

An Aromatic Universe—A Physical Chemistry Perspective

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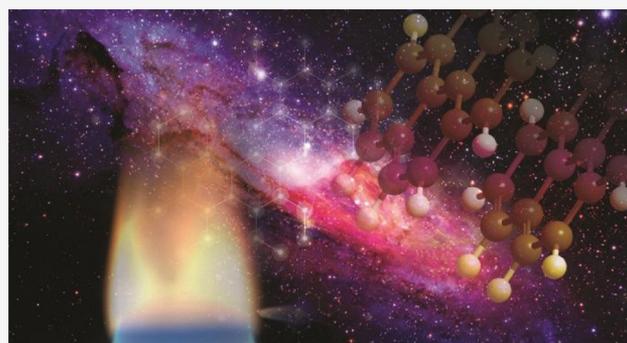
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ABSTRACT: This Perspective presents recent advances in our knowledge of the fundamental elementary mechanisms involved in the low- and high-temperature molecular mass growth processes to polycyclic aromatic hydrocarbons in combustion systems and in extraterrestrial environments (hydrocarbon-rich atmospheres of planets and their moons, cold molecular clouds, circumstellar envelopes). Molecular beam studies combined with electronic structure calculations extracted five key elementary mechanisms: Hydrogen Abstraction–Acetylene Addition, Hydrogen Abstraction–Vinylacetylene Addition, Phenyl Addition–DehydroCyclization, Radical–Radical Reactions, and Methylidyne Addition–Cyclization–Aromatization. These studies, summarized here, provide compelling evidence that key classes of aromatic molecules can be synthesized in extreme environments covering low temperatures in molecular clouds (10 K) and hydrocarbon-rich atmospheres of planets and their moons (35–150 K) to high-temperature environments like circumstellar envelopes of carbon-rich Asymptotic Giant Branch Stars stars and combustion systems at temperatures above 1400 K thus shedding light on the aromatic universe we live in.



1. INTRODUCTION

Ever since the postulation of polycyclic aromatic hydrocarbons (PAHs) together with their (partially) (de)hydrogenated, substituted, and ionized counterparts as the missing link between small carbon clusters, fullerenes, and carbonaceous nanoparticles (interstellar grains, soot particles),^{1,2} an intimate understanding of their fundamental formation mechanisms in the interstellar medium (ISM), in hydrocarbon-rich atmospheres of planets and their moons, in combustion systems, and in material sciences has been sought from the physical chemistry, astrochemistry, planetary science, and combustion science communities.^{3–8} PAHs are defined as a class of hydrocarbons, that is, organic compounds that contain only carbon and hydrogen, composed of multiple, often fused aromatic rings in which the π -electrons are delocalized. Naphthalene ($C_{10}H_8$) as well as indene (C_9H_8) represent the simplest members of two-ring aromatics with a six- and five-membered ring fused to a benzene moiety.

The presence of PAHs along with their methylated counterparts has been established in carbonaceous chondrites such as Allende.⁹ Laser desorption–laser multiphoton ionization mass spectrometry (L^2MS) along with D/H and $^{13}C/^{12}C$ isotopic analyses of meteoritic PAHs expose that these aromatics belong to a population of PAHs synthesized in circumstellar envelopes of carbon-rich Asymptotic Giant Branch Stars (AGB) and planetary nebulae as the descendants of AGB stars via high-temperature molecular mass growth

processes.¹⁰ These surveys propose that PAHs may encompass up to 20% of the galactic carbon budget and act as a link between resonantly stabilized free radicals (RSFRs) like propargyl ($C_3H_3\cdot$), aromatic radicals (ARs) such as phenyl ($C_6H_5\cdot$; **1**), and carbonaceous nanoparticles.¹¹ However, astrochemical models of PAH formation suggest time scales for the injection of PAHs from carbon stars into the interstellar medium of a few 10^9 years;¹² this is much longer than the predicted lifetimes of PAHs of only a few 10^8 years with interstellar PAHs rapidly destroyed by photolysis, galactic cosmic rays, and interstellar shocks.¹³ Nevertheless, the astronomical observation of interstellar PAHs along with their derivatives via the diffuse interstellar bands (DIBs), that is, discrete absorption features overlaid on the interstellar extinction curve from the blue part of the visible (400 nm) to the near-infrared (1.2 μm),¹⁴ and through unidentified infrared (UIR) emission bands in the 3–14 μm wavelength range ($3333\text{--}715\text{ cm}^{-1}$)¹⁵ implies critical, hitherto unexplained routes to their rapid chemical growth in low-temperature interstellar environments.

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These low-temperature routes to aromatic molecules are also of critical importance to explain the presence of PAHs in the hydrocarbon-rich atmospheres of planets and their moons such as Jupiter, Saturn, Titan, and Pluto. The Cassini–Huygens mission to Saturn’s moon Titan revealed that PAHs—besides polyacetylenes and polycyanoacetylenes—may dominate the organic carbon budget of Titan’s orange-brownish aerosol-based haze layers. The presence of PAHs in Titan’s atmosphere has been inferred from Cassini’s Visual and Infrared Mapping Spectrometer (VIMS) attributing the 3.28 μm ($3,049\text{ cm}^{-1}$) absorption to stratospheric PAHs.¹⁶ Likewise, Cassini’s Plasma Spectrometer detected heavy positively ($<350\text{ Da}$) and negatively ($<8000\text{ Da}$) charged particles, which have been suggested to contain aromatic molecules¹⁷ possibly formed via molecular mass growth processes of atmospheric benzene (C_6H_6) and phenyl radicals ($\text{C}_6\text{H}_5\cdot$; **1**) as benzene’s photolysis product. However, similar to circumstellar and interstellar environments, there is a lack of understanding of the molecular mechanisms that initiate and drive the formation of PAHs in Titan’s low-temperature atmosphere (70–180 K).

On Earth, PAHs arise from natural and anthropogenic sources and are commonly detected in the environment. The major source of PAHs in the environment has been identified as pyrogenic, that is, incomplete natural and anthropogenic combustion processes.¹⁸ These PAH byproducts of incomplete combustion processes are toxic and considered as severe environmental, often carcinogenic pollutants. Pericondensed PAHs, which consist of six-membered fused benzenoid rings, are known to survive high temperatures of combustion environments of above 2000 K. Compared to these pyrogenic PAHs, petrogenic PAHs, which are ubiquitous in oil seepages and the erosion of petroliferous shales, contain more five-membered ring structures.

The fundamental mechanisms leading to aromatic structures are also of interest to the organic chemistry community and are linked to material sciences, as they provide insight into reactivity, bond-breaking processes, and the synthesis of extended π -conjugated systems involving acyclic precursors with extensive applications as building blocks for molecular wires, carbon nanotubes, and graphene.^{19,20} For example, for fullerenes, the nonplanar corannulene molecule ($\text{C}_{20}\text{H}_{10}$), a pentagon surrounded by five hexagons, was identified as a molecular building block in combustion flames that should form fullerenes by pyrolysis. However, as with PAH and soot formation in flames, the mechanisms by which these nanomaterials nucleate and grow remain unclear, although high-level commonalities reveal the importance of the gas phase for the growth chemistry²¹ and the nucleation followed by mass growth through coalescence and coagulations and surface reactions.²²

Although more than half a century has passed, until very recently, mechanisms leading to aromatic molecules in extreme environments have been mainly conjectured from the identification of (precursors to) aromatic species in laboratory-scale model flames,^{23–26} high-temperature combustion models, and through hypothetical ion–molecule-dominated inter- and circumstellar networks.²⁷ While the communities converge that bottom-up molecular mass growth processes to PAHs and eventually to carbonaceous nanoparticles exist, the true nature of these elementary reactions has been only sparsely charted, since multiple mechanisms operate simultaneously in extraterrestrial and combustion environments.

Therefore, this complexity requires a systematic elucidation of the fundamental, elementary reactions involved in the formation of PAHs through well-defined molecular beam studies. These experiments are conducted either under single-collision conditions as provided in crossed molecular beam experiments^{7,28} or in pyrolytic microreactors under very dilute conditions.²⁹ Furthermore, flame-sampling molecular-beam studies can provide immediate insights into PAH formation kinetics.

The overarching goal of this Perspective is to shed light on the aromatic universe we live in. We bring together emerging concepts of low- and high-temperature aromatization reactions via neutral–neutral collisions from monocyclic systems to PAHs. It compiles developing trends on the formation and molecular growth processes of PAHs via five elementary mechanisms made available by new molecular beam studies combined with high-level electronic structure calculations (for details of these calculations, we refer the reader to the original literature): Hydrogen Abstraction– C_2H_2 (acetylene) Addition (HACA),^{30–33} Hydrogen Abstraction–Vinylacetylene Addition (HAVA),^{1,3,7,28,29,34–38} Phenyl Addition–DehydroCyclization (PAC),³⁹ Radical–Radical Reactions (RRR),⁴⁰ and Methylidyne Addition–Cyclization–Aromatization (MACA).⁴¹ The experimental and computational verification of these reaction networks provides a constrained framework of PAH formation chemistry in extreme environments from low temperatures in molecular clouds (10 K) and hydrocarbon-rich atmospheres of planets and their moons (35–150 K) to high-temperature environments like circumstellar envelopes of carbon-rich AGB stars and combustion systems at a few 1000 K.

2. MOLECULAR MASS GROWTH MECHANISMS

2.1. Hydrogen Abstraction–Acetylene Addition (HACA). Initially proposed by Frenklach and Wang in 1991 for high-temperature combustion systems and circumstellar envelopes of dying carbon-rich AGB stars like IRC+10216 ($<2500\text{ K}$), the HACA mechanism involves a repetitive reaction sequence of an abstraction of a hydrogen atom from the reacting aromatic hydrocarbon (ArH) by a hydrogen atom followed by an addition of an acetylene molecule (C_2H_2) to the radical site with $\text{Ar}\cdot$ being an aromatic radical.⁴² The following sequences of hydrogen abstraction, internal hydrogen transfer, acetylene addition, and stabilization through hydrogen atom losses are controversially discussed in the literature. Also, flame models are plagued by an overwhelming number of possible reaction pathways, and it is complicated to ascertain from which reactants distinct PAHs are formed. Therefore, detailed mechanistical studies are imperative to define the role of HACA in the formation mechanisms leading to PAHs.

Starting with benzene (C_6H_6), HACA leads first to the phenyl radical ($\text{C}_6\text{H}_5\cdot$; **1**) via hydrogen abstraction (Figure 1a).³ Molecular beam experiments coupled with electronic structure calculations revealed that the phenyl radical (**1**) may add to the carbon–carbon triple bond of acetylene forming the styrenyl radical ($\text{C}_6\text{H}_5\text{HCCH}\cdot$; **2**) as the central reaction intermediate via a barrier of 15 kJ mol^{-1} (Figure 1a). The latter can either lose a hydrogen atom forming phenylacetylene ($\text{C}_6\text{H}_5\text{CCH}$) or isomerize via a hydrogen shift to the ortho-vinylphenyl radical ($\text{C}_6\text{H}_4\text{C}_2\text{H}_3\cdot$; **3**). Chemical microreactor and computational studies revealed that both **2** and **3** may add an acetylene molecule via barriers of 24 and 17 kJ mol^{-1} to

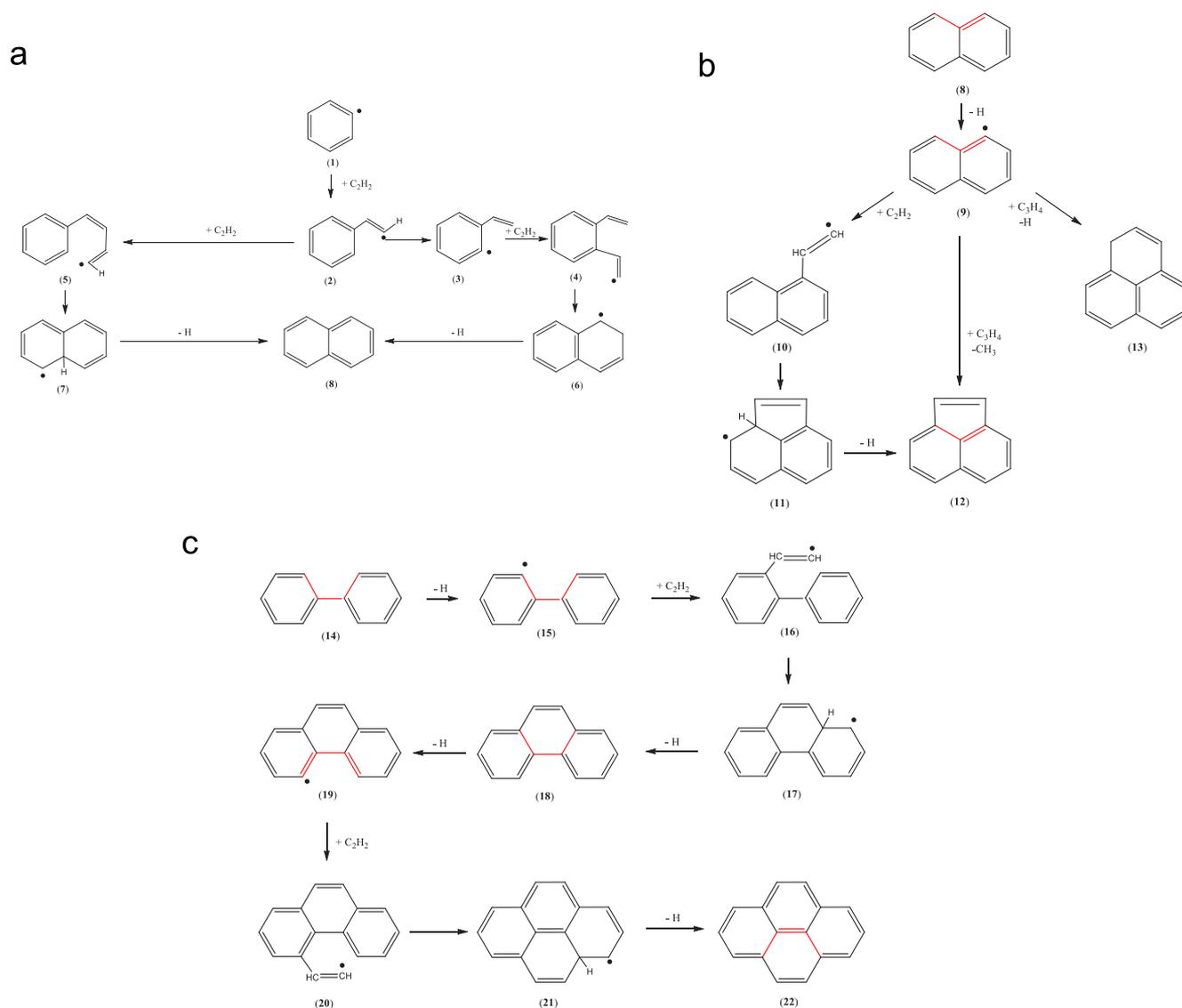


Figure 1. (a) Key routes leading to naphthalene ($C_{10}H_8$; **8**) via a [2 + 2 + 2] ring annulation through the HACA mechanism. (b) Key routes leading to acenaphthylene ($C_{12}H_8$; **12**) and 1H-phenalene ($C_{13}H_{10}$; **13**) via [3 + 2] and [3 + 3] bay closure through the HACA mechanism. The carbon skeleton in red indicates the three-carbon-bay moiety in the reactant and products. (c) Key routes leading to phenanthrene ($C_{14}H_{10}$; **18**) and pyrene ($C_{16}H_{10}$; **22**) via [4 + 2] bay closure through the HACA mechanism. The carbon skeleton in red indicates the four-carbon-bay moiety in the reactant and products.

yield resonantly stabilized collision complexes **4** and **5**, respectively. These complexes undergo ring closure to **6** and **7** followed by hydrogen loss, aromatization, and formation of naphthalene ($C_{10}H_8$; **8**)—the simplest PAH carrying two six-membered rings.^{30,31} Although the aforementioned molecular beam studies did not allow to distinguish between these two different pathways, this work provided evidence that molecular mass growth processes involving the HACA reaction sequence effectively lead, via a ring annulation of an aromatic phenyl radical (C_6H_5 ; **1**), to naphthalene ($C_{10}H_8$; **8**) (Figure 1a).

However, the general applicability of HACA has come under scrutiny. After a formation of naphthalene ($C_{10}H_8$; **8**), HACA sequences have been proposed to continue through hydrogen atom abstractions from the naphthalene leading to anthracene and phenanthrene ($C_{14}H_{10}$). Nevertheless, comprehensive electronic structure calculations and molecular beam studies demonstrated that, upon formation of the 1-naphthyl radical ($C_{10}H_7$; **9**), addition of acetylene (C_2H_2) would form a

$C_{12}H_9$ intermediate **10**, which undergoes a rapid cyclization by bay closure forming the five-membered intermediate **11** followed by an atomic hydrogen loss to acenaphthylene ($C_{12}H_8$; **12**).⁴³ This ring-closure process is much faster than the addition of a second acetylene molecule to **10** followed by the cyclization, hydrogen loss, and formation of a third aromatic ring: anthracene and/or phenanthrene ($C_{14}H_{10}$). Data from combustion flames also reveal that HACA only accounts for up to 6% of phenanthrene and anthracene at combustion-relevant temperatures from 1000 to 2000 K.⁴⁴ Recent chemical microreactor studies exploiting an isomer-selective identification of the products of reaction of the 1-naphthyl radical ($C_{10}H_7$; **9**) with acetylene deliver solid experimental evidence that acenaphthylene ($C_{12}H_8$; **12**) represents the major reaction product with no formation of the previously postulated tricyclic PAHs phenanthrene and anthracene ($C_{14}H_{10}$).⁴⁵ It shall be noted that acenaphthylene ($C_{12}H_8$; **12**) is also accessible via the reaction of the 1-naphthyl

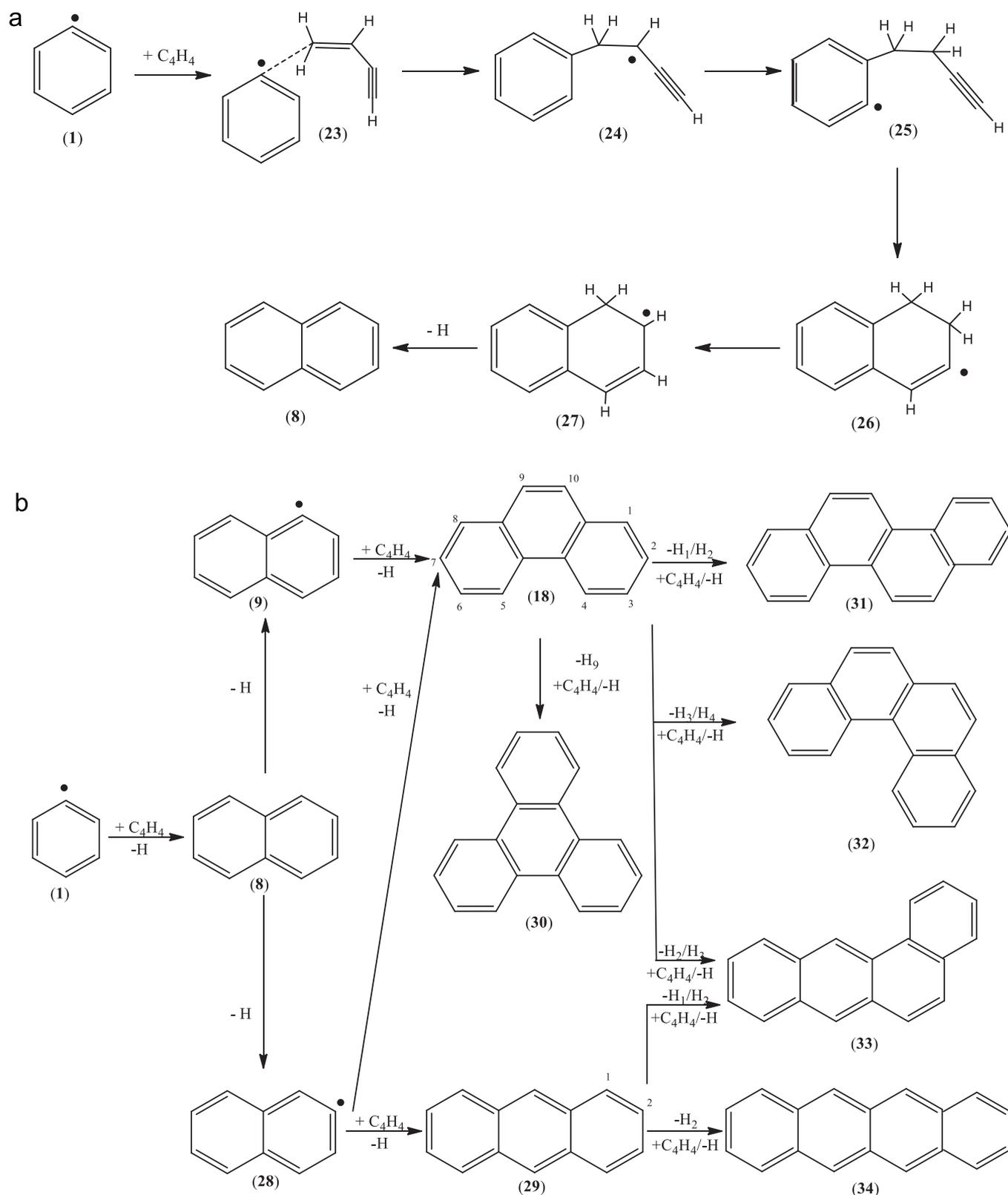


Figure 2. (a) Key routes leading to naphthalene ($C_{10}H_8$; **8**) via a [2 + 4] ring annulation through the HAVA mechanism. (b) Key routes leading to PAHs via a [2 + 4] ring annulation through the HAVA mechanism.

radical ($C_{10}H_7$; **9**) with methylacetylene (CH_3CCH) via a methyl group loss.⁴⁶ Along with 1-naphthyl/allene, this system also leads to 1*H*-phenalene ($C_{13}H_{10}$; **13**) via 10π -aromatic, resonantly stabilized free radical intermediates (Figure 1b) following a [3 + 3] bay closure.

These findings can be further generalized: Rather than forming additional six-membered rings beyond naphthalene ($C_{10}H_8$; **8**), aromatic radicals carrying the radical center at the terminal carbon atom of a three-carbon-bay moiety react with acetylene via a [3 + 2] ring closure to a five-membered ring.

Hence, HACA occurring at zigzag edges of PAH molecules tends to form a five-membered ring instead of a six-membered one. Chemical reactor studies combined with electronic structure calculations disclosed that the concept of a [3 + 2] bay closure to a five-membered ring can be expanded to [4 + 2] bay closures yielding a six-membered ring (Figure 1c).^{32,33} Hydrogen abstraction from the α -carbon atom of biphenyl ($C_6H_5C_6H_5$; **14**) leads to the biphenyl radical ($C_6H_5C_6H_4$; **15**) and the radical center at the terminal carbon atom of the four-carbon-bay moiety. Note that biphenyl ($C_6H_5C_6H_5$; **14**) can be formed in high-temperature systems via the bimolecular reaction of the phenyl radical (C_6H_5) with benzene (C_6H_6).⁴⁷ Upon reaction with acetylene via a barrier of 10 kJ mol^{-1} , the collision complex **16** undergoes ring closure to **17** followed by a hydrogen loss and aromatization to phenanthrene ($C_{14}H_{10}$; **18**). This reaction sequence is mirrored by the conversion of phenanthrene ($C_{14}H_{10}$; **18**) via 4-phenanthrenyl ($C_{14}H_9$; **19**) through a 20 kJ mol^{-1} entrance barrier for acetylene addition involving doublet radical intermediates **20** and **21** to yield pyrene ($C_{16}H_{10}$; **22**).

2.2. Hydrogen Abstraction–Vinylacetylene Addition (HAVA). The HAVA reaction mechanisms revolutionized our understanding of molecular mass growth processes of PAHs via the ring annulation and “addition” of a six-membered ring to an existing aromatic moiety (Figure 2a,b). Initially unraveled via the crossed molecular beam reaction of the phenyl radical (C_6H_5 ; **1**) with vinylacetylene ($HCCC_2H_3$) leading to naphthalene ($C_{10}H_8$; **8**),^{1,7,34} HAVA is initiated via the barrierless formation of a van der Waals complex (**23**) in the entrance channel of the reaction. Generally speaking these van der Waals complexes are weakly stabilized by $8\text{--}19 \text{ kJ mol}^{-1}$ with respect to the reactants and isomerize via an addition of the radical center of the aromatic radical reactant to the H_2C moiety of the vinylacetylene molecule leading to a resonantly stabilized free radical (RSFR) intermediate (**24**) residing in deep potential energy wells of typically $179\text{--}195 \text{ kJ mol}^{-1}$ with respect to the separated reactants.^{29,35–38} A small barrier to addition of $4\text{--}9 \text{ kJ mol}^{-1}$ does exist, but it is located below the energy of the separated reactants and hence is called a *submerged barrier*. Therefore, the reaction of the aromatic radical with vinylacetylene leading to the resonantly stabilized free doublet radical intermediate (**24**) is essentially barrierless and hence can operate even in low-temperature environments of, for example, 10 K as in cold molecular clouds. These RSFRs undergo hydrogen migration from the aromatic ring to the acetylenic moiety of the vinylacetylene reactant forming (**25**) followed by cyclization to (**26**), hydrogen migration to (**27**), and atomic hydrogen loss through tight exit transition states located typically $16\text{--}29 \text{ kJ mol}^{-1}$ above the separated products accompanied by aromatization to, for example, naphthalene ($C_{10}H_8$; **8**), in overall exoergic reactions of $237\text{--}287 \text{ kJ mol}^{-1}$. HAVA represents a versatile pathway and involves only one single collision event leading eventually to a *barrierless* [2 + 4] ring annulation of an aromatic doublet radical via RSFR intermediates (Figure 2a). It is important to note that, unlike HACA, HAVA is not limited to the formation of naphthalene (**8**) (Figure 2b).

Extensive molecular beam studies coupled with isomer-selective vacuum ultraviolet (VUV) photoionization detection of the nascent reaction products revealed *barrierless* molecular mass growth processes from naphthalene (**8**) via naphthyl radicals ($C_{10}H_7$; **9/28**) to phenanthrene ($C_{14}H_{10}$; **18**) and anthracene ($C_{14}H_{10}$; **29**),³⁵ from phenanthrene ($C_{14}H_{10}$; **18**)

via 9-phenanthrenyl radicals ($C_{14}H_9$) to triphenylene ($C_{18}H_{12}$; **30**),³⁶ from phenanthrene ($C_{14}H_{10}$; **18**) and anthracene ($C_{14}H_{10}$; **29**) via distinct phenanthrenyl and anthracenyl radicals ($C_{14}H_9$) to [4]phenacene ($C_{18}H_{12}$; **31**), [4]helicene ($C_{18}H_{12}$; **32**), benz[a]anthracene ($C_{18}H_{12}$; **33**), and tetracene ($C_{18}H_{12}$; **34**), for example, key representatives of acenes, phenacenes, and racemic helicenes.^{29,37} These isomers are differentiated by linear, zigzag, and ortho-condensed arrangements of fused benzene rings. Recent molecular beam studies revealed the first synthesis of a PAH with five benzene rings involving HAVA: pentacene ($C_{22}H_{14}$; **35**), thus highlighting the versatility of HAVA leading to PAHs via bottom-up molecular mass growth processes.³⁸ If the reacting aromatic doublet radical moiety carries an alkyl group such as methyl, HAVA can also lead to the formation of, for example, methyl-substituted PAHs such as 1- and 2-methylnaphthalene as demonstrated via crossed molecular beam experiments of tolyl (C_7H_7) radicals with vinylacetylene in which the methyl group acts as a spectator.⁴⁸ Modified HAVA routes involving hydrogenated reactants, for example, 1,3-butadiene along with their methyl-substituted counterparts, lead to (methyl-substituted) dihydrogenated naphthalenes.²⁸

To sum up, HAVA has the capability to expand PAHs by “adding” a benzene ring to an existing PAH moiety via a *single collision event* involving two neutral reactants. The barrierless nature of this mechanism is driven by the initial formation of a van der Waals complex, a submerged barrier to addition, and formation of an RSFR intermediate that successively isomerizes via hydrogen shifts and cyclization prior to the atomic hydrogen loss and PAH formation. Because of the barrierless nature of HAVA, HAVA can even operate in cold molecular clouds (10 K) and in hydrocarbon-rich atmospheres of planets and their moons such as Saturn’s moon Titan, thus challenging conventional wisdom that PAHs can only be formed in high-temperature settings such as in combustion systems and in high-temperature circumstellar envelopes of carbon-rich AGB stars. The only exception to the barrierless nature of HAVA known currently is the reaction of the 4-phenanthrenyl radical reaction with vinylacetylene, in which a steric hindrance elevated the barrier to addition slightly above the energy of the separated reactants.³⁷ On a final note, it should be stressed that, similar to methylacetylene, vinylacetylene can be classified as a substituted acetylene derivative. Therefore, [4 + 2] bay closures via HACA yielding a vinyl-substituted six-membered ring may compete with ring annulation through HAVA as demonstrated in the formation of vinyl-substituted pyrene in high-temperature systems;³⁷ however, the barrierless nature of HAVA directs low-temperature mass growth processes to ring annulation forming PAHs with at least five six-membered rings (Figure 2b).

2.3. Phenyl Addition–DehydroCyclization (PAC). Originally postulated by Koshi et al.⁴⁹ and Li et al.,⁵⁰ the high-temperature PAC mechanism involves an initial addition of a phenyl radical (C_6H_5 , **1**) to an aromatic hydrocarbon at a three- or four-carbon-atom bay as found in, for example, biphenyl ($C_6H_5C_6H_5$; **14**) and naphthalene ($C_{10}H_8$; **8**), respectively, followed by hydrogen loss. The resulting phenyl-substituted aromatic system undergoes a successive dehydrogenation, cyclization, and aromatization effectively converting three- and four-carbon bays at aromatic hydrocarbons to indene and naphthalene moieties, respectively, via [6 + 3] and [6 + 4] molecular mass growth processes (Figure 3a,b, respectively). This mechanism may overcome previous

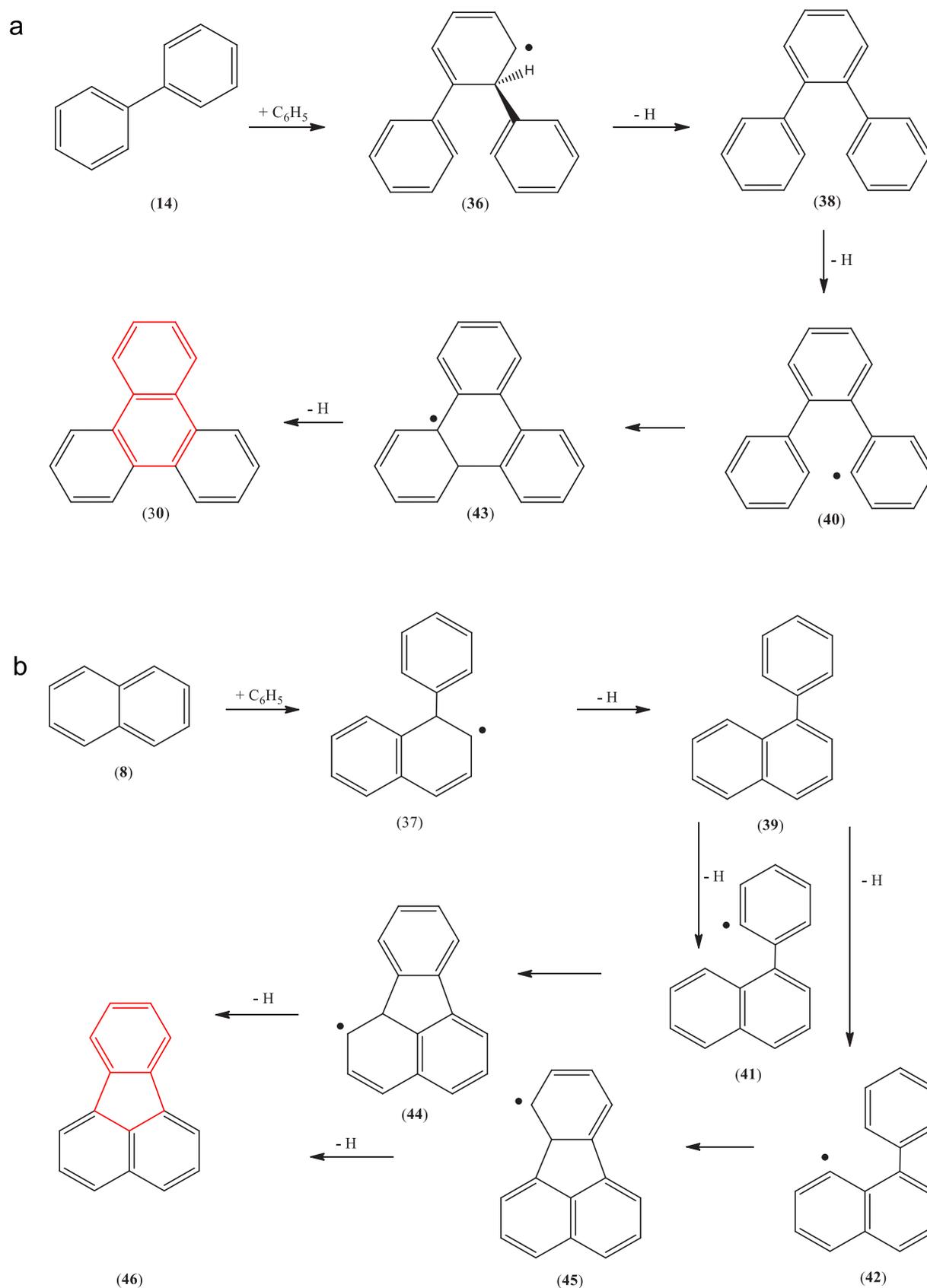


Figure 3. (a) Key routes leading to triphenylene ($C_{18}H_{12}$; **30**) via a [6 + 4] ring annulation through the PAC mechanism. The carbon skeleton in red indicates the naphthalene moiety. (b) Key routes leading to fluoranthene ($C_{16}H_{10}$; **46**) via a [6 + 3] ring annulation through the PAC mechanism. The carbon skeleton in red indicates the indene moiety.

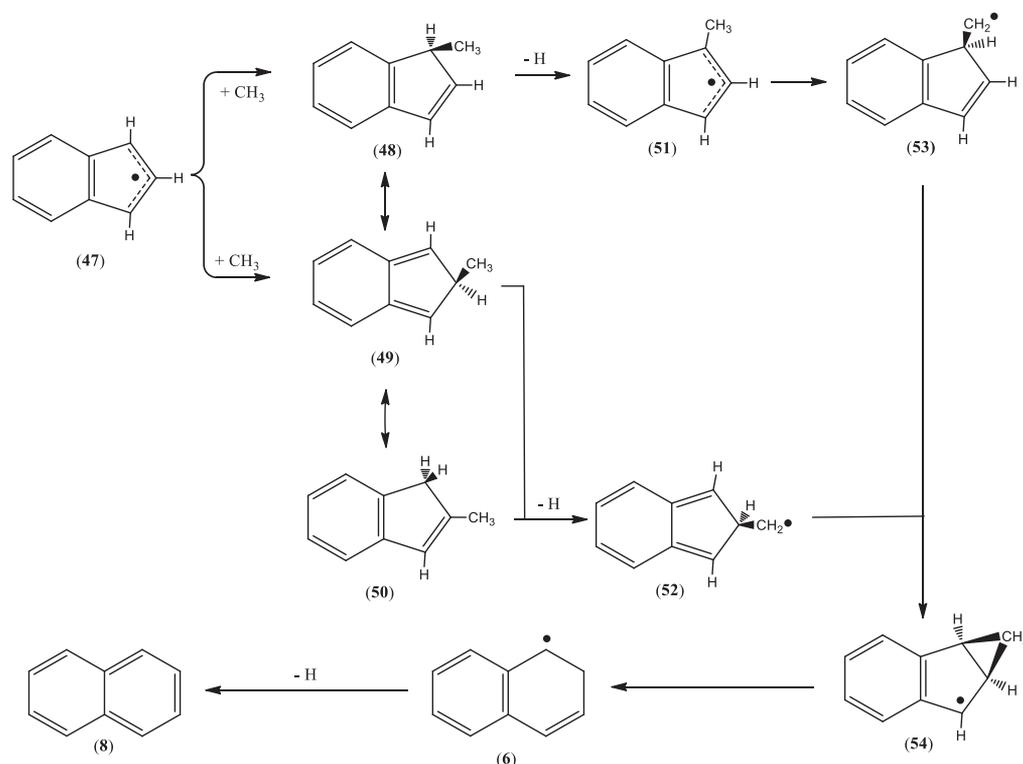


Figure 4. Key routes leading to naphthalene ($C_{10}H_8$; **8**) via the RRR mechanism.

obstacles of the high-temperature HACA framework as deduced from recent flame modeling inferring that a stepwise addition of acetylene leading to PAHs as complex as coronene ($C_{24}H_{12}$) is inefficient and too slow to reproduce the quantified mass fractions of PAHs in combustion flames and in circumstellar environments.

In detail, PAC commences with an addition of the phenyl (C_6H_5 ; **1**) radical to the terminal carbon atom of a four-carbon or three-carbon bay of aromatic hydrocarbons as found in, for example, biphenyl ($C_6H_5C_6H_5$; **14**) and naphthalene ($C_{10}H_8$; **8**) via barriers of 22 and 21 kJ mol^{-1} leading to doublet radical intermediates **36** and **37** stabilized by 108 and 137 kJ mol^{-1} with respect to the separated reactants. These transients undergo hydrogen atom losses via tight exit transition states located 42 and 44 kJ mol^{-1} above the separated *o*-terphenyl ($C_{18}H_{14}$; **38**) and the hydrogen and 1-phenylnaphthalene ($C_{16}H_{12}$; **39**) and hydrogen products, respectively. These species lose a hydrogen atom either from the phenyl moiety or from the naphthalene core via a hydrogen abstraction through barriers of 76–101 kJ mol^{-1} yielding intermediates **40–42**. These doublet radicals undergo ring closure to **43–45** followed by atomic hydrogen loss yielding triphenylene ($C_{18}H_{12}$; **30**) and fluoranthene ($C_{16}H_{10}$; **46**), respectively. The 18π aromatic triphenylene (**30**)—a benchmark of a fully benzenoid PAH—and fluoranthene (**46**)—a prototype of a nonalternant PAH—represent key building blocks in molecular mass growth processes of two-dimensional (2D) and three-dimensional (3D) PAHs leading eventually to 2D and 3D nanostructures such as graphenes and buckminsterfullerene (C_{60}) along with carbon nanotubes, respectively. Here, five-membered rings as prepared in fluoranthene (**46**) are critical to “bent” PAHs out of plane. PAHs carrying five-membered rings have been detected in sooting hydrocarbon flames. The formation of triphenylene ($C_{18}H_{12}$; **30**) is the perfect example

to illustrate the complexity of the problem to model the PAH formation accurately under a wide range of conditions. Detailed mechanistical insights are critical to understand the importance of the HAVA versus the PAC pathways at different reaction temperatures.

2.4. Radical–Radical Reactions (RRR). Reactions between two hydrocarbon radicals such as propargyl (C_3H_3)-propargyl (C_3H_3), methyl (CH_3)-cyclopentadienyl (C_5H_5),^{51–53} and cyclopentadienyl (C_5H_5)-cyclopentadienyl (C_5H_5)^{54,55} have been suggested to lead to aromatic systems such as benzene (C_6H_6) and naphthalene ($C_{10}H_8$), respectively. However, the validity of elementary reactions between free hydrocarbon radicals leading to aromatic hydrocarbons at high temperatures have been scarce under well-defined experimental conditions in molecular beams. With the exception of the reaction of the methyl radical (CH_3) with indenyl (C_9H_7 ; **47**) leading to naphthalene ($C_{10}H_8$; **8**),^{40,56,57} no experimental data are available under high-temperature conditions that have followed the kinetics and mechanism of a hydrocarbon free radical with a second hydrocarbon radical limited to self-recombination. Therefore, the methylation of the indenyl radical (C_9H_7 ; **47**) via a barrierless RRR provides a well-defined benchmark for the conversion of a five-membered ring to a six-membered ring in PAHs at temperatures of ~ 1400 K (Figure 4).

Molecular beam studies of the methyl–indenyl system coupled with isotopic substitution experiments, VUV detection of the nascent reaction products, and electronic structure calculations revealed that the reaction between the methyl radical and the indenyl radical (C_9H_7 ; **47**) is initiated by a barrierless radical–radical recombination to the C1/C3 and/or C2 carbon atom of 1-indenyl leading to 1-methylindene ($C_{10}H_{10}$; **48**) and 2-methyl-2H-indene ($C_{10}H_{10}$; **49**). These isomers can be converted via a barrier of 228 kJ mol^{-1} with

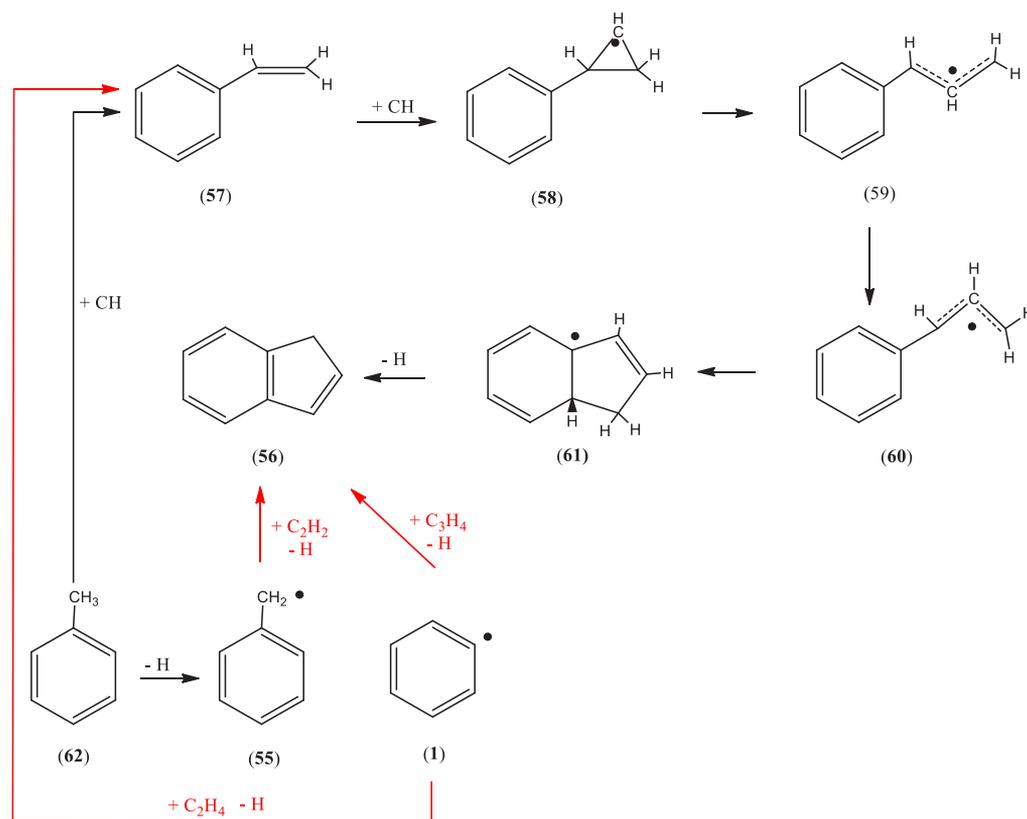


Figure 5. Key routes leading to indene (C_9H_8 ; **56**) via the low-temperature MACA mechanism. Alternative high-temperature mechanisms to indene are color coded in red.

respect to 1-methylindene ($C_{10}H_{10}$; **48**). Further, 2-methyl-2*H*-indene ($C_{10}H_{10}$; **49**) could isomerize to the thermodynamically more stable 2-methylindene isomer ($C_{10}H_{10}$; **50**) through a barrier of 64 kJ mol^{-1} . 1-Methylindene ($C_{10}H_{10}$; **48**) and 2-methyl-2*H*-indene/2-methylindene ($C_{10}H_{10}$; **49/50**) may decompose via an atomic hydrogen loss in overall endoergic reactions with respect to the separated reactants yielding $C_{10}H_9$ radicals (**51/52**). Therefore, although the radical–radical reaction is initiated via a barrierless recombination, the endoergicities of the aforementioned atomic hydrogen losses dictate that these pathways are only open in high-temperature environments. Consecutive isomerization processes lead to intermediates **53** and eventually to **54**—a tricyclic intermediate. The latter ring opens to **55**, which carries the carbon backbone of the naphthalene molecule. Intermediate **55** decomposes via an atomic hydrogen loss to the naphthalene molecule ($C_{10}H_8$; **8**) via a tight exit transition state located 26 kJ mol^{-1} above the separated products. Overall, the pathways to naphthalene ($C_{10}H_8$; **8**) showcase the prototype of a Radical–Radical Recombination that facilitates molecular mass growth processes via a ring expansion through the conversion of a five-membered ring to a six-membered ring in PAH radicals. This mechanism between a methyl radical and (annulated) cyclopentadienyl radical displays a versatile ring expansion mechanism converting postulated nonreactive end members of aromatic growth processes carrying five-membered rings to planar aromatic systems. It shall be highlighted that, although the initial recombination of two radicals such as in the methyl–indenyl system is barrierless, transition states in successive isomerization processes could reside above the

energy of the separated reactants, thus blocking bimolecular radical–radical reactions in cold interstellar environments.

2.5. Methylidyne Addition–Cyclization–Aromatization (MACA). The recently established low-temperature MACA mechanism effectively converts a vinyl side chain (C_2H_3) of a PAH into a five-membered ring via a ring annulation.⁴¹ In strong contrast to the high-temperature pathways to indene via the reactions of phenyl ($C_6H_5\cdot$, **1**) radicals with methylacetylene (CH_3CCH) and allene (H_2CCCH_2)^{58–60} (or propargyl) and of benzyl ($C_7H_7\cdot$, **55**) with acetylene (C_2H_2),^{3,61} which are characterized by entrance barriers between 14 and 51 kJ mol^{-1} (Figure 5), MACA represents a barrierless mechanism to indene (C_9H_8 ; **56**) via the reaction of the methylidyne radical (CH) with styrene ($C_6H_5C_2H_3$; **57**). Vinyl side chains can be incorporated into PAHs via three pathways as demonstrated in molecular beam experiments through (i) the reaction of an aryl radical such as phenyl ($C_6H_5\cdot$) with ethylene (C_2H_4) involving an entrance barrier to addition of 10 kJ mol^{-1} ,⁶² (ii) the reaction of an aryl radical with the acetylenic moiety of vinylacetylene via bay closure though entrance barriers to addition of $8–31 \text{ kJ mol}^{-1}$, and (iii) the barrierless reaction of a methylidyne radical with a methyl side chain of a PAH.⁴¹

In detail, the methylidyne radical can add barrierlessly either to the π electron density of the carbon–carbon double bond of the vinyl moiety (C_2H_3) or to the aromatic ring of styrene ($C_6H_5C_2H_3$; **57**). Analogously to ethylene (C_2H_4) and benzene (C_6H_6), methylidyne does not insert into any carbon–hydrogen bond of the phenyl or vinyl functional groups. The addition of methylidyne to the vinyl moiety leads to a phenyl-substituted cyclopropanyl intermediate **58**, which

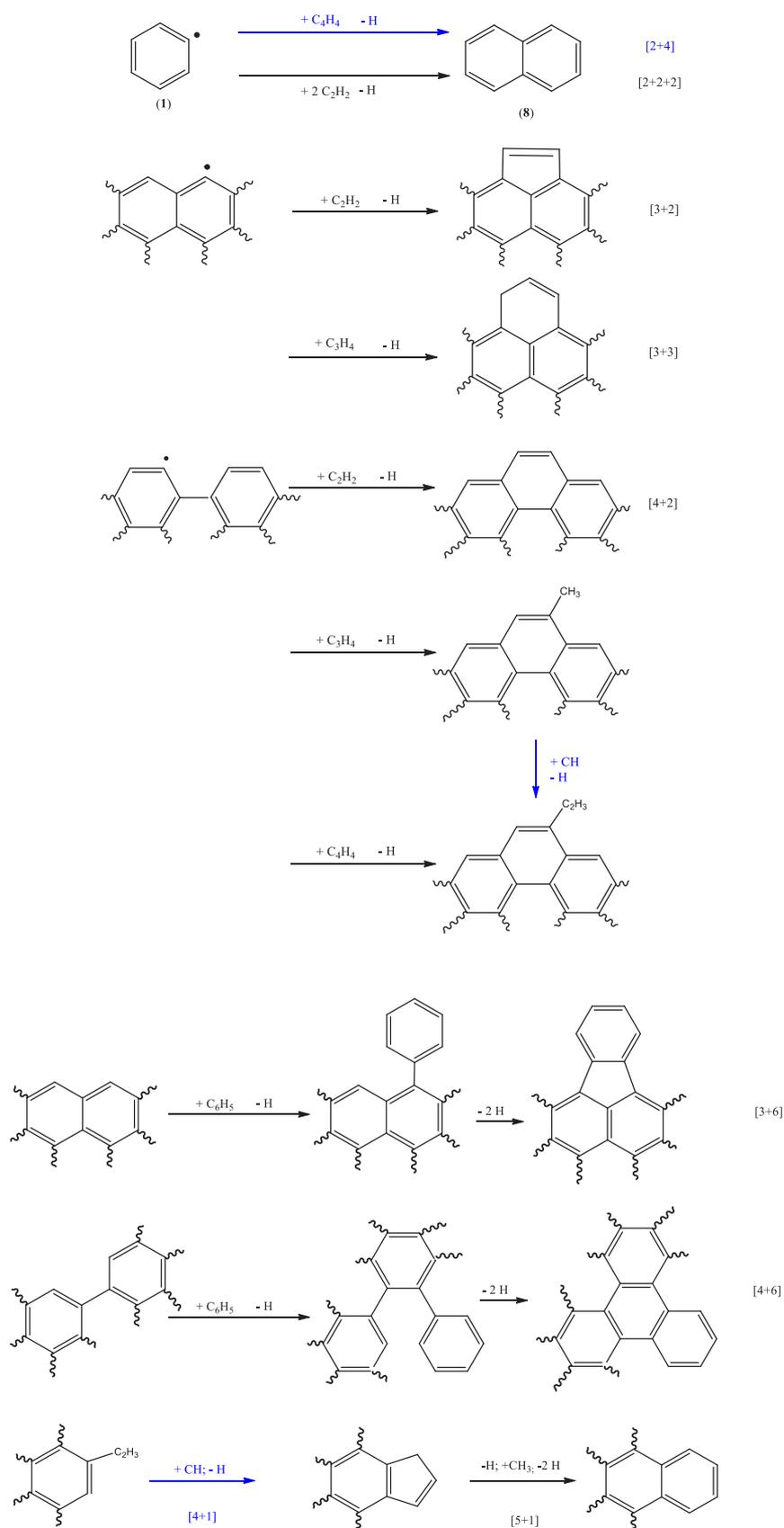


Figure 6. Compilation of molecular mass growth mechanisms to PAHs. Waved lines indicate the incorporation into an extended aromatic system. Pathways color coded in blue represent barrierless reaction mechanisms.

ring-opens to the thermodynamically preferred phenyl-substituted allylic radical intermediate **59**. The latter undergoes a cis–trans isomerization to **60** followed by a ring closure to **61**; this reaction sequence is terminated by a hydrogen atom emission from the bridging C4 carbon atom along with the aromatization and formation of indene **56** in an overall exoergic ($-356 \pm 8 \text{ kJ mol}^{-1}$) reaction through a tight exit transition state. The addition of methylidyne to the benzene ring may also lead to indene **56**, but the aromatic ring undergoes a complete reorganization of the carbon skeleton thus leading to a complete “loss of memory” of the molecular structure of the six-membered ring; this pathway is rather exceptional, as traditional molecular mass growth processes to aromatic systems via HACA, HAVA, PAC, and RRR simply “add” rings to an existing aromatic structure. MACA represents an excellent example that the underlying chemistry is important to synthesize aromatic systems such as indene: whereas MACA likely drives the low-temperature formation of indene **56** in cold molecular clouds due to the abundance of methylidyne radicals, the role of MACA in combustion systems still has to be elucidated given the apparent low concentrations of the methylidyne radicals.

3. CONCLUSIONS

Recent molecular-beam studies combined with high-level electronic structure calculations revealed the mechanisms of five key reaction pathways involving molecular mass growth processes in aromatic systems through neutral–neutral reactions: Hydrogen Abstraction–Acetylene Addition, Hydrogen Abstraction–Vinylacetylene Addition, Phenyl Addition–DehydroCyclization, Radical–Radical Reactions, and Methylidyne Addition–Cyclization–Aromatization. These experiments under well-defined and controlled experimental conditions in molecular beams and with the help of a pyrolytic microreactor combined with high-level electronic structure and model calculations has resulted in the realization that multiple key mechanisms well beyond the “established” (partially valid) HACA mechanism through radical–molecule and radical–radical reactions contribute to PAH formation. The following findings shall be highlighted (Figure 6).

HACA operates solely at high temperatures, involves barriers to addition between 5 and 30 kJ mol^{-1} , and can convert phenyl radicals ($\text{C}_6\text{H}_5\cdot$; **1**) via successive reactions with two acetylene molecules through ring annulation to naphthalene (C_{10}H_8 ; **8**), that is, an overall $[2 + 2 + 2]$ annulation with two carbon atoms originating from the aromatic radical and two plus two carbon atoms from the acetylene reactants. If the radical center is located at the terminal carbon atom of a three- or four-carbon bay of an aryl radical, $[3 + 2]/[3 + 3]$ or $[4 + 2]$ bay closures are preferable, thus forming five- and six-membered rings. $[4 + 2]$ bay closures can also be achieved with substituted acetylenes like methylacetylene (propyne) and vinylacetylene yielding methyl and vinyl-substituted rings. With a barrierless reaction with methylidyne radicals, methyl groups can be converted into vinyl groups.

HAVA controls low-temperature, barrierless molecular mass growth processes via ring annulation by “adding” a six-membered ring to an aromatic system. These $[2 + 4]$ pathways involve the initial formation of van der Waals complexes in the entrance channel and the addition of the aryl radical with its radical center to the H_2C moiety via submerged barriers leading to RSFR intermediates, which eventually isomerize

(hydrogen shifts, cyclization) and undergo decomposition via an atomic hydrogen loss accompanied by aromatization. If the aromatic radical carries a methyl side group, this aliphatic group acts as a spectator thus leading to the formation of methyl-substituted PAHs like methyl-naphthalenes. The barrierless nature of HAVA’s ring annulation is unique among all molecular mass growth processes leading to PAHs and provides a unique pathway to PAHs in low-temperature environments such as molecular clouds and hydrocarbon-rich atmospheres of planets and their moons.

PAC functions solely at high temperatures and involves $[6 + 3]$ and $[6 + 4]$ molecular mass growth processes to indene and naphthalene moieties as demonstrated through the formation of fluoranthene **46** and of triphenylene **30**. These initial addition processes of the phenyl radical have to overcome barriers to addition between 5 and 30 kJ mol^{-1} . Considering these barriers, HACA and PAC may compete in high-temperature environments with the dominating pathways to PAH formation dictated by the availability of the reactants.

RRR pathways are challenging to study experimentally, and currently only one system has been studied under controlled environments in molecular beams. At least it has been demonstrated that a ring expansion from a five- to a six-membered ring can occur via a reaction of a methyl radical with an (annulated) cyclopentadienyl radical. Although this $[5 + 1]$ molecular growth pathway is initiated by a barrierless radical–radical recombination, endoergic reaction intermediates and/or transition states higher in energy than separated reactants dictate that these $[5 + 1]$ RRRs are only open at high temperatures.

MACA directs the low-temperature chemistry and a $[4 + 1]$ bay-closure pathway to an (annulated) cyclopentadiene moiety upon the addition of a methylidyne radical to a vinyl side group attached to an aromatic molecule. Since these pathways are barrierless, these routes open up the formation of a five-membered ring within PAHs—a critical prerequisite to bent PAHs out of plane. Alternative barrierless pathways to PAHs carrying five-membered rings involve HAVA, in which aryl-type radicals already carrying a five-membered ring undergo ring annulation by adding a six-membered ring to an existing benzene moiety as demonstrated, that is, in the formation of benzindenes^{63,64} or, as shown in Figure 5, reactions of acetylene with benzyl-type radicals and/or phenyl with methylacetylene/allene.

Overall, these concepts provide solid, experimentally and computationally verified frameworks to molecular mass growth processes of PAHs in extreme environments from low temperatures in molecular clouds (10 K) and hydrocarbon-rich atmospheres of planets and their moons (35–150 K) to high-temperature environments like circumstellar envelopes of carbon-rich AGB stars and combustion systems at a few 1000 K. Whereas in high-temperature environments, initial aryl radical reactants can be accessed via a hydrogen abstraction (combustion flames, circumstellar envelopes) or photodissociation through photons in circumstellar environments emitted from the central star, a photolysis of aromatics from photons of the internal VUV field present even deep inside molecular clouds initiates molecular mass growth in low-temperature interstellar environments. Further, PAHs such as naphthalene **8** (HACA, HAVA, RRR), phenanthrene **18** (HACA, HAVA), and triphenylene **30** (HAVA, PAC) can be formed *through multiple (competing) pathways* in high- and/or low-temperature environments; this also refers to reactive radical

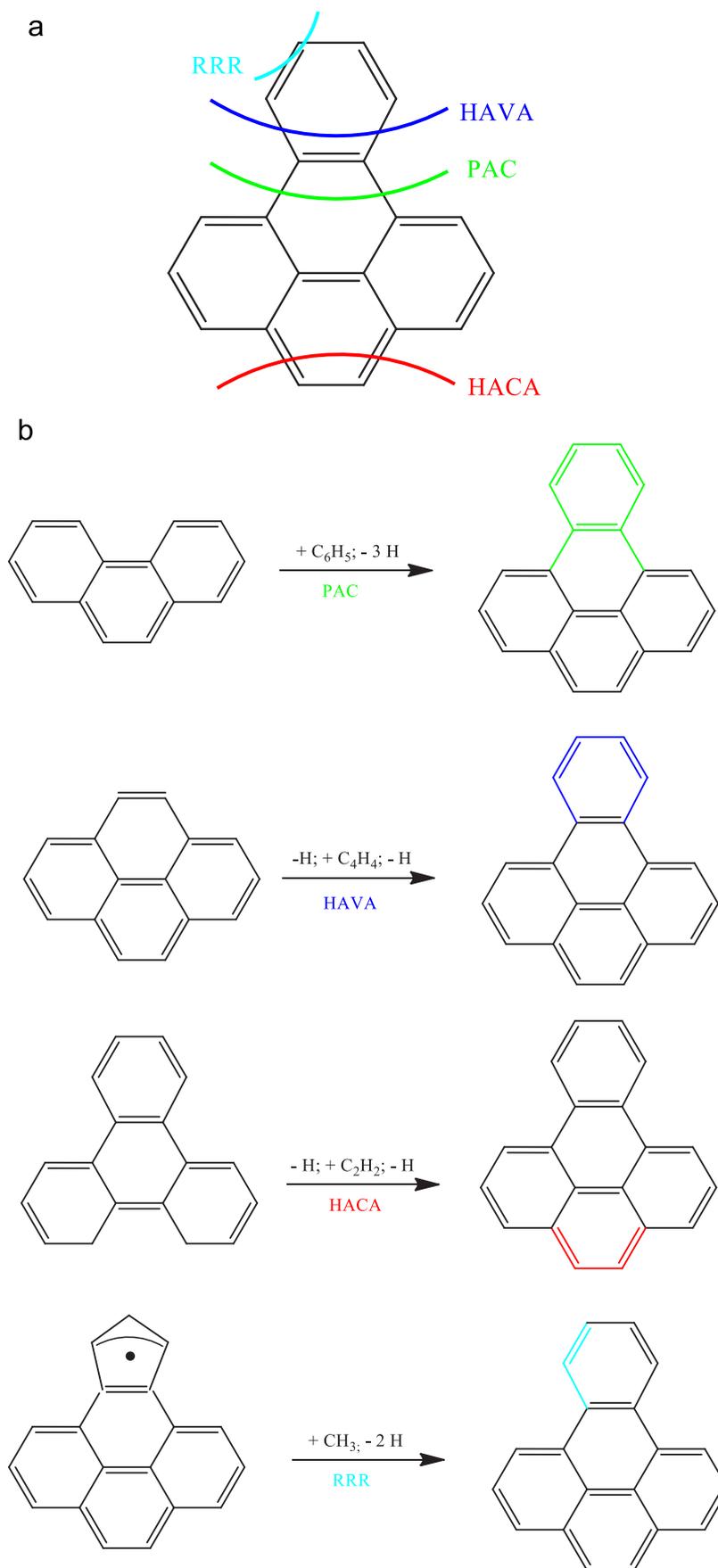


Figure 8. (a) Retrosynthetic approach to deconstruct benzo[e]pyrene into molecular building blocks required for HACA, HAVA, RRR, and PAC. (b) Forward synthesis to benzo[e]pyrene involving fundamental molecular building blocks required for HACA, HAVA, RRR, and PAC. The incorporated building blocks are color-coded.

nanotubes and fullerenes.⁶⁵ An application of these findings to authentic chemical reaction networks modeling the chemistry of aromatic species in, for example, combustion and extraterrestrial settings must be based on solid laboratory and computational data rather than guesswork based on often unstudied, speculative “paper chemistry”. Naturally, true progress in this field requires letting go of traditional concepts of “HACA-only PAH modeling” or ion–molecule reactions—a formidable task considering that entire research projects are linked to these hypotheses. However, despite mounting evidence on the importance of well-defined elementary reaction mechanisms involving a series of successive bimolecular reactions, the mechanisms revealed here have just scratched the surface. Open topics for future research include the discovery and investigation of yet unknown reaction pathways pushing the experimental limits to ever-larger PAHs. The elementary mechanisms elucidated can be exploited to conduct a retrosynthesis (on paper) for individual PAHs of interest and to extract possible formation pathways based on the aforementioned mechanisms. These predicted pathways have to be explored then experimentally via crossed beams and/or chemical microreactor studies as was done here, for instance, for the formation of corannulene ($C_{20}H_{10}$; **64**) via HAVA combined with HACA and PAC via benzo[ghi]-fluoranthene ($C_{18}H_{10}$; **63**) (Figure 7). Further, as an explicit example, our findings are applied for benzo[e]pyrene—a rather complex PAH and molecular building block of coronene ($C_{24}H_{12}$): a retrosynthetic (Figure 8a) and forward-synthetic approach (Figure 8b) revealed that four mechanisms elucidated here can form benzo[e]pyrene thus demonstrating the true complexity of modeling studies of combustion systems and extraterrestrial environments. In addition to identifying formation pathways of PAHs under these extreme low- and high-temperature conditions, understanding the importance of distinct reaction classes is of interest. Furthermore, it should be probed to what extent PAH growth chemistry can be studied successfully using relatively small molecular structures followed by extrapolation to larger systems with identical structural molecular features. From the experimental perspective, detailed crossed molecular beams and synchrotron-based studies represent a versatile approach for the study of the chemistry under the controlled conditions. These pathways yielded fundamental molecular building blocks of 2D and 3D nanostructures such as triphenylene and fluoranthene along with corannulene, respectively, but bottom-up synthetic routes to, for example, fullerenes in combustion systems and in deep space based on molecular beam studies are still lacking. Despite the similarities of the molecular weight growth mechanisms at the low and high temperatures highlighted here, the mechanisms for particle inception at the extreme conditions are likely to be different.

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Notes

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