical for Titan and reducing atmospheres of outer planets in the solar system. In 2008, our group proposed an ethynyl addition mechanism (EAM) feasible for the PAH synthesis under low-temperature conditions[15] as an alternative to HACA. In EAM, ethynyl radical additions replace the H abstraction and C_2H_2 addition steps of HACA. Because C_2H addition to unsaturated hydrocarbons (including aromatics) is barrierless, it may occur rapidly even at temperatures as low as 10−15 K. At the first step of EAM, the ethynyl group substitutes a hydrogen atom in benzene to exothermally produce phenylacetylene and then a second C_2H addition to the *ortho*-carbon atom of $C_6H_5C_2H$ followed by a H loss leads to 1,2-diethynylbenzene. The latter can react with a third ethynyl radical via addition to a carbon atom of one of the ethynyl side chains, and a consecutive ring closure results in an ethynyl-substituted naphthalene core. We have also shown that EAM starting from styrene, $C_6H_5C_2H_3$, may directly lead to the formation of ethynylnaphthalene via two consecutive C_2H addition reactions: styrene + C_2H → phenylvinylacetylene/*o*-ethynylstyrene + H and phenylvinylacetylene/*o*-ethynylstyrene + C_2H → ethynylnaphthalene + H.[16]

For understanding the origin and evolution of Titan's haze layers, it is important to find synthetic routes leading to N-PACs from small molecules, abundant in Titan's atmosphere, and radicals, which can be produced by their photodissociation. However, the formation and growth mechanisms of N-PACs are generally less understood than those of PAHs. Ricca et al.[17] have studied potential pathways for nitrogen inclusion into an aromatic ring theoretically, using density functional B3LYP calculations of potential energy profiles for reaction sequences analogous to HACA, but with HCN or cyanoacetylene HCCCN replacing C_2H_2 at some reaction steps. The presence of a nitrogen atom appeared to increase the barrier heights relative to the pure hydrocarbons to about 15 kcal/mol, and thus the calculated barriers are too high to allow reactions to occur in Titan's atmosphere unless the reaction rates are enhanced by vibrational energy of the aromatic molecule. Similar to the HACA mechanism, the reactions suggested by Ricca et al.[17] are more relevant to high-temperature conditions. Our group[18] computed potential energy surfaces (PES) for possible formation mechanisms of N-PACs with one or two nitrogen atoms in an aromatic ring, analogous to EAM but with cyano radical additions taking turns with C_2H additions. In particular, we found that two consecutive C_2H and CN additions to C_6H_6 occur through the C_2H-for-H and CN-for-H exchanges and can lead to the formation of 2-ethynylbenzonitrile, the reaction of which with C_2H, $C_6H_4(CN)(C_2H)$ + C_2H → 2-aza-4-ethynyl-1-naphthyl/2-aza-1-ethynyl-4-naphthyl, may produce N-PAC ethynylazanaphthyl radicals. Although these reactions were found to be feasible at low temperatures owing to their barrierless and exothermic character, they can form ethynylazanaphthyl radicals as final products only upon collisional stabilization of these radicals or if radiative stabilization is faster than their dissociation. Alternatively, an N-PAC with two N atoms in a ring, 4-ethynylquinazoline, can be synthesized from *N*-methylenebenzenamine via two consecutive reactions with C_2H and CN: $C_6H_5(NCH_2)$ + CN → $C_6H_4(NCH_2)(CN)$ + H and $C_6H_4(NCH_2)(CN)$ + C_2H →4-ethynylquinazoline + H, in which collisional stabilization of the radical adducts is not required.

In the present work, we expand our studies to find formation mechanisms of stable (substituted) azanaphthalenes that can be attained both at low temperatures and low pressures (without the requirement of collisional stabilization). In particular, we investigate consecutive reactions of styrene with CN and C_2H and reactions of *N*-methylenebenzenamine with two C_2H radicals using ab initio calculations of their PESs combined with RRKM calculations of reaction rate constants and product branching ratios under single-collision conditions. We will show that N-PACs, such as 2-ethynyl-1-azanaphthalene (2-ethynylquinoline) and 1-ethynyl-2-azanaphthalene (1-ethynylisoquino-

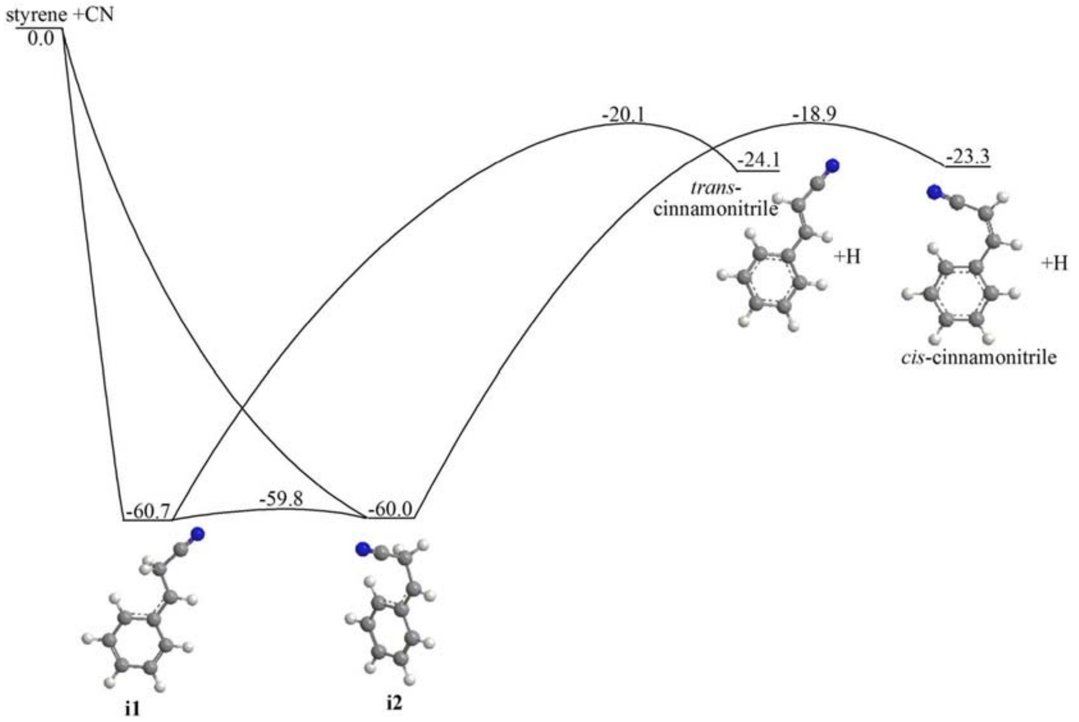

Figure 1. Potential energy diagram for CN addition to the side chain of styrene calculated at the G3(MP2,CC)/B3LYP/6-311G** level of theory. The numbers show relative energies in kcal mol^{-1}. Only the most important reaction channels are shown. (See Figure S1 in Supporting Information for a more complete diagram).

line), can indeed be synthesized by these reactions with significant relative yields.

■ COMPUTATIONAL METHODS

All structures were optimized at the B3LYP/6-311G** level of theory.[19] Afterward, vibrational frequency calculations were performed for the resulting optimized geometries. If the frequency calculations yield all real frequencies, then the structure is categorized as a local minimum (an intermediate or a product), and if the result is that there is one imaginary frequency, then the structure is categorized as a transition state. To obtain chemically accurate energies, a series of single-point calculations, known as a modification[20] of the original G3 scheme,[21] G3(MP2,CC), was carried out at all optimized structures. The G3(MP2,CC) total energy is computed as

$$E[\mathrm{G3(MP2,\ CC)}] = E[\mathrm{CCSD(T)/6\text{-}311G(d,\ p)}] + \Delta E(\mathrm{MP2}) + \mathrm{ZPE(B3LYP/6\text{-}311G^{**})}$$

where ΔE(MP2) is the basis set correction, formally, E[MP2/G3Large] − E[MP2/6-311G(d,p)], and ZPE is a zero-point vibrational energy. ΔE(SO), the spin−orbit correction, and ΔE(HLC), the higher level correction, from the original G3 scheme were not included in our calculations, as they do not make significant contributions into relative energies here. All density functional and ab initio calculations of PESs were carried out using the Gaussian 09[22] and Molpro 2002.6[23] program packages.

In an effort to describe the reaction kinetics and to predict branching ratios of various products, we used Rice−Ramsperger−Kassel−Markus (RRKM) theory.[24] Rate constants for all unimolecular reaction steps were calculated as a function of available energy (relative energy of a species + collision energy), and one energy level was considered throughout as for a zero pressure limit. Sums and densities of states required to compute the rate constants were obtained within the harmonic approximation. Meanwhile, we did not consider absolute rate constants for bimolecular reactions because all of them occur by C_2H and CN additions to aromatic rings or to unsaturated side chains. Such additions are generally found to be barrierless and, based on the analogy with the reactions of C_2H and CN with benzene as well as with alkenes and alkynes, are expected to have rate constants in the 10^{-10} cm^3 $molecule^{-1}$ s^{-1} range, i.e., to approach collision-limited kinetics even at very low temperatures.[25−33] After the unimolecular rate constants for various transformations of initial adducts and other intermediates on pertinent PESs were computed, phenomenological rate expressions were solved, yielding product branching ratios at different collision energies. The RRKM and branching ratio calculations were performed using a code developed in our group.[34]

To access the possibility of collisional stabilization of radical intermediates, RRKM-Master Equation (RRKM-ME) calculations were carried out using the MultiWell Suite of programs.[35−37] In these calculations, N_2 was used as the bath gas and the temperature was varied from 90 to 200 K in increments of 10 K at the pressures of 3, 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} mbar. For each set of conditions, 1000 simulations were run, with the simulation time of 1 ms, which ensured convergence of the results. Densities of states were determined using the Stein−Rabinovitch implementation of the Bayer−Swinehart algorithm in MultiWell, with an energy grain of 10 cm^{-1}. The Lennard−Jones parameters σ and ε/k_b for the species involved in the considered reaction were taken equal to those for benzene, 5.46 Å and 401 K, respectively.

■ RESULTS AND DISCUSSION

Styrene + CN, the C_9H_8N PES. The cyano radical can attack various sites in styrene, including unsaturated carbon atoms in this molecule, two C atoms forming the vinyl group in the side chain and six C atoms in the aromatic ring. Considering that the additions to each of these sites are barrierless and fast, the simplest assumption one can make is that they are equally likely and each of them has a probability of 12.5% to occur. Here, we focus our study only on those CN additions, which may eventually, after a consecutive C_2H addition to a primary product of the CN + styrene reaction, lead to the production of substituted azanaphthalenes. Let us first consider the CN attack toward the terminal CH_2 group in

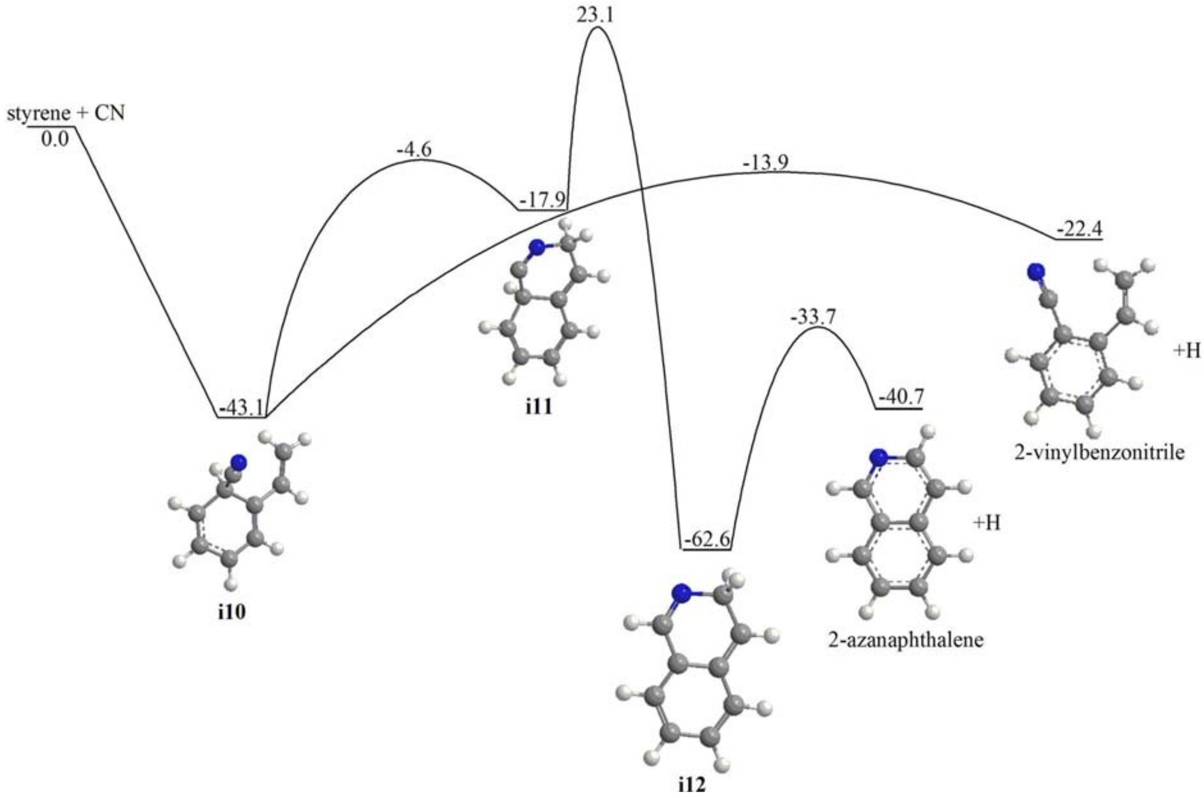

Figure 2. Potential energy diagram for CN addition to the *ortho*-carbon of styrene calculated at the G3(MP2,CC)/B3LYP/6-311G** level of theory. The numbers show relative energies in kcal mol^{-1}.

Table 1. Microcanonical Rate Constants (s^{-1}) for Individual Reaction Steps Following the Formation of Initial Adducts in the Styrene + CN Reaction Calculated at Collision Energies of 0−5 kcal/mol at the Zero-Pressure Limit

	collision energy, kcal mol^{-1}					
rate constants	0.0	1.0	2.0	3.0	4.0	5.0
k_{1-2}	5.18×10^{11}	5.19×10^{11}	5.21×10^{11}	5.23×10^{11}	5.24×10^{11}	5.26×10^{11}
k_{2-1}	6.21×10^{11}	6.21×10^{11}	6.21×10^{11}	6.21×10^{11}	6.21×10^{11}	6.22×10^{11}
k_{1-3}	1.89×10^{-3}	4.42×10^{-3}	9.63×10^{-3}	1.98×10^{-2}	3.87×10^{-2}	7.24×10^{-2}
k_{3-1}	2.82×10^{8}	4.50×10^{8}	6.79×10^{8}	9.81×10^{8}	1.37×10^{9}	1.85×10^{9}
$k_{1\text{-}\mathit{trans}\text{-cinnamonitrile}}$	1.91×10^{4}	2.73×10^{4}	3.85×10^{4}	5.34×10^{4}	7.33×10^{4}	9.95×10^{4}
k_{3-4}	1.23×10^{-14}	2.60×10^{-13}	5.56×10^{-12}	1.24×10^{-10}	2.12×10^{-9}	4.84×10^{-8}
k_{4-3}	2.66×10^{-21}	7.38×10^{-20}	2.06×10^{-18}	5.81×10^{-17}	1.65×10^{-15}	4.70×10^{-14}
k_{4-5}	1.09×10^{4}	1.67×10^{4}	2.51×10^{4}	3.68×10^{4}	5.30×10^{4}	7.49×10^{4}
k_{5-4}	1.40×10^{10}	1.62×10^{10}	1.85×10^{10}	2.11×10^{10}	2.38×10^{10}	2.66×10^{10}
k_{5-7}	2.86×10^{11}	2.88×10^{11}	2.91×10^{11}	2.93×10^{11}	2.95×10^{11}	2.97×10^{11}
k_{7-5}	4.11×10^{1}	6.38×10^{1}	9.71×10^{1}	1.45×10^{2}	2.14×10^{2}	3.10×10^{2}
k_{5-6}	2.75×10^{11}	2.87×10^{11}	2.98×10^{11}	3.08×10^{11}	3.19×10^{11}	3.29×10^{11}
k_{6-5}	9.77×10^{3}	1.46×10^{4}	2.14×10^{4}	3.07×10^{4}	4.34×10^{4}	6.00×10^{4}
$k_{7-\text{2-azanaphthalene}}$	1.13×10^{7}	1.35×10^{7}	1.61×10^{7}	1.90×10^{7}	2.24×10^{7}	2.63×10^{7}
k_{2-8}	2.90×10^{-1}	4.82×10^{-1}	7.81×10^{-1}	1.23×10^{0}	1.91×10^{0}	2.89×10^{0}
k_{8-2}	8.72×10^{10}	1.02×10^{11}	1.18×10^{11}	1.35×10^{11}	1.54×10^{11}	1.73×10^{11}
$k_{2\text{-}\mathit{cis}\text{-cinnamonitrile}}$	4.86×10^{3}	7.07×10^{3}	1.01×10^{4}	1.43×10^{4}	1.99×10^{4}	2.74×10^{4}
k_{8-9}	5.28×10^{-8}	8.20×10^{-8}	1.30×10^{-7}	2.08×10^{-7}	3.40×10^{-7}	5.64×10^{-7}
k_{9-8}	1.26×10^{-14}	2.60×10^{-14}	5.41×10^{-14}	1.13×10^{-13}	2.38×10^{-13}	5.01×10^{-13}
$k_{9-\text{1-azanaphthalene}}$	4.61×10^{9}	5.23×10^{9}	5.92×10^{9}	6.68×10^{9}	7.50×10^{9}	8.39×10^{9}
k_{10-11}	7.36×10^{-1}	1.63×10^{0}	6.54×10^{0}	6.54×10^{0}	1.21×10^{1}	2.13×10^{1}
k_{11-10}	3.39×10^{7}	5.87×10^{7}	1.48×10^{8}	1.48×10^{8}	2.19×10^{8}	3.14×10^{8}
$k_{10-\text{2-vinylbenzonitrile}}$	1.44×10^{5}	2.15×10^{5}	3.15×10^{5}	4.53×10^{5}	6.39×10^{5}	8.87×10^{5}

styrene. In this case, the CN addition can yield two conformers **i1** and **i2** with exothermicities of 60.7 and 60.0 kcal mol^{-1}, respectively (Figure 1).

Both entrance channels are found to be barrierless, and so they may occur rapidly even at low temperatures. This conclusion is supported by experimentally measured constants

Table 2. Microcononical Rate Constants (s^{-1}) for Individual Reaction Steps Following the Formation of Initial Adducts in the $C_9H_6N + C_2H$ and *N*-Methylenebenzenamine + $2C_2H$ Reactions Calculated at Collision Energies of 0−5 kcal/mol at the Zero-Pressure Limit

rate constants	collision energy, kcal mol^{-1}					
	0.0	1.0	2.0	3.0	4.0	5.0
$k_{13\_\mathit{cis}\text{-}13}$	2.87×10^{8}	3.41×10^{8}	4.05×10^{8}	4.77×10^{8}	5.57×10^{8}	6.51×10^{8}
k_{13-13_cis}	1.26×10^{8}	1.52×10^{8}	1.82×10^{8}	2.16×10^{8}	2.55×10^{8}	3.01×10^{8}
k_{13-14}	5.53×10^{3}	7.77×10^{3}	1.07×10^{4}	1.47×10^{4}	1.97×10^{4}	2.62×10^{4}
k_{14-13}	1.56×10^{6}	2.16×10^{6}	2.95×10^{6}	3.96×10^{6}	5.26×10^{6}	6.89×10^{6}
$k_{13\text{-}(\mathit{E})\text{-}3\text{-}(2\text{-ethynylphenyl})\text{-acrylonitrile}}$	1.05×10^{5}	1.50×10^{5}	2.12×10^{5}	2.96×10^{5}	4.06×10^{5}	5.50×10^{5}
$k_{13\text{-}(\mathit{Z})\text{-}3\text{-}(2\text{-ethynylphenyl})\text{-acrylonitrile}}$	1.44×10^{4}	2.22×10^{4}	3.36×10^{4}	4.98×10^{4}	7.24×10^{4}	1.04×10^{5}
k_{13-16}	1.23×10^{1}	2.22×10^{1}	3.89×10^{1}	6.64×10^{1}	1.10×10^{2}	1.79×10^{2}
k_{16-13}	5.30×10^{-1}	9.96×10^{-1}	1.81×10^{0}	3.21×10^{0}	5.54×10^{0}	9.32×10^{0}
k_{14-15}	1.86×10^{3}	2.89×10^{3}	4.40×10^{3}	6.57×10^{3}	9.65×10^{3}	1.40×10^{4}
k_{15-14}	7.55×10^{-7}	1.44×10^{-6}	2.69×10^{-6}	4.89×10^{-6}	8.71×10^{-6}	1.52×10^{-5}
k_{15-16}	6.89×10^{5}	8.12×10^{5}	9.54×10^{5}	1.12×10^{6}	1.31×10^{6}	1.52×10^{6}
k_{16-15}	2.55×10^{11}	2.57×10^{11}	2.61×10^{11}	2.64×10^{11}	2.67×10^{11}	2.70×10^{11}
$k_{15-3\text{-cyanoazanaphthalene}}$	1.50×10^{9}	1.62×10^{9}	1.74×10^{9}	1.88×10^{9}	2.02×10^{9}	2.17×10^{9}
$k_{16\text{-}(\mathit{E})\text{-}3\text{-}(2\text{-ethynylphenyl})\text{acrylonitrile}}$	3.00×10^{4}	4.39×10^{4}	6.30×10^{4}	8.93×10^{4}	1.25×10^{5}	1.72×10^{5}
$k_{17\_\mathit{trans}\text{-}17}$	6.13×10^{-2}	1.65×10^{-1}	4.04×10^{-1}	9.15×10^{-1}	1.94×10^{0}	3.90×10^{0}
k_{17-17_trans}	4.90×10^{-1}	1.28×10^{0}	3.04×10^{0}	6.67×10^{0}	1.37×10^{1}	2.69×10^{1}
k_{19-17}	3.40×10^{6}	4.84×10^{6}	6.76×10^{6}	9.31×10^{6}	1.26×10^{7}	1.69×10^{7}
k_{17-19}	2.55×10^{6}	3.41×10^{6}	4.51×10^{6}	5.88×10^{6}	7.58×10^{6}	9.65×10^{6}
k_{18-19}	2.32×10^{9}	2.63×10^{9}	2.96×10^{9}	3.26×10^{9}	3.71×10^{9}	4.13×10^{9}
k_{19-18}	3.11×10^{9}	3.79×10^{9}	4.58×10^{9}	5.49×10^{9}	6.55×10^{9}	7.76×10^{9}
$k_{18\text{-p2}}$	3.57×10^{3}	6.93×10^{3}	1.28×10^{4}	2.27×10^{4}	3.87×10^{4}	6.39×10^{4}
$k_{17\_\mathit{trans}\text{-p3}}$	1.21×10^{3}	2.37×10^{3}	4.41×10^{3}	7.90×10^{3}	1.36×10^{4}	2.28×10^{4}
$k_{19-2\text{-cyano-}1\text{-azanaphthalene}}$	2.31×10^{9}	2.64×10^{9}	2.99×10^{9}	3.39×10^{9}	3.81×10^{9}	4.28×10^{9}
k_{20-21}	7.86×10^{12}	8.12×10^{12}	8.39×10^{12}	8.65×10^{12}	8.92×10^{12}	9.18×10^{12}
k_{21-20}	5.78×10^{10}	6.71×10^{10}	7.76×10^{10}	8.96×10^{10}	1.03×10^{11}	1.17×10^{11}
$k_{20\text{-p4}}$	1.08×10^{3}	1.91×10^{3}	3.26×10^{3}	5.39×10^{3}	8.66×10^{3}	1.36×10^{4}
$k_{21-1\text{-ethynyl-}2\text{-azanaphthalene}}$	3.30×10^{7}	3.90×10^{7}	4.58×10^{7}	5.35×10^{7}	6.23×10^{7}	7.23×10^{7}
$\mathrm{k}_{22-2\text{-ethynyl-}\mathit{N}\text{-methylenebenzenamine}}$	1.90×10^{6}	2.58×10^{6}	3.47×10^{6}	4.59×10^{6}	6.01×10^{6}	7.77×10^{6}
k_{23-24}	5.24×10^{13}	5.25×10^{12}	5.26×10^{12}	5.27×10^{12}	5.27×10^{12}	5.28×10^{12}
k_{24-23}	1.24×10^{11}	1.28×10^{11}	1.36×10^{11}	1.45×10^{11}	1.54×10^{11}	1.63×10^{11}
$k_{23\text{-p5}}$	8.39×10^{5}	1.07×10^{6}	1.37×10^{6}	1.73×10^{6}	2.17×10^{6}	2.72×10^{6}
$k_{24-4\text{-ethynyl-}1\text{-azanaphthalene}}$	1.90×10^{10}	1.99×10^{10}	2.11×10^{11}	2.22×10^{10}	2.34×10^{10}	2.46×10^{10}

for CN addition to carbon double bond sites in different molecules, although the kinetics of the CN + styrene has not yet been studied. For example, most recently, Morales et al. used the CRESU (reaction kinetics in uniform supersonic flow) technique to determine rate constants for CN addition to the double bond in 1,3-butadiene and obtained the values of 4.33 ± 0.50 and 4.66 ± 0.64 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 83 K and 120 K, respectively. These results indicate that the reaction is fast and occurs without an entrance barrier.[30] Both **i1** and **i2** can eject a hydrogen atom from the attacked carbon atom forming *trans*- and *cis*-cinnamonitriles, respectively. The barriers for the H elimination pathways are 40.6 and 41.1 kcal mol^{-1} relative to **i1** and **i2** and the corresponding transition states reside 20.1 and 18.9 kcal mol^{-1} below the initial reactants, respectively. **i1** and **i2** can easily rearrange to each other by rotation around the CH−CH_2 bond via a low barrier of less than 1 kcal mol^{-1}. Other possible isomerization pathways of **i1** and **i2** might lead to the formation of 1- and 2-azanaphthalenes, but they appeared to not be competitive with the direct H losses (see Supporting Information).

Aside from the addition of CN to the vinyl side chain, CN can also attack the *ortho*-carbon position in the phenyl ring. This addition occurs without a barrier and is 43.1 kcal mol^{-1} exothermic (see Figure 2). Again, the finding that the CN addition to the aromatic ring in styrene is barrierless is in line with the previous experimental and theoretical studies of the reaction of cyano radicals with benzene[18,26,33] and toluene.[26] Once the adduct **i10** forms, it may lose the H atom from the attacked *ortho*-carbon, yielding 2-vinylbenzonitrile. A barrier of 29.2 kcal mol^{-1} must be surmounted for the hydrogen loss to proceed. The process alternative to the H loss is a six-member ring formation leading to **i11**, which requires a barrier of 38.5 kcal mol^{-1}. Once the ring is formed, 1,2-H migration may occur from a carbon atom common for the two rings to its neighbor in the N-containing ring, forming **i12**. However, this process is unlikely to be competitive under low-temperature conditions because the associated transition state resides 23.1 kcal mol^{-1} above the reactants. Theoretically, if **i12** is formed, it can undergo a H loss from the CH_2 carbon, producing 2-azanaphthalene.

With PESs in hand, energy-dependent rate constants were calculated for individual reaction steps starting from the initial adducts using RRKM theory under collision-free conditions, in the collision energy range of 0 to 5 kcal mol^{-1} (see Tables 1 and 2).

Subsequently, rate expressions were solved, yielding branching ratios for various possible products (Table 3).

Table 3. Product Branching Ratios (%) as a Function of Collision Energy at the Zero-Pressure Limit

	collision energy (kcal mol^{-1})					
	0.0	1.0	2.0	3.0	4.0	5.0
Figure 1						
trans-cinnamonitrile	77.1	76.8	76.5	76.2	76.0	75.7
cis-cinnamonitrile	22.9	23.2	23.5	23.8	24.0	24.3
1-azanaphthalene	0	0	0	0	0	0
2-azanaphthalene	0	0	0	0	0	0
p1	0	0	0	0	0	0
Figure 2						
2-vinylbenzonitrile	100	100	100	100	100	100
1-azanaphthalene	0	0	0	0	0	0
Figure S2						
3-cyanonaphthalene	0	0	0	0	0	0
(*E*)-3-(2-ethynylphenyl)acrylonitrile	94.3	93.8	93.3	92.9	92.4	91.9
(*Z*)-3-(2-ethynylphenyl)-acrylonitrile	5.7	6.2	6.7	7.1	7.6	8.1
Figure 4						
starting from *cis*-cinnamonitrile						
2-ethynyl-1-azanaphthalene	100	100	100	100	100	100
p2	0	0	0	0	0	0
p3	0	0	0	0	0	0
starting from *trans*-cinnamonitrile						
2-ethynyl-1-azanaphthalene	0	0	0	0	0	0
p2	0	0	0	0	0	0
p3	100	100	100	100	100	100
Figure 5						
1-ethynyl-2-azanaphthalene	100	100	100	100	100	100
p4	0	0	0	0	0	0
Figure 6						
4-ethynyl-1-azanaphthalene	100	100	100	100	100	100

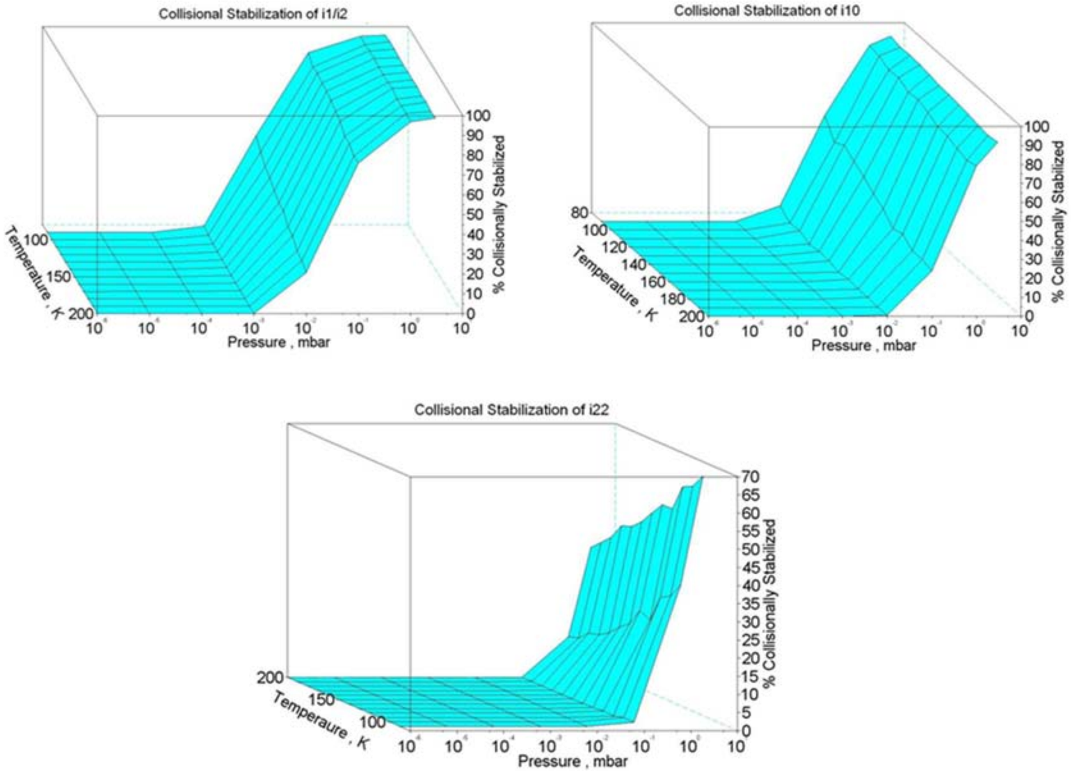

Figure 3. Relative yields of collisionally stabilized adducts **i1**/**i2**, **i10**, and **i22** computed using the RRKM-ME approach at pressures of 3 to 10^{-6} mbar and temperatures of 90−200 K.

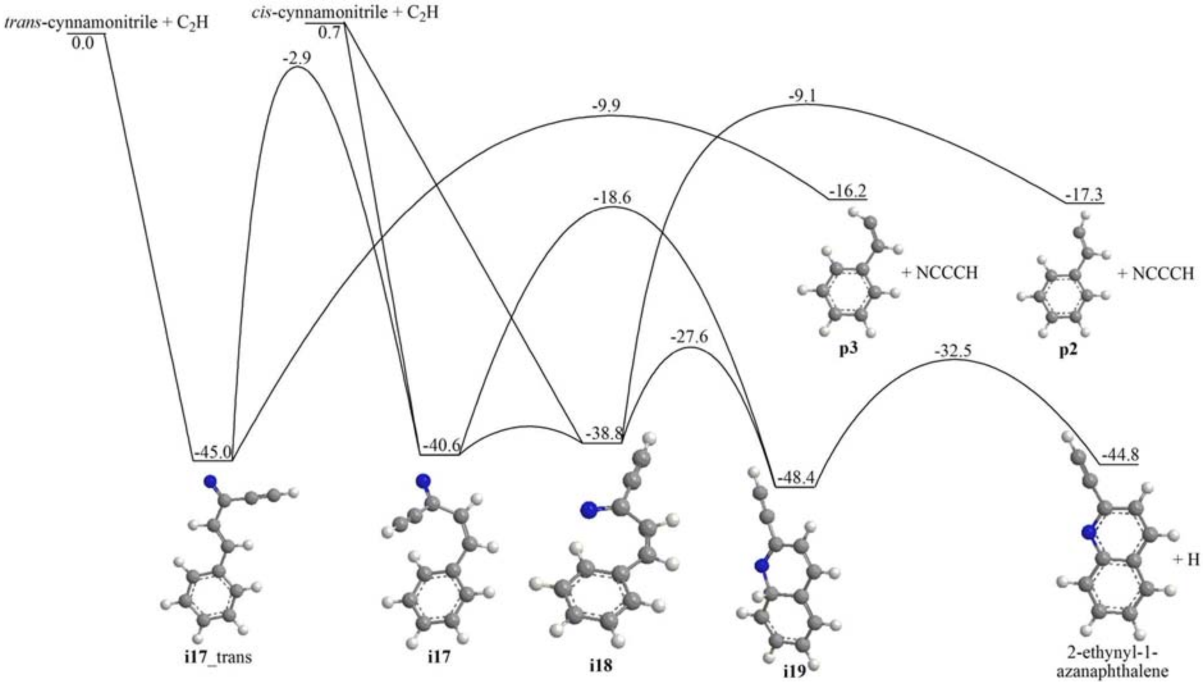

Figure 4. Potential energy diagram for C_2H addition to the CN carbon of *trans*/*cis*-cinnamonitrile calculated at the G3(MP2,CC)/B3LYP/6-311G** level of theory. The numbers show relative energies in kcal mol^{-1}.

The branching ratio of *trans*- versus *cis*-cinnamonitrile is found to be ~3:1 in favor of the trans isomer. This value is insensitive to the collision energy regardless of whether **i1** or **i2** is formed as the initial adduct because the two can rearrange to one another much faster than dissociate via the H loss (see Table 1). The branching ratios of *trans*- and *cis*-cinnamonitriles are controlled by the relative energies of the H elimination transition states leading to the formation of the trans and cis isomer; the former resides 1.2 kcal mol^{-1} lower than the latter. The results also show that 2-vinylbenzonitrile is an exclusive product of CN addition to the *ortho*-carbon of styrene under single-collision conditions.

Can the primary products of the CN + styrene reaction potentially lead to the formation of azanaphthalene through some other processes? Recently, Sebree et al. used ultraviolet photoexcitation to probe the isomerization channels of benzylallene.[38] Their results supplemented with DFT calculations revealed isomerization pathways from benzylallene which yield naphthalene. In particular, one of the mechanisms identified in their work involved photoisomerization of benzylallene to 1-phenyl-1,3-butadiene and then to 1,2-dihydronaphthalene, which loses two hydrogen atoms to ultimately produce naphthalene. Alternatively, naphthalene was also formed by H loss from benzylallene leading to benzylallenylradical, which then undergoes a ring closure and a second H elimination. *E*- and *Z*-Phenylvinylacetylenes (PVAs), which are isoelectronic analogues of *trans*- and *cis*-cinnamonitriles predicted to be formed in the CN + styrene reaction, were also produced. Though no similar experiments have yet been performed on nitrogen-containing analogues such as cinnamonitriles, it seems plausible that their isomerization (or that of 2-vinylbenzonitrile) promoted by ultraviolet photoexcitation and/or by encounters with radicals may lead to azanaphthalene production.

It may be possible that the initial adducts of the CN + styrene reaction, **i1**, **i2**, or **i10**, could be collisionally stabilized. While the pressure on the surface of Titan is about 1.4 bar, the PAH-forming region of the atmosphere has been determined to exist between the altitudes of 140 to 300 km above the surface.[2] The pressures at these altitudes range from 3 to 0.1 mbar[39] with T being approximately 160−180 K and the average time between collisions is in the 20−600 ns range at these conditions. According to the calculated rate constants (Table 1), the lifetimes of **i1**/**i2** and **i10** are 52 and 7 μs, respectively, at zero collision energy and decrease with E_{col}, meaning that collisional stabilization may play a significant role. To verify this, we carried out more sophisticated RRKM-ME simulations at pertinent temperatures (90−200 K) and pressures (3−10^{-6} mbar). The results are illustrated in Figure 3, whereas the numerical values of relative yields of stabilized **i1**/**i2** and **i10** are given in Table S1 of Supporting Information. It appears that at 160−180 K and 3 mbar **i1** and **i2** are almost completely collisionally stabilized (98−99%) and do not fragment. However, the relative yield of the stabilized intermediates decreases to ~80% and 24−29% at 0.1 and 0.01 mbar, respectively. The collisional stabilization is more significant at lower temperatures at the same pressure. For **i10** which has a lower dissociation barrier (~30 kcal/mol vs ~40 kcal/mol for **i1**/**i2**), the collisional stabilization in the same temperature interval is less significant and decreases from about 90% at 3 mbar to ~80% at 1 mbar, 25−30% at 0.1 mbar, and ~1% at 0.01 mbar. At 10^{-3} mbar and lower pressures, the collisional stabilization of **i1**/**i2** and **i10** becomes negligible. These results show that at higher altitudes, where the pressure is in the range of 0.1 mbar, the fragmentation products of **i1**/**i2** (*trans*- and *cis*-cinnamonitriles) and **i10** (2-vinylbenzonitrile) will constitute ~20% and 70−75% of the total product yield for the CN addition to the CH_2 group and *ortho*-carbon in styrene, respectively. Taking into account the assumed equal probabilities of CN additions to each unsaturated carbon atom in styrene and the computed branching ratios, we estimate relative yields of *trans*- and *cis*-cinnamonitriles and 2-vinylbenzonitrile

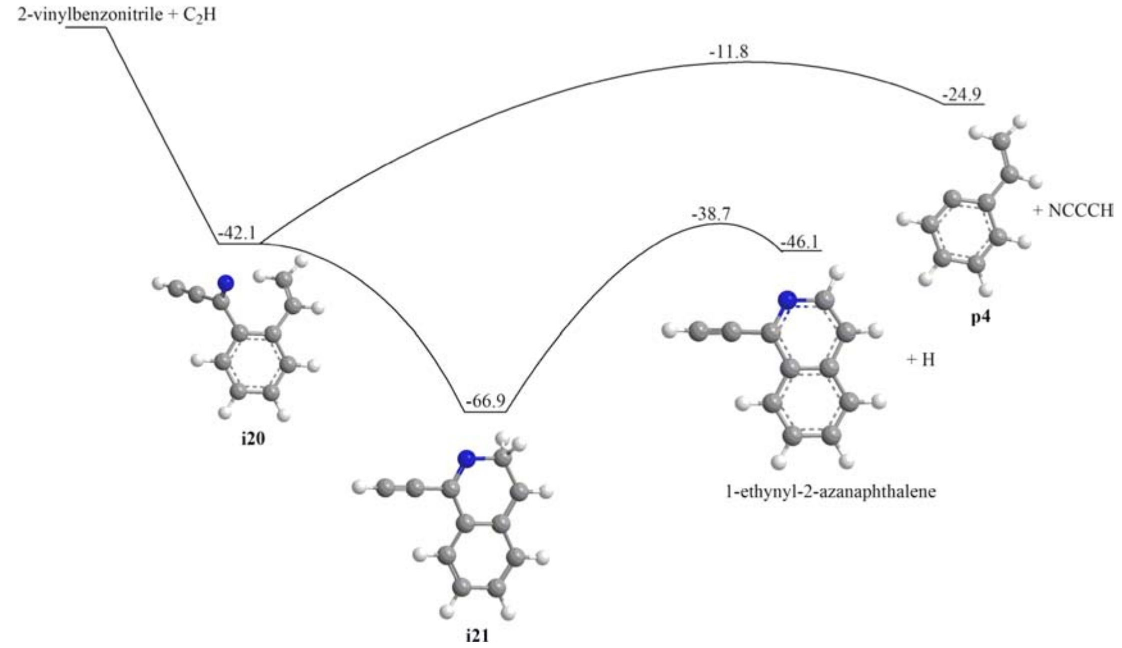

Figure 5. Potential energy diagram for C_2H addition to the CN carbon of 2-vinylbenzonitrile calculated at the G3(MP2,CC)/B3LYP/6-311G** level of theory. The numbers show relative energies in kcal mol^{-1}.

in the CN + styrene reaction at 0.1 mbar and 160−180 K as 1.9%, 0.6%, and 18−19%, respectively.

Meanwhile, infrared radiative stabilization of the intermediates under these conditions can be ruled out. The radiative stabilization rate constants k_{rad} were computed using the approach by Klippenstein et al.[40] at average temperatures corresponding to the available internal energies of the intermediates, if they were produced in the corresponding bimolecular reactions at zero collision energy, and utilizing B3LYP/6-311G** vibrational frequencies and IR intensities. The radiative stabilization rate constants, 21.2 and 11.5 s^{-1} for **i1** and **i10**, respectively, are 3−4 orders of magnitude lower than the decomposition rate constants of these intermediates (Table 1), and thus infrared radiative stabilization is not competitive with dissociation. If the radical adducts **i1**, **i2**, and **i10** are collisionally stabilized, they may react with other species or be processed photochemically. However, because the formation of azanaphthalenes directly from these radicals is not favorable, here we do not pursue their fate further. Meanwhile, this analysis indicates that significant amounts of *trans*- and *cis*-cinnamonitriles and 2-vinylbenzonitrile can be produced at the pressure of 0.1 mbar and lower in the temperature range of 160−180 K, i.e., at the conditions relevant to the PAH forming region of Titan's atmosphere.

With the result being that neither of the considered mechanisms of the CN + styrene reaction offer viable pathways toward the immediate formation of N-PACs, we move to investigate consequent reaction of the CN + styrene primary products. In particular, we study addition of the ethynyl radical, C_2H, to *trans*- and *cis*-cinnamonitrile, along with 2-vinylbenzonitrile, to see whether it can lead to the formation of substituted N-PACs. Earlier, our group demonstrated that C_2H addition to $C_{10}H_8$ products of the C_2H + styrene reaction may yield considerable amounts of substituted naphthalene,[16] with the reaction proceeding by ring closure, following the initial C_2H attack on various carbon centers, and finally by hydrogen loss to form PAH molecules. The PAH growth is attainable in these reactions because the cyclization process becomes more favorable than the direct hydrogen loss mechanism. One can expect that the analogous C_2H reactions with cinnamonitrile and 2-vinylbenzonitrile may lead to the formation of substituted azanaphthalenes and hence we consider them here.

C_9H_7N + C_2H, the $C_{11}H_8N$ PES. Addition of the ethynyl radical to the ortho positioned carbon in *trans*- or *cis*-cinnamonitriles eventually results in the formation of (*E*)- and (*Z*)-3-(2-ethynylphenyl)acrylonitriles by direct H losses from the initial adducts **i13** and **i13**_cis, respectively. Because the targeted (substituted) azanaphthalenes cannot be produced here, these reaction channels are described in Supporting Information.

C_2H addition may alternatively occur to the CN carbon of *trans*- or *cis*-cinnamonitriles (Figure 4). The addition to *cis*-cinnamonitrile leads to two rotational isomers, **i17** and **i18**, with exothermicities of 40.6 and 38.8 kcal mol^{-1}, respectively, which can easily rearrange to one another via a very low barrier. **i17** can undergo a ring closure via a barrier of 22.0 kcal mol^{-1} forming **i19** in the process. Next, elimination of the hydrogen from C common for the two fused six-member rings in **i19** leads to the formation of 2-ethynyl-1-azanaphthalene via a 15.9 kcal mol^{-1} barrier. The ring closure in **i18**, also to form **i19**, is even more facile than that in **i17**, as this process requires a barrier of only 11.2 kcal mol^{-1}. The only competitive alternative to the ring closure in **i18** is elimination of cyanoacetylene, NCCCH, leading to the formation of the C_6H_5CHCH radical **p2**, but the associated barrier of 29.7 kcal mol^{-1} is almost a factor of 3 higher than that for the **i18** → **i19** cyclization process. One can clearly see that the C_2H + *cis*-cinnamonitrile reaction provides a favorable path to synthesize ethynyl-substituted 1-azanaphthalene if C_2H adds to the carbon atom of the cyano group. This, however, is not the case for the similar reaction involving *trans*-cinnamonitrile because isomerization of the initial adduct **i17**_trans to **i17** involves a rotation around a double C═C bond and is not expected to compete with the loss of cyanoacetylene due to a high, ∼42 kcal mol^{-1},

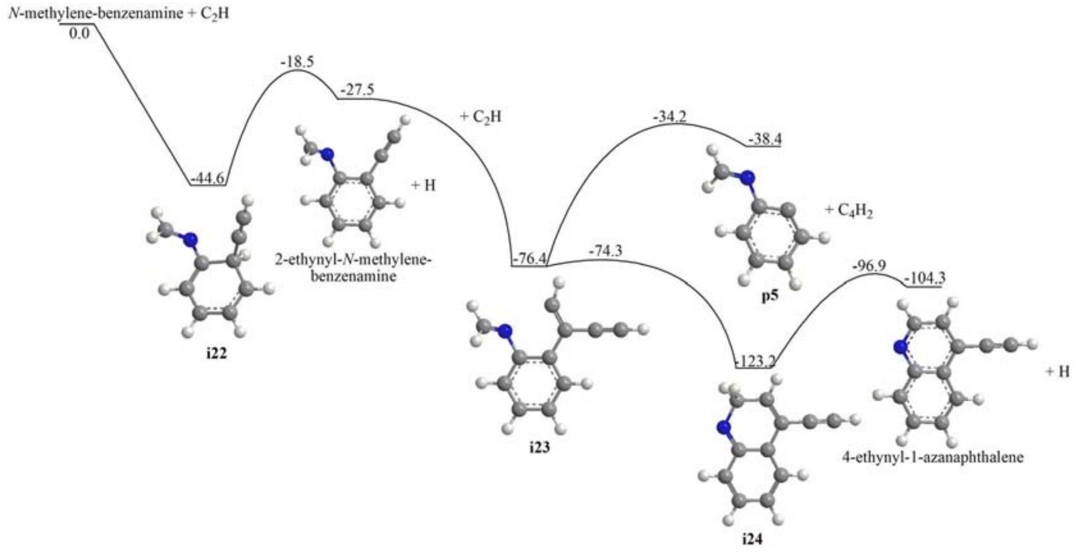

Figure 6. Potential energy diagram for two sequential C_2H additions to *N*-methylenebenzenamine calculated at the G3(MP2,CC)/B3LYP/6-311G** level of theory. The numbers show relative energies in kcal mol^{-1}.

barrier. The wave function of the transition state associated with this rotation was found to have a strong multireference character, and hence its energy was evaluated by multireference perturbation theory CASPT2(5,5)/6-311G** single-point calculations at the optimized B3LYP geometry, relative to the reference **i17** energy calculated at the same level.

Finally, C_2H can also add to the carbon atom of the CN group in 2-vinylbenzonitrile (Figure 5). This occurs with an exothermicity of 43.1 kcal mol^{-1} and leads to **i20**. This adduct can feature a spontaneous ring closure to form a bicyclic structure **i21.** A very low barrier for this process was found at the B3LYP level where **i20** is a local minimum. However, the transition state energy at the G3(MP2,CC)/B3LYP/6-311G** level is computed to be lower than that of **i20**, indicating a metastable character of this intermediate. Hydrogen elimination can then occur from **i21** via a barrier of 28.2 kcal mol^{-1}, leading to the formation of an N-PAC molecule, 1-ethynyl-2-azanaphthalene. Alternatively, NCCCH can be lost from the initial adduct **i20**, leading to the $C_6H_4CHCH_2$ radical **p4** via a barrier of 30.3 kcal mol^{-1}. Clearly, the cyanoacetylene elimination is less preferable than the ring closure followed by a H loss.

Tables 2 and 3 list rate constants for each unimolecular reaction as a function of collision energy and associated branching ratios under single-collision conditions (a zero-pressure limit). One can see that the monocyclic 3-(2-ethynylphenyl)acrylonitrile molecule (in two *E* and *Z* conformers) is the sole product of the C_2H + *trans*/*cis*-cinnamonitrile reactions when C_2H attacks the ortho carbon in the ring. The branching ratio of the *E* and *Z* conformers, 94−92/6−8, is insensitive to whether C_2H reacts with *trans*- or *cis*-cinnamonitrile because isomerization between **i13** and **i13**_cis is much faster than their dissociation via the H loss. The reactions do not lead to the formation of bicyclic substituted azanaphthalenes for the same reasons as those for the CN + styrene reaction channels illustrated in Figures 1, S1 (in Supporting Information), and 2: the initial cyclization steps appear to be nearly competitive to the direct hydrogen loss, but the subsequent 1,2-H migration impedes the progress toward the formation of N-PAC molecules. In contrast, N-PACs can be achieved through processes involving incorporation of CN into the second ring (Figures 4 and 5). In particular, 2-ethynyl-1-azanaphthalene is calculated to be the exclusive product of the C_2H + *cis*-cinnamonitrile reaction if the ethynyl radical adds to the CN carbon, as the **i17** and **i18** adducts preferably undergo a ring closure and H elimination to produce N-PACs instead of losing cyanoacetylene. The unpaired electron in **i17** and **i18** is mostly localized on the hydrogen-less nitrogen atom, and no viable pathway exists of losing hydrogen. For the reaction channels shown in Figures 1−3, a H loss is favored because it results in the formation of a closed shell stable species, but that cannot happen for **i17** and **i18**. The formation of a stable closed shell molecule through a H loss can only occur after the cyclization process is completed. Once the second ring is closed, the radical center is redistributed to carbon atoms in the C_6 ring, allowing for a closed shell species to form through hydrogen elimination. Figure 5 shows that 1-ethynyl-2-azanaphthalene can also be formed, again as the exclusive product, in the C_2H + 2-vinylbenzonitrile reaction if the ethynyl radical adds to the C atom of the cyano moiety. Here too, the reason for the success of the N-PAC formation is the inability of the initial adduct **i20** to lose a hydrogen atom. This illustrates an important general mechanistic aspect of the PAH (or N-PAC) synthesis. Hydrogen elimination from an initial adduct almost always outcompetes any cyclization event. Therefore, successful routes to PAHs (N-PACs) should have such adducts formed in an entrance channel, for which a direct hydrogen loss cannot occur or is not competitive as compared to a ring closure.

RRKM-ME calculations at $p = 3{-}10^{-6}$ mbar and $T = 90{-}200$ K do not show any collisional stabilization of the initial adduct **i17** and other intermediates **i18** and **i19** in Figure 4, which is explained by rather low barriers on the pathway to the dissociation products, where the highest in energy transition state (**i18** → **i19**) resides only 13.0 kcal/mol above **i17**. The calculated radiative stabilization rate constant of **i17** at zero collision energy, 16.9 s^{-1}, is several orders of magnitude lower than the rate constants for its isomerization and for the H loss from **i19**. Thus, under the conditions of Titan's atmosphere, **i17** formed in the C_2H + *cis*-cinnamonitrile reaction is expected to decompose to 2-ethynyl-1-azanaphthalene + H rather than to be collisionally or radiatively stabilized. On the other hand,

i17_trans, the initial adduct of the C_2H + *trans*-cinnamonitrile separated from the fragmentation products by a much higher barrier of 35.1 kcal/mol, is expected to be largely collisionally stabilized or otherwise form the **p3** + cyanoacetylene products. No collisional stabilization was found also for intermediate **i21** in Figure 5, and its radiative stabilization rate constant, 51.2 s^{-1}, is much lower than that for the loss from **i21**, 3.30 × 10^7 s^{-1} at zero collision energy. Although the barrier for the H elimination reaction involving **i21** is relatively high, 28.2 kcal/mol, the transition state resides 38.7 kcal/mol below the reactants, making the collisional stabilization of **i21** unlikely, as verified by RRKM-ME calculations. Thus, the C_2H + 2-vinylbenzonitrile reaction may produce 1-ethynyl-2-azanaphthalene not only under single-collision conditions but also in the PAH-forming region of Titan's atmosphere if C_2H attacks the C atom of the CN group. Assuming equal probabilities of C_2H additions to each unsaturated C atom in *cis*-cinnamonitrile and 2-vinylbenzonitrile (11.1%), up to ~2% of styrene molecules can be converted to ethynyl-substituted azanaphthalenes under Titan's atmospheric conditions by consecutive reactions with CN and C_2H, predominantly to 1-ethynyl-2-azanaphthalene via 2-vinylbenzonitrile.

***N*-Methylenebenzenamine + 2C_2H.** In our previous work,[18] we found that 4-ethynylquinazoline, an N-PAC molecule with two N atoms in an aromatic ring, can be produced from *N*-methylenebenzenamine via two consecutive additions of C_2H and CN: $C_6H_5(NCH_2)$ + CN → $C_6H_4(NCH_2)(CN)$ + H and $C_6H_4(NCH_2)(CN)$ + C_2H → 4-ethynylquinazoline + H. Here, we investigate a similar mechanism starting from *N*-methylenebenzenamine but involving two C_2H additions with an expectation that this process can produce an ethynyl-substituted quinoline molecule with one N atom in a ring. The computed potential energy profile is illustrated in Figure 6. The addition of C_2H to an *ortho*-carbon in *N*-methylenebenzenamine occurs barrierlessly with an exothermicity of 44.6 kcal mol^{-1}. Next, a direct loss of the hydrogen from the attacked carbon leads to the formation of 2-ethynyl-*N*-methylenebenzenamine, which lies 27.5 kcal mol^{-1} below the initial reactants, via a barrier of 26.1 kcal/mol. Addition of another C_2H unit then forms the **i23** adduct with an exothermicity of 48.9 kcal mol^{-1}. **i23** can undergo a fast ring closure through a very low barrier of 2.1 kcal mol^{-1}, leading to intermediate **i24**, which can then lose hydrogen to form 4-ethynyl-1-azanaphthalene (4-ethynylquinoline) via a barrier of 26.3 kcal mol^{-1}. 4-ethynylquinoline lies 76.8 kcal mol^{-1} below the initial reactants 2-ethynyl-*N*-methylenebenzenamine + C_2H. The only alternative fate of **i23** could be elimination of the C_4H_2 (diacetylene) side-chain group. However, this process requires a relatively high barrier of 42.2 kcal mol^{-1} and thus is not competitive with the ring closure followed by the H loss leading to 4-ethynylquinoline.

According to RRKM calculations at the zero-pressure limit, 4-ethynylquinoline is the dominant product of the 2-ethynyl-*N*-methylenebenzenamine + C_2H reaction in the range of collision energies of 0−5 kcal mol^{-1} if C_2H adds to the α carbon of the ethynyl side chain. RRKM-ME calculations at pressures in the 3−10^{-6} mbar range and temperatures of 90−200 K show little collisional stabilization of **i22** in the first C_2H addition reaction for pressures up to 1 mbar (see Figure 3 and Table S1) and no collisional stabilization of **i23** and **i24** in the second reaction. Also, the computed radiative stabilization rate constants, 19.6, 21.9, and 60.3 s^{-1}, are too low for this process to compete with dissociation of these intermediates.

Thus, if *N*-methylenebenzenamine and C_2H radicals are available, two consecutive reactions described above can lead to the production of substituted quinoline under low-temperature and low-pressure conditions. Assuming equal probabilities of C_2H additions to each carbon of *N*-methylenebenzenamine (14.3%) and 2-ethynyl-*N*-methylenebenzenamine (11.1%), ~3% of the former can converted to 4-ethynylquinoline at pressures up to 0.1 mbar. Previously[18] we discussed that *N*-methylenebenzenamine itself can be formed in various reactions under different conditions, including recombination of phenyl and methylene-amidogen radicals followed by collisional stabilization of the product (low temperature and high pressure), the barrierless C_6H_5 + CH_3N → $C_6H_5(NCH_3)$ → $C_6H_5(NCH_2)$ + H reaction (low temperature and low pressure), and the reaction of phenyl with methyleneimine, C_6H_5 + CH_2NH → $C_6H_5(NHCH_3)$ → $C_6H_5(NCH_2)$ + H featuring 3−5 kcal mol^{-1} barriers (elevated/high temperature and low pressure).

■ CONCLUDING REMARKS

Ab initio calculations of potential energy surfaces combined with RRKM calculations of reaction rate constants and product branching ratios under single-collision conditions demonstrate that ethynyl-substituted 1- and 2-azanaphthalenes (ethynylquinoline and -isoquinoline) can be produced by two consecutive CN and C_2H additions to styrene or by two C_2H additions to *N*-methylenebenzenamine. In particular, 2-ethynyl-1-azanaphthalene can be formed via the following reaction sequence: styrene + CN → **i1**/**i2** → *cis*-cinnamonitrile + H, *cis*-cinnamonitrile + C_2H → **i17**/**i18** → cyclization → **i19** → 2-ethynyl-1-azanaphthalene + H. 1-Ethynyl-2-azanaphthalene can be synthesized via the styrene + CN → **i10** → 2-vinylbenzonitrile + H and 2-vinylbenzonitrile + C_2H → **i20** → cyclization → **i21** → 1-ethynyl-2-azanaphthalene + H consecutive reactions and 4-ethynyl-1-azanaphthalene can be produced via *N*-methylenebenzenamine + C_2H → **i22**→ 2-ethynyl-*N*-methylenebenzenamine + H and 2-ethynyl-*N*-methylenebenzenamine + C_2H → **i23** → cyclization → **i24** → 4-ethynyl-1-azanaphthalene + H. All reactions in these sequences are computed to be exothermic overall and to have no entrance barriers, with all intermediates and transition states along the favorable pathways residing lower in energy than the respective initial reactants. These features of the potential energy surfaces make the reactions feasible even at very low temperatures. In addition, all the reactions are completed by dissociation of chemically activated reaction adducts (or their isomers formed afterward) via a hydrogen atom loss leading to the final products. This means that substituted azanaphthalenes can be produced through these reaction sequences under single-collision conditions (i.e., at very low or zero pressure) because the chemical energy released in the reactions can be converted into kinetic and internal energy of the dissociation fragments and thus collisional stabilization of energized intermediates is not required. The viability of the suggested mechanism for the low temperature/very low (zero) pressure conditions makes it especially significant for astrochemical environments, such as planetary atmospheres and the ISM. For the PAH-forming region of Titan's stratosphere, our RRKM-ME calculations show that, although collisional stabilization of the radical adducts may be significant, the initial CN reaction with styrene may produce substantial amounts of *cis*-cinnamonitrile and especially 2-vinylbenzonitrile at p = 0.1 mbar and T = 160−180 K, which in turn may react with C_2H to form ethynyl-substituted azanaphthalenes. Collisional stabilization of the adduct in the reaction of C_2H with *N*-methylenebenzenamine is insignificant or small for pressures up to 1 mbar, whereas no contribution from collisionally stabilized intermediates to the total product yield is predicted for the C_2H reactions with *cis*-cinnamonitrile, 2-vinylbenzonitrile, and 2-ethynyl-*N*-methylenebenzenamine in the pressure/temperature range of $3-10^{-6}$ mbar/90−200 K relevant to the atmosphere of Titan. Radiave association processes are shown not to be competitive for the considered CN and C_2H addition reactions.

The discovery of a novel synthetic route toward a cold temperature synthesis of N-PACs may have significant implications for Titan's atmospheric chemistry. Even though nitrogen analogues of aromatics are yet to be positively identified on Titan, the inclusion of the reactions leading to the formation of N-PACs into chemical models of Titan's atmosphere may help better understanding of its chemical processes and reveal other interesting avenues of research. Moreover, additions of CN and C_2H to (substituted) 1- and 2-azanaphthalene can lead to the formation of N-PACs with three and more aromatic rings. For example, C_2H addition to either the nitrogen or carbon positions adjacent to the ethynyl group in 2-ethynyl-1-azanaphthalene followed by cyclization may lead to the formation of a third ring. After that, a similar ethynyl addition mechanism may lead to a further growth of polycyclic aromatic structures. The mechanism suggested and theoretically investigated here may be generally applicable to an expansion of a substituted PAH or N-PAC molecule by an extra aromatic ring. If such a molecule contains an out-of-ring vinyl group, it may undergo consecutive CN and C_2H additions analogous to the reactions presented here, resulting in the formation of an additional ring incorporating a nitrogen atom. Also, if a polycyclic aromatic molecule contains a side-chain methyleneamino group (methyleneamino-PAH or -N-PAC), two sequential barrierless ethynyl radical additions may lead to the formation of an N-PAC with an extra azabenzene ring.

It should be noted that the second C_2H addition serves to enhance the extra ring closure and may be in principle replaced by an addition of any other radical R. As illustrated in Figure 7, an addition of a radical R to the CN carbon atom in *cis*-cinnamonitrile and 2-vinylbenzonitrile or to the α carbon atom of the C_2H side chain in 2-ethynyl-*N*-methylenebenzenamine would result in a shift of the radical site to a terminal atom of the attacked side chain, nitrogen in the case of the *cis*-cinnamonitrile and 2-vinylbenzonitrile reactions or carbon in the case of 2-ethynyl-*N*-methylenebenzenamine. This is expected to make the extra ring closure facile and more competitive than the alternative process of elimination of RCN or RCCH, as actually demonstrated in the present work for $R = C_2H$. If R is a hydrogen atom, then unsubstituted 1- and 2-azanaphthalenes can be formed via this mechanism. The feasibility of the reactions shown in Figure 7 under different conditions will be governed by the barrier height for the addition of the radical R to the molecules involved. For instance, C_2H and CN normally add to a triple bond (here, in *cis*-cinnamonitrile, 2-vinylbenzonitrile, and 2-ethynyl-*N*-methylenebenzenamine) without a barrier, making the proposed mechanism facile even in very low-temperature environments. However, the addition of a H atom to a triple bond proceeds via a significant barrier, for example, ~6 kcal mol^{-1} for the $H + C_2H_2 \rightarrow C_2H_3$ reaction.[41] Hence, the formation of unsubstituted azanaphthalenes via the pathways shown in Figure 7 with *R* = H may be possible only at elevated temperatures. Noteworthy, a barrier height for a reaction between a radical and an unsaturated hydrocarbon molecule can be correlated to the difference of the ionization energy of the molecule (I.E.) and electron affinity of the radical (E.A.). According to a semiempirical criterion derived by Smith et al.,[42] for such a reaction to be barrierless and fast at low temperatures the I.E. − E.A. value should be below 8.75 eV. On the basis of this criterion, one can expect the mechanism of R addition followed by the ring closure and H elimination to be more probable for the radicals with a high electron affinity.

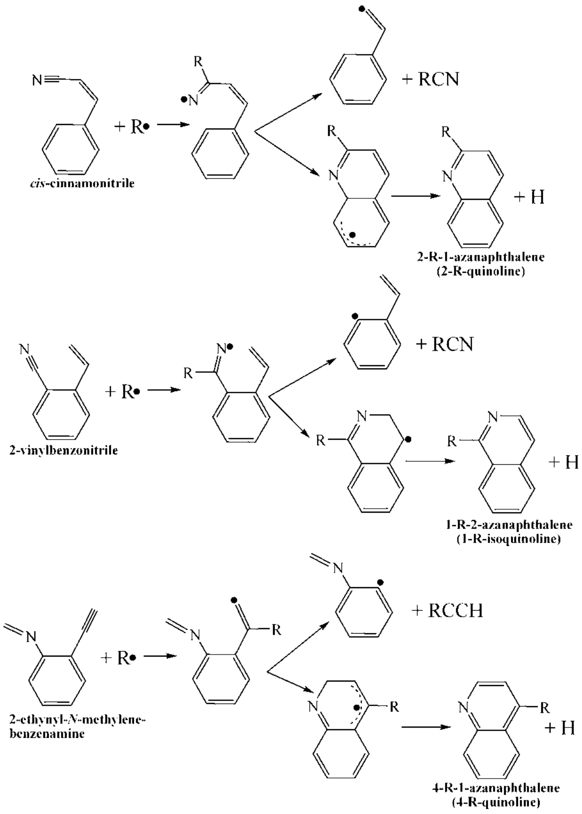

Figure 7. Schematic mechanism of a radical addition to *cis*-cinnamonitrile, 2-vinylbenzonitrile, and *N*-methylenebenzenamine followed by cyclization and H atom elimination.

Experimental verification of the theoretically proposed mechanism, though difficult, may be achieved through a two-step study of elementary chemical reactions. First, this requires demonstrating that the CN addition to styrene indeed can produce *trans*- and *cis*-cinnamonitriles and 2-vinylbenzonitrile. Although experimental routes to generate CN radicals are readily available and styrene is commercially accessible, a crossed molecular beams experiment with the universal mass spectrometric product detection may not be sufficient for this purpose because the three products are separated in energy by less than 2 kcal mol^{-1}. These products may be distinguished by their spectroscopic identification or by measuring their photoionization energy curves upon irradiation with VUV light. If cinnamonitrile and 2-vinylbenzonitrile are identified as primary products of the CN + styrene reaction, their branching ratios may also be deduced. At the second step, one would need to study the reactions of these products with C_2H to confirm that they are able to produce ethynyl-substituted azanaphthalenes. Both cinnamonitrile and 2-vinylbenzonitrile are commercially available, and such an experiment is in principle possible. Because the NCCCH loss products and substituted azanaphthalenes have different masses and the ethynylazanaphthalenes are expected to be clearly separated in energy from other $C_{11}H_7N$ isomers, the crossed molecular beam experimental technique may be used to verify whether the N-PACs can be formed. Alternative experimental techniques where styrene can interact with both CN and C_2H radicals (or *N*-methylenebenzenamine with C_2H radicals) in a reaction chamber under conditions allowing for secondary reactions to occur, with spectroscopic or VUV photoionization mass spectrometric identification of products, may be also employed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of alternative isomerization pathways of the initial adducts **i1** and **i2** in the CN + styrene reaction and C_2H additions to *ortho*-C atoms in cinnamonitriles (including Figures S1 and S2), RRKM-ME calculated relative yields of collisionally stabilized adducts **i1**/**i2**, **i10**, and **i22** at pressures of 3 to 10^{-6} mbar and temperatures of 90−200 K (Table S1), optimized Cartesian coordinates, rotational constants, vibrational frequencies, and G3(MP2,CC) total energies of various structures (Table S2), and total energies calculated at different levels of theory, ZPE corrections, and T1 diagnostic values (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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