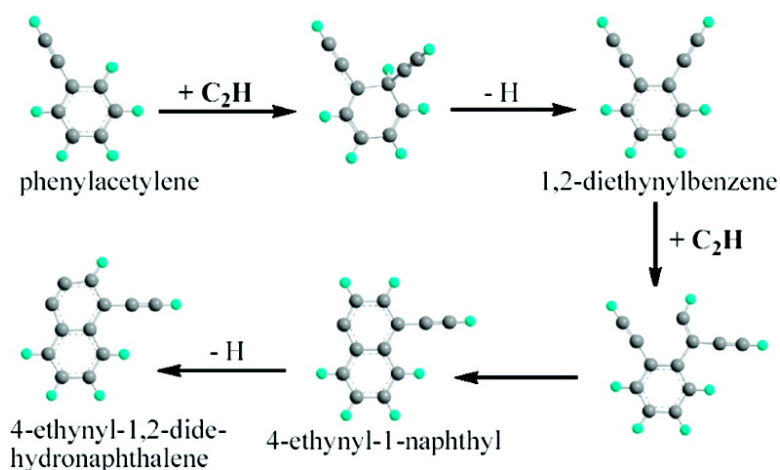


Photoinduced Mechanism of Formation and Growth of Polycyclic Aromatic Hydrocarbons in Low-Temperature Environments via Successive Ethynyl Radical Additions

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Photoinduced Mechanism of Formation and Growth of Polycyclic Aromatic Hydrocarbons in Low-Temperature Environments via Successive Ethynyl Radical Additions

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Abstract: A novel ethynyl addition mechanism (EAM) has been established computationally as a practicable alternative to high-temperature hydrogen-abstraction-C₂H₂-addition (HACA) sequences to form polycyclic aromatic hydrocarbon (PAH)-like species under low-temperature conditions in the interstellar medium and in hydrocarbon-rich atmospheres of planets and their moons. Initiated by an addition of the ethynyl radical (C₂H) to the ortho-carbon atom of the phenylacetylene (C₆H₅C₂H) molecule, the reactive intermediate loses rapidly a hydrogen atom, forming 1,2-diethynylbenzene. The latter can react with a second ethynyl molecule via addition to a carbon atom of one of the ethynyl side chains. A consecutive ring closure of the intermediate leads to an ethynyl-substituted naphthalene core. Under single-collision conditions as present in the interstellar medium, this core loses a hydrogen atom to form ethynyl-substituted 1,2-didehydronaphthalene. However, under higher pressures as present, for example, in the atmosphere of Saturn's moon Titan, three-body reactions can lead to a stabilization of this naphthalene-core intermediate. We anticipate this mechanism to be of great importance to form PAH-like structures in the interstellar medium and also in hydrocarbon-rich, low-temperature atmospheres of planets and their moons such as Titan. If the final ethynyl addition to 1,2-diethynylbenzene is substituted by a barrierless addition of a cyano (CN) radical, this newly proposed mechanism can even lead to the formation of cyano-substituted naphthalene cores in the interstellar medium and in planetary atmospheres.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the Earth environment in the form of atmospheric aerosols, soot, and volatile particles and are formed as a result of incomplete combustion processes of fossil fuels.^{1–5} Because of the harmful environmental effects attributed to PAHs, which have been shown to be major air pollutants exhibiting mutagenic and tumorigenic activities,^{1–3} their formation mechanism is one of the central areas in combustion research.^{6,7} In the meantime, PAHs and their cations are also found to play an important role in interstellar chemistry.^{8,9} For instance, PAH molecules could

account for 2–30% of the carbon in the galaxy and may provide nucleation sites for the formation of carbonaceous dust particles.⁸ PAHs are also believed to be responsible for emission features in astronomical infrared spectra⁹ and remain strong candidates for carriers of diffuse interstellar bands (DIB),^{10–13} which are ubiquitously observed toward reddened stars throughout the Milky Way¹⁴ and also in extragalactic lines of sight.^{13,15–19} Circumstellar shells of carbon-rich stars are among the more

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promising places for the formation of PAHs,²⁰ but they can also be found in interplanetary dust^{21,22} and are suggested to be omnipresent in the interstellar medium.²³

PAHs are also relevant to the atmospheric chemistry of planets and moons in the solar system.²⁴ Although they are yet to be directly observed in planetary atmospheres, PAHs have been identified in laboratory experiments simulating Jupiter's atmosphere and also the atmospheric chemistry of Saturn's moon Titan together with its colored organic haze layers.²⁵ Furthermore, detection of the simplest aromatic hydrocarbon, benzene (C₆H₆), which is considered as the building block and hence precursor of complex PAHs, in the low-temperature atmospheres of Jupiter and Saturn²⁶ and recently on Titan²⁷ strongly suggests that the PAH synthesis may proceed in these environments. For instance, it is widely believed that PAHs are responsible for the formation of organic haze layers in Titan's atmosphere,²⁴ but the nature of PAHs on Titan and their formation and growth mechanisms are not well understood. Surprisingly, the present models of PAH growth in low-temperature environments such as on Titan or in the interstellar medium are inspired by the models of PAH and soot formation in combustion processes^{7,28,29} and assume that similar mechanisms are important both at combustion temperatures (1000–2500 K) and in the extraterrestrial, low-temperature environments (10–150 K).²⁴ Wilson et al.,³⁰ for instance, suggested that benzene is formed in Titan's atmosphere primarily via the pressure-induced recombination of propargyl radicals; once the first aromatic ring has been formed, the further growth of PAHs proceeds by the hydrogen-abstraction-acetylene-addition

(HACA) mechanism,^{24,31} which is believed to be the most important PAH formation mechanism in combustion flames.⁷ However, the elementary reactions involved in the HACA sequence, such as hydrogen abstraction from benzene and acetylene (C₂H₂) addition to the phenyl radical, exhibit significant barriers in the range of 17 and 4 kcal/mol, respectively.³² Consequently, these processes are too slow at the low-temperature conditions of Titan's atmosphere. For example, the reaction that is assumed to initiate PAH synthesis in combustion flames, C₆H₅ + C₂H₂ → C₆H₅C₂H + H reaction producing phenylacetylene, follows the rate expression $k = (2.14 \times 10^{-14}) T^{0.834} \exp(-2320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ³³ with T being the temperature in kelvins. This gives *low rate constants* of 8.4×10^{-23} – $1.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ between 100 and 200 K. On the contrary, an alternative reaction to form phenylacetylene, C₆H₆ + C₂H → C₆H₅C₂H + H, can proceed by barrierless addition of the ethynyl radical (C₂H) to benzene followed by a hydrogen atom elimination to form phenylacetylene with overall exothermicity of ~28 kcal/mol.^{34,35} This pathway has been found to be *very fast* at low temperatures, with $k = (3.0\text{--}4.0) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 105–298 K.³⁶ Therefore, on Titan, the reaction of benzene with the ethynyl radical (C₆H₆ + C₂H → C₆H₅C₂H + H) is certainly expected to play a role similar to that of reaction of phenyl radicals with acetylene (C₆H₅ + C₂H₂ → C₆H₅C₂H + H) in combustion to efficiently produce phenylacetylene.³⁵

These considerations suggest that in low-temperature environments such as those found in the atmosphere of Titan, fast ethynyl radical (C₂H) addition sequences may present a viable alternative to the HACA reaction sequences. The prerequisite for the ethynyl mechanism to work is the presence of benzene (as observed on Titan) and also the availability of ethynyl radicals. On Titan, ethynyl radicals (C₂H) can be produced easily by the photolysis of acetylene.^{37–40} Therefore, C₂H has been included in the current photochemical models of Titan,^{24,30,41–47} where this radical is shown to play an important role in the formation of polyynes CH₃(C≡C)_{*n*}-H, H-(C≡C)_{*n*}-H, and H-(C≡C)_{*n*} and thus in the complexation of the organic haze layers via such reactions as C₂H + H(C≡C)_{*n*}H → H(C≡C)_{*n*}+1H + H and C₂H + CH₃(C≡C)_{*n*}H → CH₃(C≡C)_{*n*}+1H + H. In this paper, due to the lack of experimental and computational studies on the proposed ethynyl radical reaction mechanism with aromatic species, we utilize high-level ab initio calculations of

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potential energy surfaces (PES) to tackle computationally the reactions of ethynyl radicals with phenylacetylene and diethynylbenzene and their role in the formation of PAHs and related structures in low-temperature environments. These investigations present compelling evidence that PAH-like molecules can indeed readily grow from benzene (C_6H_6) via phenylacetylene ($C_6H_5C_2H$) and diethynylbenzene [$C_6H_4(C_2H)_2$] by barrierless and sequential ethynyl (C_2H) radical addition steps in low-temperature environments. These findings can revolutionize the understanding of the formation of PAHs not only in low-temperature solar system environments, such as in the atmospheres of hydrocarbon-rich planets and their moons like Titan, but also in cold molecular clouds where temperatures can drop as low as 10 K.

Computational Methods

Geometries of all intermediates and transition states on the $C_{10}H_7$ ($C_6H_5C_2H + C_2H$) and $C_{12}H_7$ [$C_6H_4(C_2H)_2 + C_2H$] PESs as well as bimolecular fragments of these radicals were optimized by the hybrid density functional B3LYP method⁴⁸ with the 6-311G** basis set. The same method was used to obtain vibrational frequencies, molecular structural parameters, and zero-point energy (ZPE) corrections and to characterize the stationary points as minima or first-order saddle points. To obtain more accurate energies, we applied the G3(MP2,CC)//B3LYP modification⁴⁹ of the original GAUSSIAN-3 (G3) scheme⁵⁰ for high-level single-point energy calculations. The final energies at 0 K were obtained by use of the B3LYP optimized geometries and ZPE corrections according to the formula $E_0[G3(MP2,CC)] = E[CCSD(T)/6-311G(d,p)] + \Delta E_{MP2} + E(ZPE)$, where $\Delta E_{MP2} = E[MP2/G3large] - E[MP2/6-311G(d,p)]$ is the basis set correction and $E(ZPE)$ is the zero-point energy. $\Delta E(SO)$, a spin-orbit correction, and $\Delta E(HLC)$, a higher-level correction, from the original G3 scheme were not included in our calculations, as they are not expected to make significant contributions into relative energies. Here and below we denote this G3-type approach used in our computations as G3 for brevity. We applied the *Gaussian98*⁵¹ program package to carry out B3LYP and MP2 calculations, and the MOLPRO 2006⁵² program package to perform calculations of spin-restricted coupled cluster RCCSD(T) energies. Relative yields of various products in the $C_6H_5C_2H + C_2H$ and $C_6H_4(C_2H)_2 + C_2H$ reactions under single-collision conditions were evaluated by Rice–Ramsperger–Kassel–Marcus (RRKM) calculations⁵³ of energy-dependent rate constants for individual unimolecular steps and of branching ratios of different channels. The computational procedure for these calculations has been described in detail in our previous works.⁵⁴ We calculated rate constants as functions of available internal energy of each intermediate or transition state; the internal energy was taken as a sum of the energy of chemical activation in each reaction considered and the collision energy, assuming that a dominant fraction of the

latter is converted to internal vibrational energy. Only a single total-energy level was considered throughout, as for single-collision conditions (zero-pressure limit). The harmonic approximation was used in calculations of numbers and densities of states needed to evaluate the rate constants. With all rate constants in hand, we computed product branching ratios by solving first-order kinetic equations for unimolecular reactions. We employed the fourth-order Runge–Kutta method to solve the equations; the product concentrations at the time when they converged were used to compute branching ratios.

Results and Discussion

Phenylacetylene + Ethynyl Reaction: (A) C_2H Addition to the Aromatic Ring. In the HACA mechanism in combustion, the phenylacetylene molecule is first activated by a hydrogen atom abstraction from the ortho position in the benzene ring (with respect to the C_2H out-of-ring group), which is followed by acetylene addition to the radical site and ring closure, producing 1-naphthyl radical. Therefore, here we first consider the C_2H addition to the ortho-carbon. As seen in Figure 1, ethynyl addition to $C_6H_5C_2H$ occurs without a barrier and produces intermediate **i1** with an exothermicity of 44.4 kcal/mol. In **i1** one of the ring carbons is linked to a C_2H group and the neighboring C atom has two out-of-ring single bonds, with H and another C_2H (sp^3 hybridization). The chemically activated **i1** adduct can use the available internal energy for either dissociation or isomerization. The most favorable fragmentation channel is a hydrogen atom elimination from the C(H)(C_2H) group, which leads to the formation of 1,2-diethynylbenzene. The diethynylbenzene plus hydrogen atom products reside 27.5 kcal/mol lower in energy than the initial reactants, $C_6H_5C_2H + C_2H$. The hydrogen atom loss from **i1** proceeds via a barrier of 29.5 kcal/mol at the transition state TS1-H, with the reverse barrier for hydrogen atom addition to diethynylbenzene being 12.6 kcal/mol. Note that the calculated energetics for the $C_6H_5C_2H + C_2H \rightarrow C_6H_4(C_2H)_2 + H$ reaction are rather similar to that for $C_6H_6 + C_2H \rightarrow C_6H_5(C_2H) + H$, where the total exothermicity was computed to be 28.4 kcal/mol. The initial hydrogen atom addition step proceeds with an energy gain of 42.2 kcal/mol, and the hydrogen atom loss barrier is somewhat lower, 24.4 kcal/mol.³⁵ TS1-H resides 14.9 kcal/mol below the reactants and therefore, unless **i1** can be collisionally stabilized, it has enough internal energy to break apart to produce diethynylbenzene plus a hydrogen atom.

It was found earlier for the $C_6H_6 + C_2H$ reaction that hydrogen atom migrations in the $C_6H_6C_2H$ adduct cannot compete with the hydrogen atom loss producing phenylacetylene (ethynylbenzene).^{34,35} The same is true for **i1**; all attempts to optimize transition states for 1,2- or 1,3-H shifts within the C(H)(C_2H) group or from this group to the neighboring C_2H fragment converged to TS1-H for the hydrogen atom elimination. In the $C_6H_6C_2H$ system, hydrogen atom migration around the ring to form a CH_2 group instead of C(H)(C_2H) was found to have a barrier of 38.6 kcal/mol, ~ 14 kcal/mol higher than that for the hydrogen atom loss, and also the subsequent hydrogen atom elimination from the CH_2 group gave the same ethynylbenzene product.^{34,35} Hence, we do not have to consider this type of hydrogen atom migrations around the ring in the present **i1** adduct. On the other hand, a new isomerization channel may be possible in **i1** as compared to $C_6H_6C_2H$. It involves a second ring closure via TS1-2 producing intermediate **i2**, 9H-1,4-didehydronaphthalene. This $C_{10}H_7$ isomer possesses two fused C_6 rings but is nonplanar and not aromatic because one of the two carbon atoms participating in the C–C bond connecting

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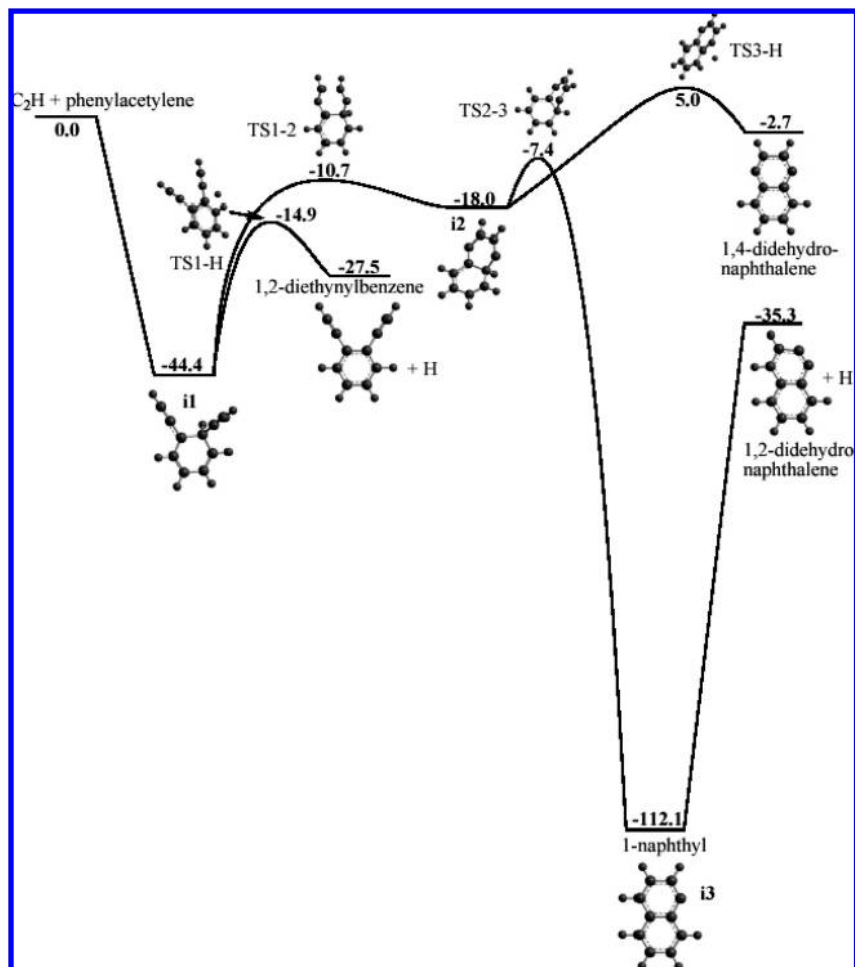


Figure 1. Potential energy diagram for the $C_2H + C_6H_5C_2H$ reaction: channels originating from C_2H addition to the ortho-carbon atom in the ring. All relative energies are calculated at the G3(MP2,CC)//B3LYP/6-311G** level and given in kilocalories per mole. Optimized geometries of all intermediates and transition states are also shown.

the rings is sp^3 -hybridized. **i2** resides 18.0 kcal/mol below phenylacetylene + ethynyl and thus is 26.4 kcal/mol less favorable than the initial **i1** adduct. The transition state for the ring closure lies 10.7 kcal/mol lower in energy than the reactants and so the ring closure barrier is 4.2 kcal/mol higher than that for the H elimination producing diethynylbenzene. Next, **i2** can undergo either hydrogen atom loss, producing 1,4-didehydronaphthalene, or 1,2-H migration, giving 1-naphthyl radical **i3**. The first scenario is clearly unfavorable because the transition state for hydrogen atom elimination, TS3-H, is 5.0 kcal/mol higher in energy than the initial reactants. Therefore, this channel is closed at low collision energies. The 1,2-H shift takes place via transition state TS2-3, residing 7.4 kcal/mol below the reactants with a barrier of 10.6 kcal/mol, and the resulting **i3** resides in a deep potential well of 112.1 kcal/mol relative to $C_6H_5C_2H + C_2H$. Depending on the reaction conditions, 1-naphthyl radical either can be stabilized by collisions, becoming the final product, or, under single-collision conditions (like in cross molecular beam experiments or in very low pressure environments), can lose the hydrogen atom in the ortho position with respect to the radical site, producing 1,2-didehydronaphthalene. The hydrogen atom loss in **i3** takes place without an exit barrier, just like hydrogen atom elimination from the phenyl radical to produce *o*-benzynes,⁵⁵ and the resulting product is 35.3 kcal/mol lower in energy than the reactants.

According to the calculated energetics, two reaction channels are open when C_2H adds to the ortho C atom of the ring of phenylacetylene, $C_6H_5C_2H + C_2H \rightarrow i1 \rightarrow TS1-H \rightarrow 1,2$ -diethynylbenzene + H and $C_6H_5C_2H + C_2H \rightarrow i1 \rightarrow TS1-2 \rightarrow i2 \rightarrow TS2-3 \rightarrow i3$ (1-naphthyl) \rightarrow 1,2-didehydronaphthalene plus a hydrogen atom. In order to compare the importance of the two channels, we performed RRKM calculations of rate constants for individual reaction steps starting from the chemically activated initial adduct **i1** under collisionless conditions. Here we assumed that, upon a single collision of $C_6H_5C_2H$ with C_2H , all collision energy E_{col} is converted into internal vibrational energy of **i1** and thus the available internal energy of this intermediate is 44.4 kcal/mol + E_{col} . The same is true for the other intermediates and transition states; their internal energies were assumed to be equal to their chemical energy relative to the $C_6H_5C_2H + C_2H$ plus collision energy. The RRKM calculation were carried out for $E_{col} = 0-5$ kcal/mol with a step of 1 kcal/mol, and the resulting rate constants were used to determine relative yields of the 1,2-diethynylbenzene and 1,2-didehydronaphthalene products. The results presented in Table 1 show that 1,2-diethynylbenzene should be the nearly exclusive product under single-collision conditions of the $C_6H_5C_2H + C_2H$ reaction; only a minute amount, $\sim 0.01\%$, of

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Table 1. Calculated Branching Ratios (%) for Various C₂H Addition Reactions under Single-Collision Conditions Depending on the Collision Energy, E_{col}

product	E_{col} , kcal/mol					
	0.0	1.0	2.0	3.0	4.0	5.0
C₂H + C₆H₅C₂H → i1 → products (Figure 1)						
1,2-didehydronaphthalene(via 1-naphthyl)	0.01	0.01	0.01	0.01	0.01	0.01
1,2-diethynylbenzene	99.99	99.99	99.99	99.99	99.99	99.99
C₂H + C₆H₅C₂H → i4 → products (Figures 2 and 3)						
phenyldiacetylene	89.88	89.71	89.59	89.42	89.28	89.15
1,2(2,3)-didehydronaphthalene (via 2-naphthyl)	0.09	0.09	0.10	0.10	0.10	0.11
1,3-didehydronaphthalene	0.00	0.00	0.00	0.00	0.00	0.00
C ₆ H ₅ + C ₄ H ₂	10.03	10.19	10.30	10.47	10.61	10.74
C₂H + C₆H₅C₂H → i11 → products (Figures 3 and 2)						
phenyldiacetylene	23.50	22.83	22.19	21.63	21.01	20.44
1,2(2,3)-didehydronaphthalene (via 2-naphthyl)	0.01	0.01	0.01	0.01	0.01	0.01
1,3-didehydronaphthalene	0.00	0.00	0.00	0.00	0.00	0.00
C ₆ H ₅ + C ₄ H ₂	76.49	77.16	77.80	78.36	78.97	79.55
C₂H₂ + C₆H₅CC → i12 → products (Figure 4)						
phenyldiacetylene	99.96	99.96	99.96	99.96	99.96	99.96
1,2-didehydronaphthalene	0.04	0.04	0.04	0.04	0.04	0.04
C₂H + C₆H₄(C₂H)₂ → i14 → products (Figure 5)						
4-ethynyl-1,2-didehydronaphthalene (via 4-ethynyl-1-naphthyl)	97.79	97.65	97.50	97.34	97.18	97.00
ethylbutadiynylbenzene	1.94	2.06	2.18	2.31	2.43	2.57
C ₈ H ₅ + C ₄ H ₂	0.26	0.29	0.32	0.35	0.39	0.43
C₂H + C₆H₄(C₂H)₂ → i17 → products (Figure 5)						
4-ethynyl-1,2-didehydronaphthalene(via 4-ethynyl-1-naphthyl)	55.76	54.89	54.12	53.31	52.56	51.70
ethylbutadiynylbenzene	43.93	44.77	45.52	46.30	47.02	47.85
C ₈ H ₅ + C ₄ H ₂	0.31	0.34	0.36	0.39	0.42	0.44

1,2-didehydronaphthalene with the naphthalene core can be formed in this case. Note also that more sophisticated pressure- and temperature-dependent RRKM calculations followed by solution of kinetic master equations will be required to evaluate the rate constants and product branching ratio under particular conditions of Titan's atmosphere. Under nonzero pressure, collisions may stabilize the **i1** adduct and especially 1-naphthyl radical **i3**, which represents one of the most stable local minima in the C₁₀H₇ system. Calculations of p, T -dependent rate constants and branching ratios is beyond the scope of the present paper, as our main goal here is to test the viability of the PAH growth mechanism from benzene to naphthalene core via barrierless ethynyl radical addition reactions. Note that in analogy with the ethynyl addition to the ortho position of the aromatic ring of C₆H₅C₂H, which is most likely to produce 1,2-diethynylbenzene, we can expect that meta and para additions will proceed by similar mechanisms and will form, after H elimination, 1,3- and 1,4-diethynylbenzenes, respectively. Since neither 1,3- and 1,4-diethynylbenzenes nor their C₁₀H₇ precursors can immediately form the naphthalene core, the details of these channels will not be further pursued here. Summarized, the reaction of ethynyl radicals with phenylacetylene can proceed via a barrierless addition, forming an intermediate **i1**. The latter was found to decompose predominantly to 1,2-diethynylbenzene plus atomic hydrogen.

(B) C₂H Addition to the α -Carbon of the C₂H Side Chain of Phenylacetylene. Now we consider an alternative entrance reaction channel where the ethynyl radical adds to the terminal carbon atom of the C₂H side chain (α -carbon atom) in phenylacetylene. The addition is barrierless and leads to the formation of intermediate **i4**, C₆H₅CCHCCH, with an exothermicity of 63.4 kcal/mol, as shown in Figure 2. This addition is analogous to the C₂H addition to acetylene or diacetylene and proceeds with similar energetics. For instance, ethynyl addition to acetylene gives a n -C₄H₃ radical with energy gains of 58.5 and 64.1 kcal/mol as calculated at the G2M(MP2) and CCSD(T)/

CBS levels of theory, respectively,^{56,57} whereas the C₂H addition to diacetylene produces HCCCHCCCH with exothermicities of 63.9 and 70.2 kcal/mol at the CCSD(T)/cc-pVTZ and CCSD(T)/CBS levels, respectively.⁵⁷ While the most accurate CCSD(T) calculations with extrapolation to the complete basis set (CBS) are too expensive computationally for the present system, we can expect that the C₆H₅C₂H + C₂H → **i4** reaction exothermicity should be in the range of 63–70 kcal/mol. The most favorable reaction scenarios for C₂H + C₂H₂ and C₂H + C₄H₂ following the barrierless formation of HCCCHCH and HCCCHCCCH adducts involve elimination of the central hydrogen atom, producing diacetylene and triacetylene, respectively. A similar mechanism is also favored for C₆H₅C₂H + C₂H; elimination of the hydrogen atom from the central carbon in the C₄ side chain gives phenyldiacetylene. The C₆H₅C₄H + H products reside 30.3 kcal/mol below the phenylacetylene plus ethynyl reactants; the barrier for the H loss is computed to be 37.9 and 4.8 kcal/mol in the forward and reverse directions, respectively, with the corresponding TS4-H positioned 25.5 kcal/mol below the reactants. One can see that unless **i4** can be collisionally stabilized, the C₆H₅C₂H + C₂H reaction can readily produce phenyldiacetylene in a barrierless fashion. Can the initial intermediate **i4** rearrange to a naphthalene core and will such rearrangement, if it exists, be competitive with the immediate hydrogen atom loss giving C₆H₅C₄H? As seen in Figure 2, we have found two pathways leading to the second ring closure. First, the ring closure occurs directly in **i4** to form a bicyclic structure **i5**, 9H-1,3-didehydronaphthalene. Intermediate **i5** lies 19.4 kcal/mol below the reactants and the ring formation barrier is 46.8 kcal/mol. Next, **i5** can lose the H atom from the 9-position, producing 1,3-didehydronaphthalene. The corresponding barrier at TS5-H is 12.2 kcal/mol relative to **i5** and

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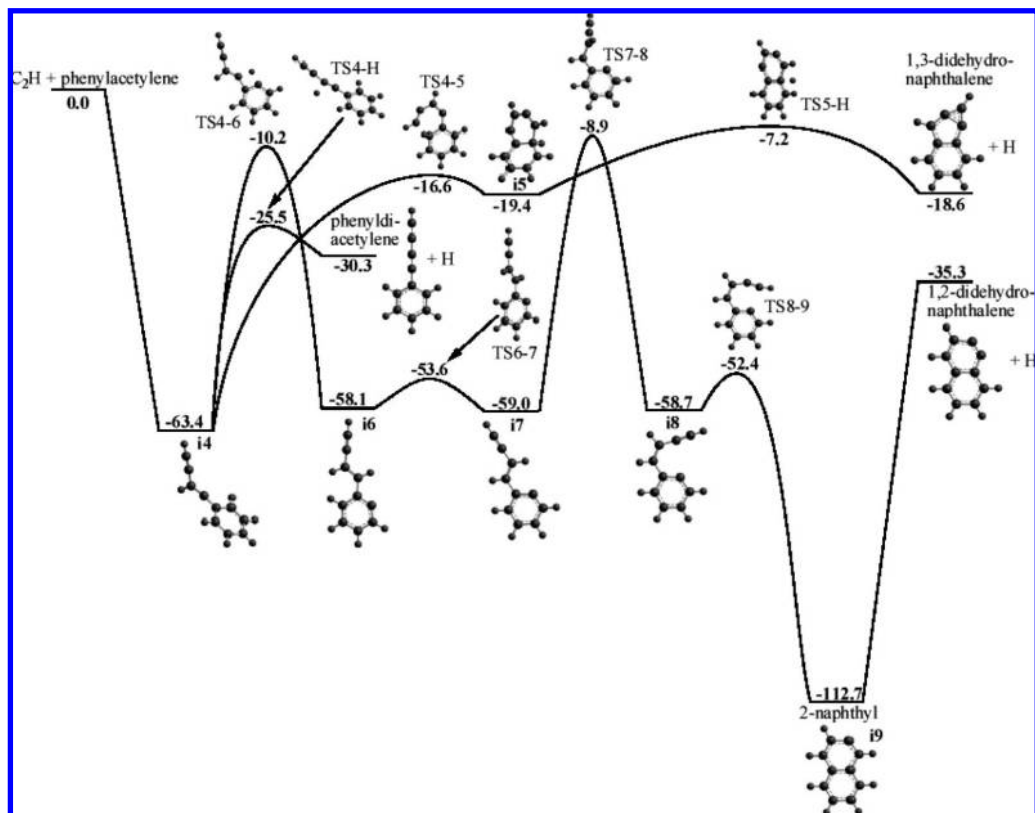


Figure 2. Potential energy diagram for the $C_2H + C_6H_5C_2H$ reaction: channels originating from C_2H addition to the terminal carbon atom in the C_2H group. All relative energies are calculated at the G3(MP2,CC)//B3LYP/6-311G** level and given in kilocalories per mole. Optimized geometries of all intermediates and transition states are also shown.

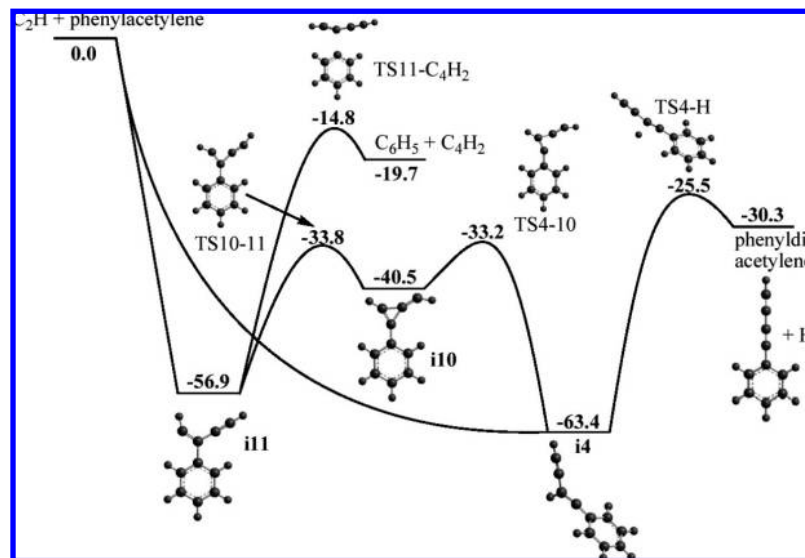


Figure 3. Potential energy diagram for the $C_2H + C_6H_5C_2H$ reaction: channels originating from C_2H addition to the middle carbon atom in the C_2H group. All relative energies are calculated at the G3(MP2,CC)//B3LYP/6-311G** level and given in kilocalories per mole. Optimized geometries of all intermediates and transition states are also shown.

the products are 18.6 kcal/mol exothermic relative to the reactants. The transition states TS4-5 and TS5-H for this two-step mechanism reside 16.6 and 7.2 kcal/mol, respectively, lower in energy than $C_6H_5C_2H + C_2H$, and hence the channel leading to 1,3-didehydronaphthalene is open even at zero collision energy. An alternative mechanism producing the 2-naphthyl radical involves hydrogen migration followed by rotations around single and double C–C bonds in the side chain and

completed by the ring closure. For instance, 1,3-H shift from the ortho position in ring of **i4** produces intermediate **i6**, $C_6H_5CHCHCCH$, lying 58.1 kcal/mol below the reactants via a barrier of 53.2 kcal/mol at TS4-6. Next, rotation around the single C_6H_5-C bond proceeding with a relatively low barrier of 4.5 kcal/mol gives another $C_6H_5CHCHCCH$ conformer **i7**. This is followed by rotation around the double $CH=CH$ bond leading to **i8**, but the barrier at the corresponding TS7-8 is high,

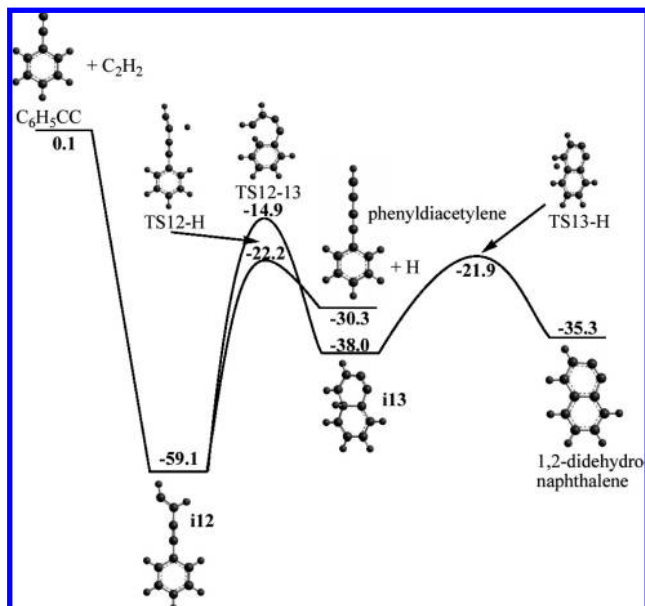


Figure 4. Potential energy diagram for the $C_2H_2 + C_6H_5CC$ reaction. All relative energies are calculated at the G3(MP2,CC)/B3LYP/6-311G** level and given in kilocalories per mole. Optimized geometries of all intermediates and transition states are also shown.

50.1 kcal/mol relative to **i7**. At the next step, **i8** undergoes ring closure to form 2-naphthyl radical **i9** via a small 6.3 kcal/mol barrier. 2-naphthyl **i9** is 112.7 kcal/mol more stable than the $C_6H_5C_2H + C_2H$ reactants and can be either collisionally stabilized or lose a hydrogen atom from the 1- or 3-position, producing 1,2- or 2,3-didehydronaphthalene with overall exothermicity of ~ 35 kcal/mol relative to the initial reactants and without an exit barrier. The highest in energy transition states on the pathway described above and resulting in the naphthalene core formation are TS4-6 and TS7-8. Both lie 10.2 and 8.9 kcal/mol lower in energy than the reactants, indicating that this channel is open in the phenylacetylene plus ethynyl reaction. TS7-8, corresponding to rotation around a double $C=C$ bond has a considerable biradical character and therefore its energy may not be accurately described by single-reference CCSD(T) calculations. However, T_1 diagnostic in the CCSD calculation for this transition state gives a value of only 0.018, indicating a rather moderate multireference character of the wave function, and therefore the CCSD(T) result should be reasonably reliable. Note also that another pathway leading from **i6** to **i8** and then to 2-naphthyl is also possible in which rotation around the double $CH=CH$ bond precedes rotation about the single C_6H_5-C bond. However, in this case the calculated rotational barrier around the double bond is even higher than that at TS7-8, and therefore this channel is not expected to be preferable.

Another reaction route illustrated in Figure 3 involves migration of the C_2H group over the double $C=C$ bond in the side chain via intermediate **i10** containing a three-membered carbon ring. Similar rearrangements were also found to be accessible for C_4H_3 and C_6H_3 adducts formed in ethynyl reactions with acetylene and diacetylene, respectively.^{56,57} **i10** is 22.9 kcal/mol less stable than **i4** but resides 40.5 kcal/mol below the reactants and, in principle, can be formed directly from them by barrierless addition of C_2H to the triple $C\equiv C$ bond of phenylacetylene. The C_2H migration leads to intermediate **i11**, 56.9 kcal/mol below the reactants, in which a C_4H_2 moiety is attached to the C_6H_5 ring through one of its two nonterminal carbon atoms. The transition states on the **i4** \rightarrow

i10 \rightarrow **i11** pathway, TS4-10 and TS10-11 both lie about 33 kcal/mol lower in energy than the reactants, making this rearrangement more favorable than the hydrogen atom loss, hydrogen atom migration, or ring closure in **i4**. Intermediate **i11** can decompose by the cleavage of the out-of-ring $C-C$ bond producing phenyl radical and diacetylene, 19.7 kcal/mol below $C_6H_5C_2H + C_2H$. The barrier for this decomposition channel is calculated to be 42.1 kcal/mol relative to **i11**, that is, 19.0 kcal/mol higher than the barrier for the reverse isomerization of **i11** to **i4** via **i10**. Thus, though the $C_6H_5 + C_4H_2$ channel with the critical TS11- C_4H_2 residing 14.8 kcal/mol lower in energy than the reactants is reachable, it is less favorable than the direct H loss from **i4**.

Summarizing ethynyl addition to the terminal carbon atom of the C_2H fragment in phenylacetylene, four competitive reaction routes are possible: (1) **i4** \rightarrow TS4-H \rightarrow phenyldiacetylene + H, (2) **i4** \rightarrow TS4-5 \rightarrow **i5** \rightarrow TS5-H \rightarrow 1,3-didehydronaphthalene + H, (3) **i4** \rightarrow TS4-6 \rightarrow **i6** \rightarrow TS6-7 \rightarrow **i7** \rightarrow TS7-8 \rightarrow **i8** \rightarrow TS8-9 \rightarrow **i9** \rightarrow 1,2- or 2,3-didehydronaphthalene + H, and (4) **i4** \rightarrow TS4-10 \rightarrow **i10** \rightarrow TS10-11 \rightarrow **i11** \rightarrow TS11- C_4H_2 \rightarrow $C_6H_5 + C_4H_2$. Although all four channels are open even at zero collision energy, the first one is clearly favorable energetically as its transition state TS4-H lies 11–18 kcal/mol lower than the highest in energy transition states for the other channels. To confirm this conclusion, we carried out RRKM calculations for the energized **i4** adduct, taking its internal energy as the energy of chemical activation in the $C_6H_5C_2H + C_2H$ reaction plus $E_{col} = 0-5$ kcal/mol. The results shown in Table 1 indicate that phenyldiacetylene should be the dominant reaction product, 89–90%, followed by phenyl + diacetylene, 10–11%, and only minuscule amounts ($\sim 0.1\%$) of didehydronaphthalene isomers can be produced.

(C) C_2H Addition to the β -Carbon of the C_2H Side Chain of Phenylacetylene. The remaining entrance channel of the $C_6H_5C_2H + C_2H$ reaction involves ethynyl addition to the middle carbon (β -carbon atom) of the C_2H side chain in phenylacetylene (Figure 3). In this case, the intermediate **i11**, $C_6H_5C(C_2H)CH$, is produced without a barrier and with energy gain of 56.9 kcal/mol. Neither a hydrogen atom elimination from any position in **i11** nor the synthesis of the naphthalene core by rearrangements in **i11** are favorable. Any H atom loss would result in the formation of a radical site on a terminal side-chain carbon atom or on the aromatic ring and therefore the resulting $C_{12}H_6$ product would have a biradical character. Hence, the only feasible dissociation mechanism is the rupture of the single $C-C$ bond between the ring and the side chain, producing phenyl radical and diacetylene. Alternatively, as seen in the previous section, **i11** can isomerize to **i4** by C_2H migration and then access the reaction channels described above. We carried out RRKM calculations for the same reaction scheme as in the previous section (Figures 2 and 3) but taking **i11** as the initial chemically activated intermediate. The computed product branching ratios appeared to be rather different if the reaction starts from **i11**; $C_6H_5 + C_4H_2$ that are formed directly from **i11** account for 76.5–79.5% of the total product yield, whereas the yield of phenyldiacetylene via a multistep mechanism is 23.5–20.5%. Again, the production of the naphthalene-core species is expected to be negligible.

In summary, the barrierless reaction of ethynyl radical with phenylacetylene can lead to a variety of $C_{12}H_6$ products depending on the site to which the C_2H addition takes place. Addition to the ortho, meta, and para positions in the aromatic ring should produce 1,2-, 1,3-, and 1,4-diethynylbenzenes,

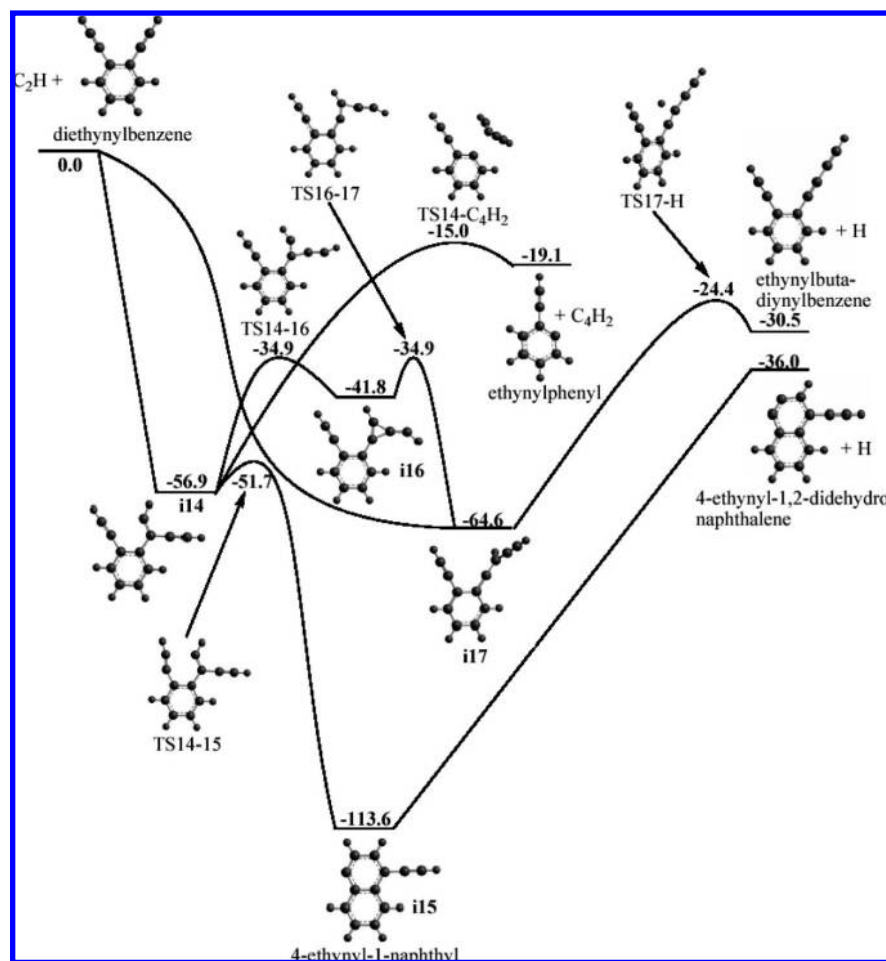


Figure 5. Potential energy diagram for the C₂H + 1,2-diethynylbenzene reaction: channels originating from C₂H addition to the C₂H side chain. All relative energies are calculated at the G3(MP2,CC)//B3LYP/6-311G** level and given in kilocalories per mole. Optimized geometries of all intermediates and transition states are also shown.

respectively, via H eliminations from the initial adducts. Addition to the terminal carbon of the C₂H side chain is most likely to yield phenyldiacetylene, whereas the ethynyl attachment to the middle C atom of the C₂H group is expected to result mostly in the C₆H₅ + C₄H₂ products. Only insignificant amounts of the products containing a naphthalene core, such as didehydronaphthalenes or naphthyl radicals (in case of collisional stabilization) can be produced at this stage.

C₆H₅CC + C₂H₂ Reaction. The reaction of the phenylethynyl radical (C₆H₅CC) with acetylene (C₂H₂) is isoelectronic to the reaction of ethynyl radicals with phenylacetylene. Therefore, we also consider this system here. A recent crossed molecular beam study by Kaiser's group⁵⁸ investigated the reaction of benzene with dicarbon molecules in their electronic ground X¹Σ_g⁺ and excited a³Π_u states and demonstrated that the phenylethynyl radical C₆H₅CC (X²A') is the major reaction product. On the basis of this result, it was suggested that C₆H₅CC can contribute to PAH growth from benzene (in particular, to formation of the naphthalene core) via its recombination with acetylene, followed by ring closure and hydrogen atom elimination, producing 1,2-didehydronaphthalene. This reaction could be an alternative to the reaction of the ethynylphenyl radical (C₆H₄C₂H) with acetylene, a well-

established route to 1-naphthyl in the HACA mechanism in combustion. Moreover, since C₆H₅CC is an analogue of ethynyl, it is likely to add to acetylene without an entrance barrier and with high exothermicity, making this reaction relevant to low-temperature conditions of the interstellar medium or Titan's atmosphere.

As seen in Figure 4, C₆H₅CC addition to acetylene is barrierless and proceeds with exothermicity of 59.1 kcal/mol to give intermediate **i12**, C₆H₅CCCHCH. The latter can eliminate the hydrogen atom from the β-CH group in the side chain to produce phenyldiacetylene, residing 30.3 kcal/mol below the C₆H₅CC + C₂H₂ reactants. The transition state for the hydrogen atom loss, TS12-H, lies 22.2 kcal/mol lower in energy than the reactants and the barrier is thus 36.9 kcal/mol relative to **i12**. Alternatively, the ring closure barrier in **i12** to produce 9H-1,2-didehydronaphthalene **i13** via TS12-13 is somewhat higher, 44.2 kcal/mol. At the next step, **i13** can lose the hydrogen atom in 9-position and form the 1,2-didehydronaphthalene product with the naphthalene core via a barrier of 16.1 kcal/mol, with the corresponding TS13-H lying 21.9 kcal/mol below phenylethynyl + acetylene. Interestingly, although the energy of C₆H₅CC + C₂H₂ is very close to that of C₆H₅C₂H + C₂H, the two reactions access different areas of the C₁₀H₇ PES. It seems that the **i12** intermediate could isomerize to **i14** by 1,2-H shift in the side chain; however, a careful search of corresponding transition states converges to

(58) Gu, X.; Guo, Y.; Zhang, F.; Mebel, A. M.; Kaiser, R. I. *Chem. Phys. Lett.* **2007**, *436*, 7.

transition states for H elimination from either **i12** or **i4**. This result indicates that the unimolecular **i12** \leftrightarrow **i4** rearrangement is unlikely and would not be competitive with hydrogen atom losses from **i12** or **i4**. Intermediate **i13** in principle can isomerize to **i5** (Figure 2) by a 1,2-H shift in the upper ring; however, this process exhibits a very high barrier with TS5-13 lying 48.3 kcal/mol above $C_6H_5C_2H + C_2H$, which effectively closes this reaction channel. Finally, on the basis of analogies with the $C_2H + C_4H_2 \rightarrow C_2H_2 + C_4H$ reaction, which features a direct hydrogen atom abstraction barrier of 9.0 kcal/mol,⁵⁷ and with $C_2H + C_6H_6 \rightarrow C_2H_2 + C_6H_5$, where no first-order saddle point was found,³⁵ we can also rule out the direct $C_2H + C_6H_5C_2H \rightarrow C_2H_2 + C_6H_5CC$ process, at least at low-temperature conditions.

We can see that the difference in barrier heights for the reaction channels involving hydrogen atom elimination, **i12** \rightarrow TS12-H $\rightarrow C_6H_5C_4H + H$, and formation of the naphthalene core, **i12** \rightarrow TS12-13 \rightarrow **i13** \rightarrow TS13-H \rightarrow 1,2-didehydronaphthalene + H, is only 7.3 kcal/mol. Nevertheless, according to RRKM calculations (Table 1), the formation of phenyldiacetylene remains the nearly exclusive reaction channel and only a trace amount of 1,2-didehydronaphthalene (0.04%) can be produced. This can be attributed to the entropic preference for the H loss in **i12** versus its cyclization; TS12-H possess three low real vibrational frequencies of 33, 70, and 77 cm^{-1} , whereas the lowest real frequencies for TS12-13 are 119, 160, and 246 cm^{-1} . Therefore, the number of states of TS12-H is significantly higher than for TS12-13, resulting in a large difference in the rate constants for the hydrogen atom loss and cyclization despite a moderate energy difference between the transition states.

Diethynylbenzene + Ethynyl Reaction. We have found so far that the reactions on the $C_{10}H_7$ PES, phenylacetylene + ethynyl and phenylethynyl + acetylene, can produce only insignificant amounts of molecules with the naphthalene core, namely, didehydronaphthalenes under single-collision conditions and naphthyl radicals under nonzero pressures. The major products of these reactions are expected to be non-PAH diethynylbenzenes, phenyldiacetylene, and phenyl radical. However, in this section we will demonstrate that the reaction of one of these major products, 1,2-diethynylbenzene, with another ethynyl radical leads predominantly to a naphthalene-core product. Consider the 1,2-diethynylbenzene plus ethynyl reaction, where the ethynyl radical adds to the β -carbon atom of a C_2H side chain (Figure 5). This addition does not exhibit any entrance barrier and produces intermediate **i14** with an energy gain of 56.9 kcal/mol. **i14** possesses the aromatic ring with two adjacent side chains, C_2H and $C(C_2H)CH$. The further fate of the initial adduct can be 3-fold. It can either lose the $C(C_2H)CH$ side chain producing ethynylphenyl radical and diacetylene, undergo ring closure to form 4-ethynyl-1-naphthyl radical **i15**, or depict C_2H migration over the side-chain $C=C$ bond to produce **i17** via a three-membered ring isomer **i16**, with **i17** further eliminating the middle H atom in the side chain and giving rise to 1-ethynyl-2-butadiynylbenzene. In this case, the ring closure is clearly preferable as it features a barrier of only 5.2 kcal/mol versus 41.9 kcal/mol for the C_4H_2 loss, 22.0 kcal/mol for C_2H migration, and 32.5 kcal/mol (relative to **i14**) for a hydrogen atom elimination from **i17**. **i15** lies in a very deep potential well of 113.6 kcal/mol relative to the reactants and therefore can be easily stabilized collisionally. Under single-collision conditions, 4-ethynyl-1-naphthyl would lose a hydrogen atom from 2-position to form another naphthalene-core molecule, 4-ethynyl-1,2-didehydronaphthalene, lying 36.0 kcal/mol

below the reactants. The intermediate **i17** can be formed directly in the ethynyl + 1,2-diethynylbenzene reaction by ethynyl addition to an α side-chain carbon. Then it can either lose the H atom or isomerize to **i14** by C_2H migration and then undergo ring closure to 4-ethynyl-1-naphthyl radical **i15**. A reaction pathway involving four-membered ring closure in **i14** followed by C_2H elimination was not found.

Therefore, we carried out RRKM calculations considering **i14** and **i17** as the initial energized intermediates. In the case of **i14** formation, the reaction channel leading to the naphthalene-core species, 4-ethynyl-1,2-didehydronaphthalene via 4-ethynyl-1-naphthyl radical, is dominant (97–98%), and only small amounts of $C_8H_5 + C_4H_2$ (0.3–0.4%) and $C_6H_4(C_2H)(C_4H) + H$ (1.9–2.6%) can be produced. If **i17** is formed first, the hydrogen atom elimination and ethynyl migration channel followed by the naphthalene core synthesis are competitive, with their branching ratios calculated to be in the range of 44–48% and 52–56%, respectively (Table 1). Clearly, C_2H addition to a side-chain carbon in 1,2-diethynylbenzene appears to be a very efficient route to form the second aromatic ring.

Other ethynyl additions are not expected to result in PAH formation immediately (Figure 6). If ethynyl radical attaches to a ring carbon of diethynylbenzenes, considering the analogy with the $C_6H_5C_2H + C_2H$ reaction, the products are expected to be 1,2,3-, 1,2,4-, or 1,3,5-triethynylbenzenes. The attack of ethynyl radicals to a side chain of 1,3- or 1,4-diethynylbenzenes should result in nonpolycyclic 1-ethynyl-3-butadiynylbenzene or 1-ethynyl-4-butadiynylbenzene, respectively, or ethynylphenyl radicals plus diacetylene. The reactions of phenyldiacetylene with ethynyl (Figure 7) are expected to produce phenyltriacetylene plus a hydrogen atom (addition to C_1 or C_2), $C_8H_5CC + C_4H_2$ (addition to C_2 or C_1), or ethynylbutadiynyl isomers (addition to the ring carbons). C_2H addition to the C_3 or C_4 atoms would produce $C_6H_5 + C_6H_2$ because, on the contrary to facile C_2H migration over a triple $C\equiv C$ bond in polyene, the migration over a single $C-C$ bond was shown to be forbidden due to a high barrier.⁵⁷ However, if a product formed after two sequential ethynyl additions to phenylacetylene features a C_2H group in combination with another C_2H or C_4H side chain in the ortho position (see 1,2,3- and 1,2,4-triethynylbenzenes or 1-ethynyl-2-butadiynylbenzene), a third addition of an extra C_2H followed by ring closure can easily lead to the formation of the naphthalene core. For instance, as illustrated in Figure 8, the 1,2,3-triethynylbenzene + C_2H reaction can produce 4,5-diethynyl-1-naphthyl radical; 1,2,4-triethynylbenzene + C_2H can give 4,6-diethynyl-1-naphthyl or 4,7-diethynyl-1-naphthyl; and 1-ethynyl-2-butadiynyl + C_2H can form 3,4-diethynyl-1-naphthyl or 2,4-diethynyl-1-naphthyl. If the naphthyl radicals cannot be collisionally stabilized, they would lose another H atom in the 2-position (or the C_2H group in 2,4-diethynyl-1-naphthyl) to produce ethynyl-substituted 1,2-didehydronaphthalenes. Meanwhile, if H atoms are available, they can react with the didehydronaphthalenes and naphthyl radicals without barriers, giving rise to substituted naphthalene molecules, and thus the synthesis of the smallest PAH molecule will be achieved.

Probabilities of PAH Growth from Phenylacetylene. On the basis of analogy with the $C_2H + C_6H_6$, $C_2H + C_2H_2$, and $C_2H + C_4H_2$ reactions, one can expect that ethynyl additions to phenylacetylene, di- and triethynylbenzenes, and ethynylbutadiynylbenzenes should be fast even at very low temperatures, with rate constants in the range of $(1.0-5.0) \times 10^{-10} cm^3$

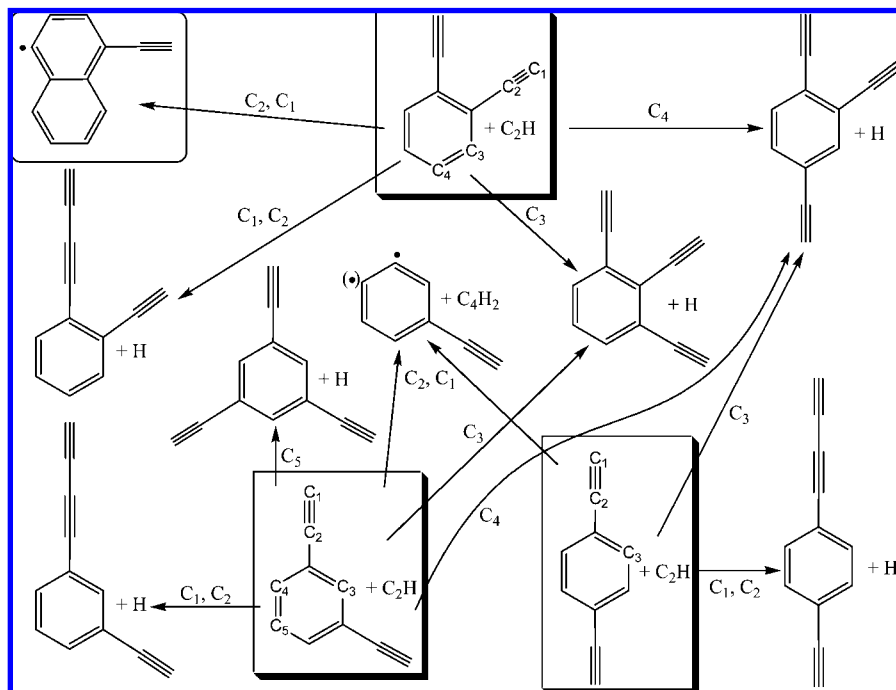


Figure 6. Schematic representation of possible outcomes for the reactions of C_2H with 1,2-, 1,3-, and 1,4-diethynylbenzenes. Carbon atoms shown on arrows indicate the direction of initial C_2H additions.

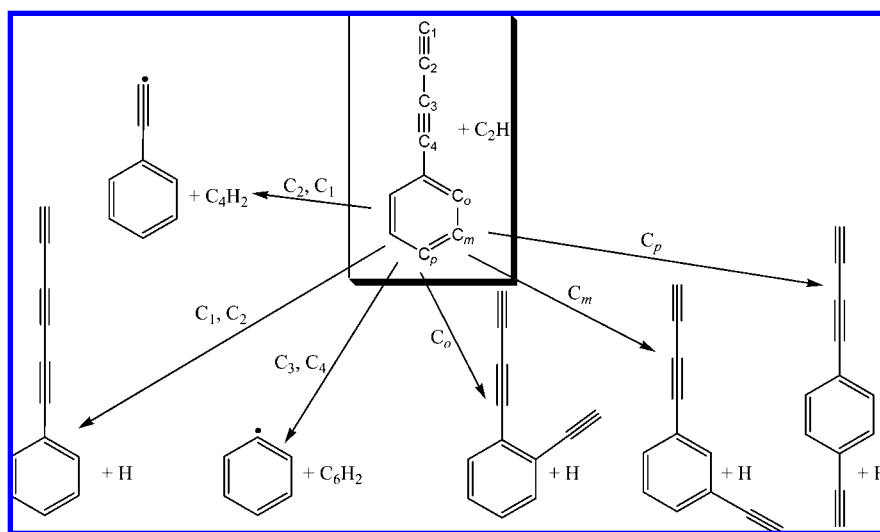


Figure 7. Schematic representation of possible outcomes for the reactions of C_2H with phenyldiacetylene. Carbon atoms shown on arrows indicate the direction of initial C_2H additions.

molecule⁻¹ s⁻¹ at 60–298 K.^{35,36,57,59} However, as seen from the discussion in the previous sections, not every reactive collision of the ethynyl radical with these molecules would result in naphthalene core formation and thus contribute to the PAH growth; a variety of nonpolycyclic products can also be formed. Assuming that ethynyl addition is roughly equally probable to every carbon atom in $C_6H_5C_2H$, $C_6H_4(C_2H)_2$, $C_6H_3(C_2H)_3$, and $C_6H_4(C_2H)(C_4H)$, we can estimate the probabilities of the naphthalene synthesis via two or three consecutive ethynyl additions to phenylacetylene. Consider the $C_2H + C_6H_5C_2H$ reaction first. It does not lead to immediate PAH formation, and the only product that can lead to naphthalene (or rather to

naphthyl radical or didehydronaphthalene) at the next C_2H addition step is 1,2-diethynylbenzene. The formation of the latter is accomplished if C_2H adds to the ortho-carbons in the ring, and therefore the probability of producing 1,2-diethynylbenzene is $2/8 = 0.25$ (two out of eight carbon atoms in phenylacetylene are in the ortho position). Note that the ring carbon atom linked to the C_2H group has to be counted also; C_2H addition to this atom is expected to restore the initial reactants. Next, C_2H addition to C_2 -type atoms in 1,2-diethynylbenzene (2 out of 10, probability 0.2; see Figure 6) will produce the naphthalene core with a relative yield of 98% (see Table 1; for simplicity we take the values corresponding to $E_{col} = 0$). Alternatively, C_2H addition to the C_1 atoms in 1,2-diethynylbenzene (probability 0.2) will give the naphthalene core with a relative yield of 56%.

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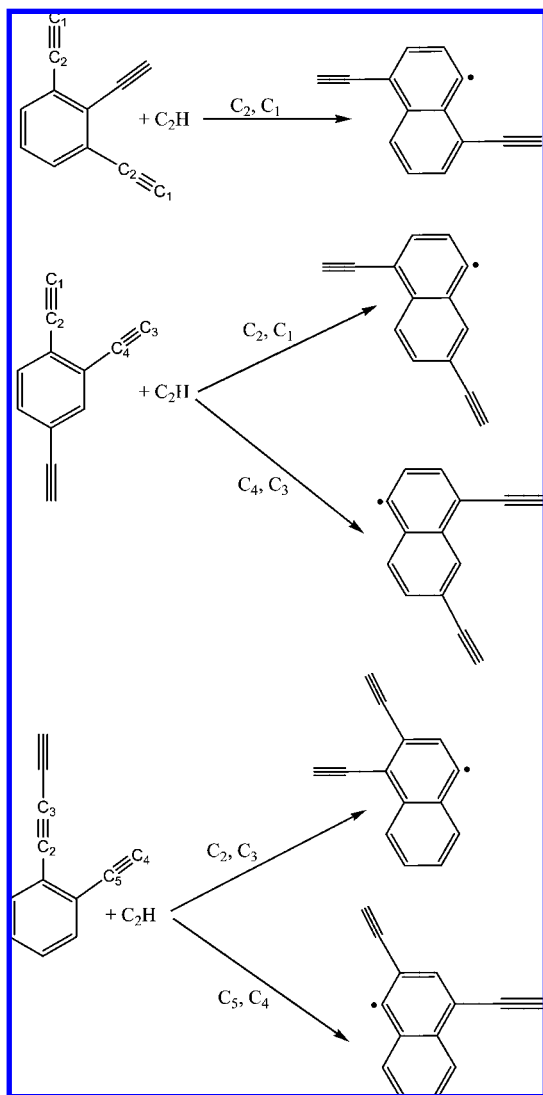


Figure 8. Possible mechanisms for the formation of substituted naphthyl radicals in the reactions of C_2H with 1,2,3- and 1,2,4-triethynylbenzenes and 1-ethynyl-2-butadiynylbenzene.

Therefore, the overall probability of naphthalene formation after two consecutive C_2H additions to $C_6H_5C_2H$ is $0.25[(0.2)(0.98) + (0.2)(0.56)] = 7.7\%$.

Next, we consider the reaction sequence including three C_2H additions starting from phenylacetylene. As seen in Figure 8, the species that can contribute to naphthalene core formation at the last step are 1-ethynyl-2-butadiynylbenzene and 1,2,3- and 1,2,4-triethynylbenzenes. 1-Ethynyl-2-butadiynylbenzene can be produced on the preceding step from 1,2-diethynylbenzene with the probability of $0.25[(0.2)(0.02) + (0.2)(0.44)] = 2.3\%$; here we took into account that the branching ratios of the $C_6H_4(C_2H)(C_4H)$ product are 0.02 and 0.44, respectively, when C_2H adds to C_2 and C_1 atoms of 1,2-diethynylbenzene (Table 1). Another potential precursor of 1-ethynyl-2-butadiynylbenzene is phenyldiacetylene. This molecule can be formed in the first $C_2H + C_6H_5C_2H$ reaction when ethynyl adds to the α -C atom of the C_2H group ($1/8$) with a relative yield ~ 0.9 (Table 1, for $E_{col} = 0$) or to the middle C in C_2H ($1/8$) with a relative yield of 0.23. Thus, the probability to form phenyldiacetylene at the initial step is 0.14. When $C_6H_5C_4H$ reacts with C_2H , it can produce 1-ethynyl-2-butadiynylbenzene only if ethynyl attacks ortho-C atoms ($2/10$, see Figure 7). Therefore,

the probability to form 1-ethynyl-2-butadiynylbenzene in this sequence is $(0.14)(0.2) = 3.8\%$ and the overall probability to produce this molecule after two C_2H additions is $2.3\% + 3.8\% = 6.1\%$. Finally, naphthalene can be formed if C_2H adds to C_2 or C_5 ($2/12$) with a relative yield of 0.98 and to C_3 or C_4 ($2/12$) with a relative yield of 0.56. Hence, the overall probability to synthesize naphthalene in three C_2H additions steps via 1-ethynyl-2-butadiynylbenzene is $0.061[(0.167)(0.98) + (0.167)(0.56)] = 1.57\%$.

Now take 1,2,3-triethynylbenzene as a naphthalene precursor at the third C_2H addition step. It can be formed from 1,2-diethynylbenzene with probability of $(0.25)(0.2) = 0.05$ (addition to C_3 , Figure 6) or from 1,3-diethynylbenzene with probability of $(0.25)(0.1) = 0.025$ (addition to C_3). Thus, the overall probability to form 1,2,3-triethynylbenzene after two steps is 7.5%. C_2H addition to C_2 atoms in 1,2,3-triethynylbenzene ($2/12$) will produce the naphthalene core with a relative yield of 0.98, and the addition to C_1 ($2/12$) will give a PAH product with a relative yield of 0.56. Therefore, the total probability to form naphthalene in three steps via 1,2,3-triethynylbenzene is $0.075[(0.167)(0.98) + (0.167)(0.56)] = 1.9\%$. Finally, consider 1,2,4-triethynylbenzene. It can be produced from 1,2-diethynylbenzene [probability $(0.25)(0.2) = 0.05$, addition to C_4], 1,3-diethynylbenzene [$(0.25)(0.2) = 0.05$, C_4], and 1,4-diethynylbenzene [$(1/8)(0.4) = 0.05$, C_3], with the overall probability being 0.15. At the final step, addition to C_2 or C_4 and to C_1 or C_3 will give naphthalene with probabilities of $(2/12)(0.98)$ and $(2/12)(0.56)$, respectively. Then, the total probability to form naphthalene via 1,2,4-triethynylbenzene is $0.15[(0.167)(0.98) + (0.167)(0.56)] = 3.85\%$. The overall probability to achieve a PAH product in three C_2H addition steps starting from phenylacetylene is 7.32% and to do so in either two or three steps is $\sim 15\%$. Although the above consideration is only qualitative, it clearly demonstrates that a significant fraction of the products formed by consecutive C_2H additions to benzene, phenylacetylene, and so on, will possess the naphthalene core, and therefore this mechanism is a viable route for PAH growth. Molecular dynamics calculations with a mixture of benzene molecules and ethynyl radicals should be able to provide more quantitative results; however, potential energy functions used for such calculations need to be able to reproduce the main features of the ab initio potentials and to correctly describe the mechanism of elementary ethynyl addition reactions.

Conclusions

High-level ab initio G3//B3LYP calculations of the $C_{10}H_7$ and $C_{12}H_7$ potential energy surfaces demonstrate that the naphthalene core can be readily synthesized by the ethynyl addition mechanism starting from benzene via the following route: $C_2H + C_6H_6 \rightarrow C_6H_5C_2H$ (phenylacetylene) + H, $C_6H_5C_2H + C_2H \rightarrow$ 1,2-diethynylbenzene + H (addition to the ortho-carbons in the ring), and 1,2-diethynylbenzene + $C_2H \rightarrow$ 4-ethynyl-1-naphthyl radical or 4-ethynyl-1,2-didehydronaphthalene + H (addition to side-chain carbon atoms). This mechanism can also be extrapolated to the three-step C_2H addition routes starting from phenylacetylene: (I) $C_6H_5C_2H + C_2H \rightarrow$ 1,2-diethynylbenzene + H/1,3-diethynylbenzene + H (addition to meta-C atoms)/1,4-diethynylbenzene + H (addition to the para-C atoms)/phenyldiacetylene + H (addition to the side chain); (II) 1,2-diethynylbenzene + $C_2H \rightarrow$ 1,2,3-triethynylbenzene + H/1,2,4-triethynylbenzene + H/1-ethynyl-2-butadiynylbenzene + H, or 1,3-diethynylbenzene + $C_2H \rightarrow$

1,2,3-triethynylbenzene + H/1,2,4-triethynylbenzene + H, or 1,4-diethynylbenzene + C₂H → 1,2,4-triethynylbenzene + H, or phenylacetylene + C₂H → 1-ethynyl-2-butadiynylbenzene + H; and (III) 1,2,3-triethynylbenzene + C₂H → 4,5-diethynyl-1-naphthyl radical/4,5-diethynyl-1,2-didehydronaphthalene + H, or 1,2,4-triethynylbenzene + C₂H → 4,6-diethynyl-1-naphthyl/4,6-diethynyl-1,2-didehydronaphthalene + H/4,7-diethynyl-1-naphthyl/4,7-diethynyl-1,2-didehydronaphthalene + H, or 1-ethynyl-2-butadiynylbenzene + C₂H → 3,4-diethynyl-1-naphthyl/3,4-diethynyl-1,2-didehydronaphthalene + H/2,4-diethynyl-1-naphthyl/4-ethynyl-1,2-didehydronaphthalene + C₂H. Since the ethynyl radical reacts with benzene, phenylacetylene, and 1,2-diethynylbenzene without a barrier and with high exothermicity, and all subsequent transition states, intermediates, and products lie significantly lower in energy than the initial reactants, the ethynyl addition reaction sequence should be fast, with rate constants on the order of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, even at very low temperatures under conditions of the interstellar medium or planetary atmospheres, such as on Titan. The driving force of this mechanism is the presence of ethynyl radicals, which can be formed by photodissociation of acetylene below 217 nm light.^{60,61} If hydrogen atoms are also available, the substituted naphthyl radicals and didehydronaphthalenes can

recombine with them without barriers and produce substituted naphthalenes, which can be stabilized by a three-body reaction at higher pressures; these reactions should also be fast at low temperatures.

Summarized, the ethynyl addition mechanism (EAM) should be a viable alternative of the hydrogen-abstraction–C₂H₂-addition (HACA) sequences for PAH growth under low-temperature conditions if the photoinduced formation of ethynyl radicals is possible. Consequently, we anticipate this mechanism to be of great importance to form PAHs and related structures in the interstellar medium and also in hydrocarbon-rich, low-temperature atmospheres of planets and their moons such as Titan. If the final ethynyl addition to 1,2-diethynylbenzene can be replaced by a barrierless addition of the cyano (CN) radical, this newly proposed mechanism can even lead to the formation of cyano-substituted naphthalene cores in the interstellar medium and in planetary atmospheres.

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Supporting Information Available: Full references 51 and 52. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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