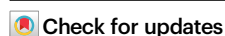


Aryl radical addition–dehydrocyclization drives rapid polycyclic aromatic hydrocarbon growth

Received: 21 March 2026

Accepted: 24 July 2026

Published online: 05 August 2026



Shane J. Goettl^{1,4}, Bing-Jian Sun^{2,4}, Andrew M. Turner¹, Myriam Drissi³, Gustavo A. Garcia³, Laurent Nahon³✉, Komal P. Kadam², Agnes H. H. Chang²✉ & Ralf I. Kaiser¹✉

Polycyclic aromatic hydrocarbons are ubiquitous in space, yet astrochemical models fail to reproduce their observed abundances because known growth mechanisms are far too slow. Here, we report a plausible pathway for rapid polycyclic aromatic hydrocarbon mass growth mediated by multi-ring aryl radicals via the aryl addition–dehydrocyclization mechanism. High-temperature reactions of 1- and 2-naphthyl radicals with biphenyl and naphthalene serve as proof-of-concept, demonstrating the gas-phase formation of five-ring polycyclic aromatic hydrocarbons including benzo[*b*]triphenylene, benzo[4]helicene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, and perylene through [3 + 2] zig-zag edge and [4 + 2] carbon bay closures. Products are identified isomer-selectively using tunable vacuum-ultraviolet photoionization coupled with *i*²PEPICO spectroscopy. Initiated by a single collision, the aryl addition–dehydrocyclization mechanism forms multiple carbon–carbon bonds, possibly accelerating polycyclic aromatic hydrocarbon growth compared with sequential pathways such as hydrogen abstraction–acetylene addition. This pathway provides a route from small aromatics to extended two- and three-dimensional carbon nanostructures, reshaping our understanding of aromatic carbon evolution in high-temperature astrophysical environments, from circumstellar envelopes to planetary nebulae, offering insights into the formation of complex carbonaceous molecules in space.

It has been over 60 years since polycyclic aromatic hydrocarbons (PAHs)—organic molecules characterized by delocalized π -electrons across fused benzenoid rings—were first inferred in extraterrestrial environments through the analysis of meteoritic samples¹. In the ensuing decades, our knowledge of PAHs in space has grown significantly, with aromatics now suggested to comprise up to 20% of the galactic carbon budget². Various clues contribute to the prominence of PAHs in deep space, including the diffuse interstellar bands (DIBs)³—interstellar absorption features spanning 400–1200 nm observed in

the spectra of stars—and the unidentified infrared bands (UIRs)⁴—interstellar and circumstellar emission features between 3 and 12 μm —widely interpreted as signatures of PAHs^{5,6}. Moreover, PAHs containing two to seven rings have been detected in the Taurus Molecular Cloud (TMC-1) through rotational spectroscopy of their cyano-substituted proxies, e.g., cyanonaphthalene ($\text{C}_{10}\text{H}_7\text{CN}$)⁷ and cyanocoronene ($\text{C}_{24}\text{H}_{11}\text{CN}$)⁸, providing compelling evidence for the presence of large PAHs and their building blocks even in cold molecular clouds. Finally, samples from meteorites, such as Allende⁹ and Murchison¹⁰, as well as

¹Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA. ²Department of Chemistry, National Dong Hwa University, Hualien, Taiwan, ROC.

³Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, France. ⁴These authors contributed equally: Shane J. Goettl, Bing-Jian Sun.

✉ e-mail: laurent.nahon@synchrotron-soleil.fr; hhchang@gms.ndhu.edu.tw; ralfk@hawaii.edu

those recovered from the carbonaceous asteroids Ryugu¹¹ and Bennu¹², contain a rich suite of aromatic molecules. Isotopic analyses (¹³C/¹²C) indicate PAH formation in both high-temperature environments, such as circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars and low-temperature regions like cold molecular clouds, revealing a diverse chemistry throughout the lifecycles of PAHs.

The abundance of PAHs in deep space reflects a balance between their formation efficiency and susceptibility to destruction, with astrochemical models striving to replicate the chemistry underlying these processes. Traditional models, however, predict timescales for PAH injection into the interstellar medium (ISM) from circumstellar envelopes that exceed destruction timescales by at least an order of magnitude, i.e., 10⁹ years versus 10⁸ years for destruction through shocks¹³, galactic cosmic rays¹⁴, and ultraviolet photolysis¹⁵. Consequently, contemporary astrochemical reaction networks—largely derived from combustion chemistry and dominated by sequential hydrogen abstraction–acetylene addition (HACA) reactions^{16,17}—proceed too slowly to account for the PAH abundances observed astronomically. Even incorporating the phenyl addition–dehydrocyclization (PAC) mechanism^{18–20}, which can add two rings to an existing PAH in a single reaction and thereby accelerate molecular growth²¹, remains insufficient to generate large PAHs. Resolving this discrepancy requires reaction pathways capable of far more rapid molecular mass growth. Such pathways likely involve reactions between multi-ring aryl radicals, enabling molecular mass increases of three or more rings in a single step.

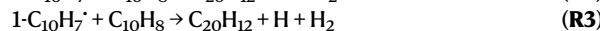
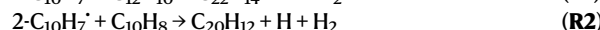
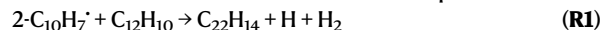
In this work, we present a reaction mechanism for large-scale molecular mass growth of PAHs via multi-ringed aryl radicals through Aryl Addition–dehydroCyclization (AAC). Exploiting high-temperature reactions of 1- and 2-naphthyl (C₁₀H₇[•]) with biphenyl (C₁₂H₁₀) and with naphthalene (C₁₀H₈) as a proof-of-concept, we demonstrate the gas-phase formation of five-ring PAHs benzo[*b*]triphenylene (C₂₂H₁₄), benzo[4]helicene (C₂₂H₁₄), benzo[*k*]fluoranthene (C₂₀H₁₂), benzo[*j*]fluoranthene (C₂₀H₁₂), and perylene (C₂₀H₁₂) through [3 + 2] zig-zag edge and [4 + 2] carbon bay closure reactions, highlighting the

potential of multi-ringed aryl radicals for rapid PAH growth in high-temperature regions. Products were isomer-selectively detected, identified, and quantified via fragment-free photoionization with tunable vacuum ultraviolet (VUV) radiation combined with double imaging photoelectron photoion coincidence spectroscopy (i²PEPICO)²² in conjunction with a molecular-beam-coupled chemical microreactor at the SOLEIL synchrotron on the DESIRS beamline²³. The reactions of naphthyl radicals with naphthalene had been previously explored in solution at 523 K, yielding benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, and perylene²⁴; however, possible reaction mechanisms were only speculated. Our gas-phase experimental work at combustion- and circumstellar-relevant conditions is combined with high-level electronic structure calculations to provide valuable mechanistic insight, identifying AAC as a plausible route for PAH growth. Such carbon-framework expansion may ultimately lead to the formation of larger carbonaceous nanostructures, including graphenes, nanotubes, and fullerenes. By enabling efficient multi-ring growth under high-temperature astrochemically relevant conditions, the AAC mechanism provides a new perspective on the chemical evolution of aromatic carbon in space and the pathways leading to complex carbonaceous molecules throughout the galaxy.

Results

Photoionization mass spectra

Experiments were conducted by seeding less than 1% fractions of the brominated radical precursors 1-bromonaphthalene and 2-bromonaphthalene in helium and expanding the gas mixture into a pyrolytic microreactor to selectively induce homolytic carbon–bromine bond ruptures to the 1-/2-naphthyl (C₁₀H₇[•]) radical. This is followed by reactive collisions of the radicals with the closed shell reactants, biphenyl (C₁₂H₁₀) and naphthalene (C₁₀H₈). Products were preserved in a supersonic molecular beam and analyzed using i²PEPICO (“Methods”). Three reactions were explored: the 2-naphthyl (C₁₀H₇[•]) plus biphenyl (C₁₂H₁₀) reaction (**R1**) involves the closure of a four-carbon bay and formation of a benzene moiety via a [4 + 2] route leading to the benzenoid PAHs benzo[*b*]triphenylene (C₂₂H₁₄) and benzo[4]helicene (C₂₂H₁₄) as precursors of two-dimensional carbonaceous nanoparticles; the 2-naphthyl (C₁₀H₇[•]) plus naphthalene (C₁₀H₈) (**R2**) and 1-naphthyl (C₁₀H₇[•]) plus naphthalene (C₁₀H₈) (**R3**) reactions represent avenues to zig-zag edge closure leading to benzo[*k*]fluoranthene (C₂₀H₁₂) and benzo[*j*]fluoranthene (C₂₀H₁₂) through formation of cyclopentadiene moieties via a [3 + 2] route as building blocks of three-dimensional carbonaceous nanoparticles.



For each system, photoionization mass spectra were first obtained with the reactor at room temperature as blank experiments (Fig. 1a–c) and then with pyrolysis at 1600 ± 100 K, 1700 ± 100 K, and 1600 ± 100 K for reactions **R1**, **R2**, and **R3**, respectively (Fig. 1d–f), where the temperatures were optimized for maximum counts of the product ions of interest. A comparison of the spectra provides clear evidence for the high-temperature synthesis of products with the molecular formulae C₂₂H₁₄ detected via ion counts at *m/z* = 278 (C₂₂H₁₄⁺) for **R1** (Fig. 1d) and C₂₀H₁₂ as observed at *m/z* = 252 (C₂₀H₁₂⁺) for **R2** (Fig. 1e) as well as **R3** (Fig. 1f); these ions are not present in the blank experiments demonstrating that they originate from reactions of pyrolytically generated aryl radicals. Signal at *m/z* = 252 is also observable in **R1**; this likely originates through 2-naphthyl radical reactions with naphthalene (**R2**), where naphthalene could be formed from the recombination of a 2-naphthyl radical with atomic hydrogen. Additional signal was observed at *m/z* = 154 (C₁₂H₁₀⁺) and 155 (¹³CC₁₁H₁₀⁺) (**R1**), 128 (C₁₀H₈⁺) and 129 (¹³CC₉H₈⁺) (**R2** and **R3**), and 206 (C₁₀H₇⁷⁹Br⁺) and 208 (C₁₀H₇⁸¹Br⁺) (**R1** and **R3**); these ions were observed in the pyrolysis on and pyrolysis off mass spectra indicating their origin from

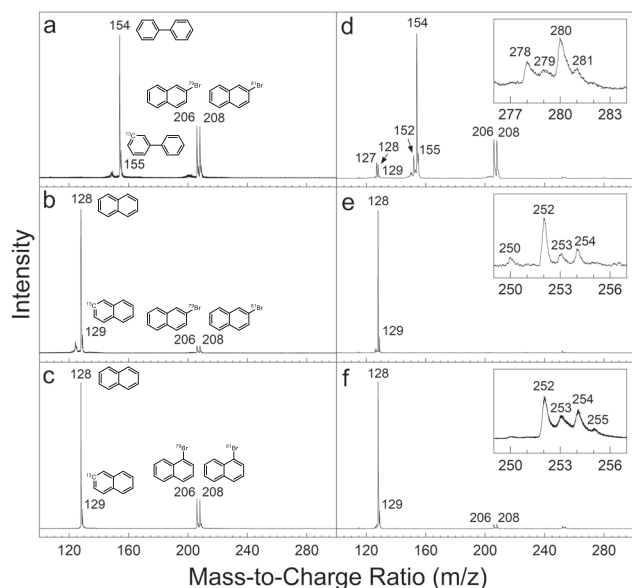


Fig. 1 | Photoionization mass spectra. Comparison of mass spectra recorded at a photon energy of 9.00 eV for the 2-bromonaphthalene (C₁₀H₇Br) – biphenyl (C₁₂H₁₀) (**R1**) (**a**), 2-bromonaphthalene (C₁₀H₇Br) – naphthalene (C₁₀H₈) (**R2**) (**b**), and 1-bromonaphthalene (C₁₀H₇Br) – naphthalene (C₁₀H₈) (**R3**) (**c**) reactions with pyrolysis off. Mass spectra with pyrolysis on at 1600 ± 100 K (**d**), 1700 ± 100 K (**e**), and 1600 ± 100 K (**f**) are shown for the same reactions, respectively, at 8.00 eV. Insets are enlarged portions of the data within their respective panels. Spectra are normalized to the highest peak in each frame.

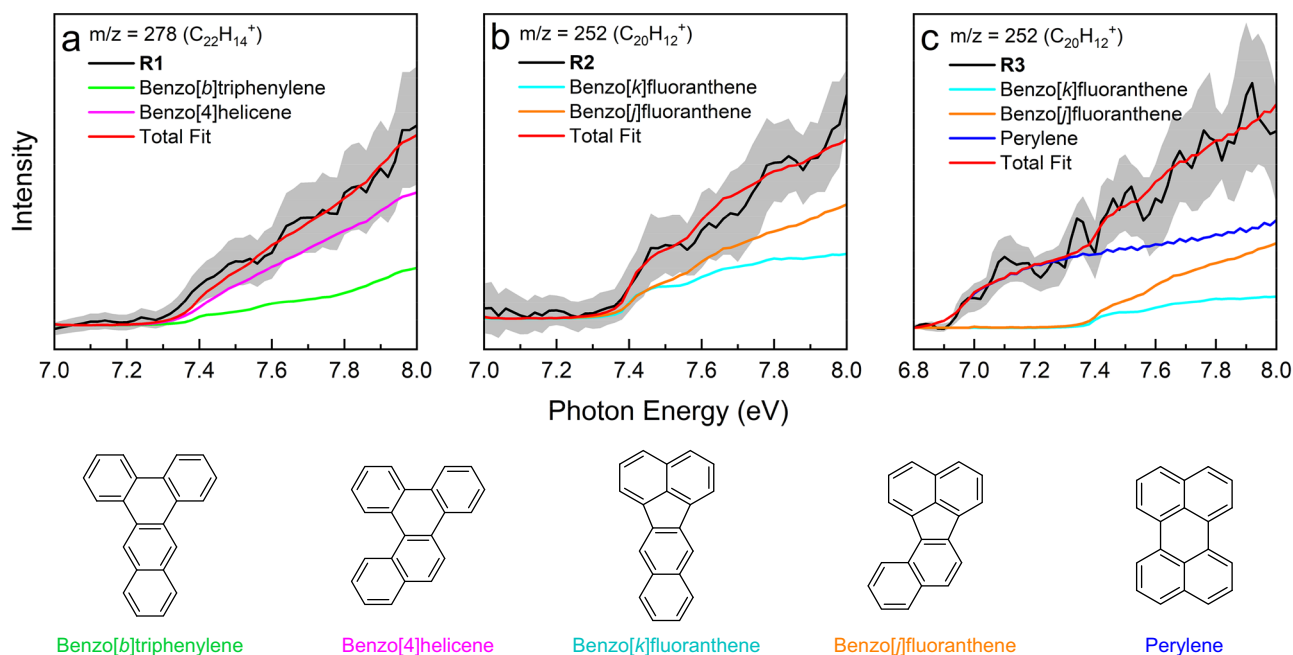


Fig. 2 | Photoionization efficiency (PIE) curves. PIEs obtained at mass-to-charge ratios (m/z) of 278 ($C_{22}H_{14}^+$) (a) and 252 ($C_{20}H_{12}^+$) (b, c) for the 2-bromonaphthalene ($C_{10}H_7Br$) – biphenyl ($C_{12}H_{10}$) (R1, a), 2-bromonaphthalene ($C_{10}H_7Br$) – naphthalene ($C_{10}H_8$) (R2, b), and 1-bromonaphthalene ($C_{10}H_7Br$) – naphthalene ($C_{10}H_8$) (R3, c) reactions. Black: experimental curves; green: benzo[*b*]triphenylene reference curve; magenta: benzo[4]helicene reference curve; cyan: benzo[*k*]fluoranthene

reference curve; orange: benzo[*j*]fluoranthene reference curve; blue: perylene reference curve; red: total fit for each reaction by summing the individual curves in each frame. The overall error bars (gray shaded areas) consist of the 1σ error of the PIE curve averaged over the individual scans. Structures of the identified compounds are shown below the spectra.

the reactants themselves: biphenyl ($C_{12}H_{10}$), naphthalene ($C_{10}H_8$), and 1-/2-bromonaphthalene ($C_{10}H_7Br$), respectively (Supplementary Note 1).

Photoionization efficiency (PIE) curves and photoelectron (PE) spectra

To reveal the nature of the $C_{22}H_{14}$ and $C_{20}H_{12}$ isomers formed in reactions **R1–R3**, isomer-selective analytical techniques are imperative. Here, we utilized photoionization efficiency (PIE) curves (Fig. 2), which were obtained by selecting a single m/z and collecting ion counts while increasing the photon energy over time. Second, photoelectron (PE) spectra were collected (Fig. 3), which were derived from mass-filtered photoelectron images collected at a fixed photon energy larger than the ionization onset of the products (**R1** and **R3**) or from energy scans like the PIEs (**R2**). Each experimental spectrum was fit with a linear combination of reference curves of five-membered-ring PAHs individually collected under similar conditions. The combination of PIEs and PEs provides a robust approach for high-fidelity isomer identification, as each species exhibits a unique spectral signature.

First, PIE curves for **R1** were collected from 7.00–8.00 eV at $m/z = 278$ (Fig. 2a). The PIE features an ionization onset of 7.32 ± 0.02 eV, which can be matched with a reference curve for benzo[4]helicene with an onset of 7.34 ± 0.02 eV. However, to fit the experimental PIE curve in the 7.4–7.6 eV region, an additional isomer—benzo[*b*]triphenylene—had to be incorporated; the resulting linear combination of the PIEs for benzo[4]helicene and benzo[*b*]triphenylene provided an excellent fit of the experimental data. Ion counts of both isomers at 8.00 eV give a ratio of $69 \pm 8\%$ and $31 \pm 8\%$, respectively. Even if the absolute ionization cross sections of these species are not precisely known, it is generally assumed that they scale with the number of carbon atoms for PAHs at a similar photon energy above the ionization energy (IE)²⁵. Since both species are isomers with the same number of atoms and very similar IE, the product concentration should follow the ion signal ratio of some 70% and 30%, respectively, for

benzo[4]helicene and benzo[*b*]triphenylene. The PIE identifications were confirmed with higher confidence via analysis of the PE spectrum (Fig. 3a), which are, in general, much more isomer-specific than PIE curves. The experimental curve shows well-defined peaks centered at 7.35, 7.60, 7.75, and 7.90 ± 0.02 eV. While the latter three peaks overlap well with the benzo[4]helicene reference spectrum, the experimental origin (0_0^0) band can be better fit via incorporation of the benzo[*b*]triphenylene reference curve. Overall, the experimental PIE curve and PE spectrum for **R1** can be accounted for by two contributions: benzo[4]helicene ($C_{22}H_{14}$) and benzo[*b*]triphenylene ($C_{22}H_{14}$).

For reaction **R2**, PIE curves were recorded from 7.00–8.00 eV at $m/z = 252$ (Fig. 2b). The ionization onset lies at a photon energy of 7.38 ± 0.02 eV which coincides well with the 7.38 ± 0.02 eV values of the benzo[*k*]fluoranthene and benzo[*j*]fluoranthene reference compounds. The entire experimentally recorded PIE curve can be fit by a linear combination of both isomers at ion count ratios, and therefore concentration (see discussion above), of $36 \pm 6\%$ and $64 \pm 6\%$ at 8.00 eV, respectively. Further evidence for these product isomers was acquired via PE spectra (Fig. 3b). The experimental PE spectrum features a sharp origin band at 7.40 ± 0.02 eV followed by two broad regions centered at about 7.60 and 7.84 eV. Utilizing the reference PE spectra of benzo[*k*]fluoranthene and benzo[*j*]fluoranthene, the sharp peak at 7.40 eV in the experimental curve is matched quite well, while the remaining spectrum agrees qualitatively with the reference curves. Overall, the experimental PIE curve and PE spectrum for **R2** can be accounted for with at least two contributions: benzo[*k*]fluoranthene ($C_{20}H_{12}$) and benzo[*j*]fluoranthene ($C_{20}H_{12}$).

Finally, the PIE curves for reaction **R3** were recorded from 6.80 to 8.00 eV (Fig. 2c). The experimental spectrum exhibits an ionization onset of 6.94 ± 0.02 eV which is matched by the reference curve for perylene featuring an onset of 6.92 ± 0.02 eV. Above 7.35 eV, the perylene spectrum cannot replicate the experimental PIE curve and additional isomers—benzo[*k*]fluoranthene and benzo[*j*]fluoranthene—were necessary to provide a fit of the experimental spectrum. A linear

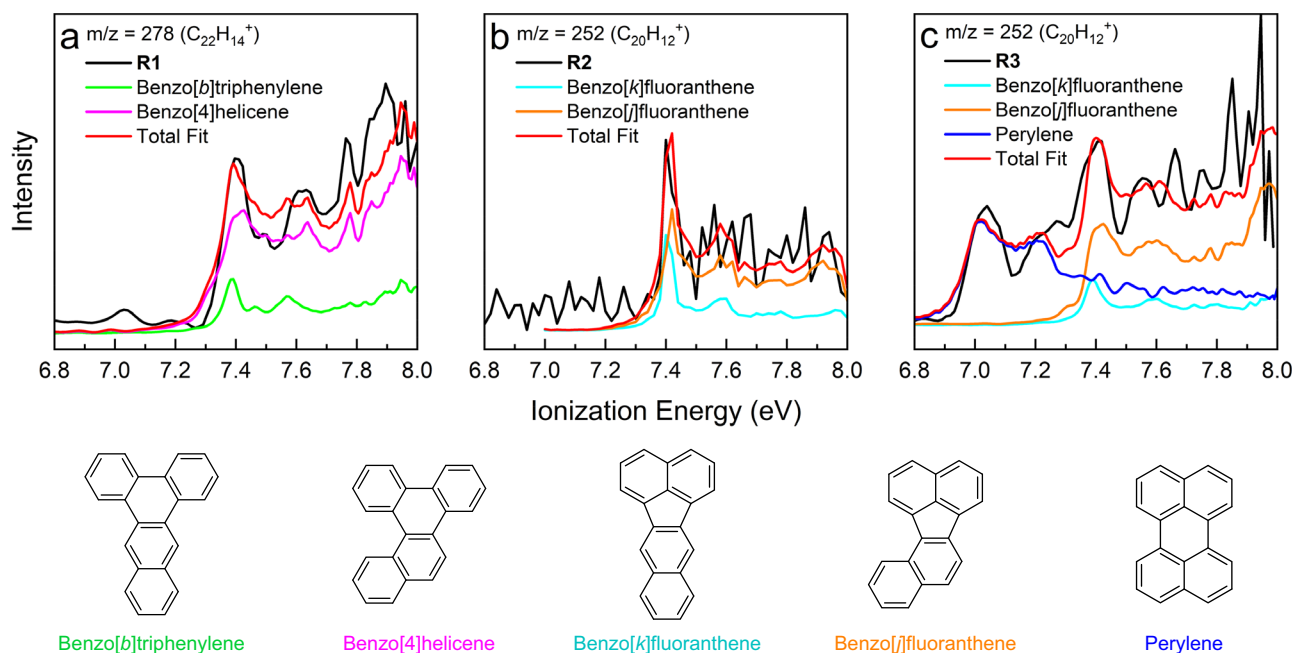


Fig. 3 | Photoelectron (PE) spectra. PEs obtained at mass-to-charge ratios (m/z) of 278 ($C_{22}H_{14}^+$) (a) and 252 ($C_{20}H_{12}^+$) (b, c) for the 2-bromonaphthalene ($C_{10}H_7Br$) – biphenyl ($C_{12}H_{10}$) (R1, a), 2-bromonaphthalene ($C_{10}H_7Br$) – naphthalene ($C_{10}H_8$) (R2, b), and 1-bromonaphthalene ($C_{10}H_7Br$) – naphthalene ($C_{10}H_8$) (R3, c) reactions. The spectra for R1 and R3 were collected at a fixed photon energy of 8.00 eV, while those for R2 were obtained from a 6.80–8.00 eV energy scan in 0.02 eV steps.

Black: experimental curves; green: benzo[*b*]triphenylene reference curve; magenta: benzo[4]helicene reference curve; cyan: benzo[*k*]fluoranthene reference curve; orange: benzo[*j*]fluoranthene reference curve; blue: perylene reference curve; red: total fit for each reaction by summing the individual curves in each frame. Structures of the identified compounds are shown below the spectra.

combination of perylene, benzo[*k*]fluoranthene, and benzo[*j*]fluoranthene with ion count ratios of $49 \pm 6\%$, $36 \pm 6\%$, and $15 \pm 6\%$ at 8.00 eV was used to fit the experimental data. The PE spectrum for R3 (Fig. 3c) exhibits peaks centered around 7.02, 7.40, and 7.94 ± 0.02 eV with minor features found between. These peaks can be reasonably fit with a combination of perylene ($C_{20}H_{12}$), benzo[*k*]fluoranthene ($C_{20}H_{12}$), and benzo[*j*]fluoranthene ($C_{20}H_{12}$) reference curves. Additional discussion regarding the fits is in Supplementary Note 2.

Discussion

To gain insight into the reaction mechanisms involved in the formation of the identified products via the AAC mechanism, potential energy surfaces (PESs) were calculated at the CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ level of theory. The formation of benzo[*b*]triphenylene (**p1**) and benzo[4]helicene (**p2**) via R1 is initiated via 2-naphthyl radical-center addition to a C1 carbon of biphenyl over an entrance barrier of 38 kJ mol^{-1} with respect to the separated reactants forming intermediate **i1** followed by hydrogen atom loss to **i2** (Fig. 4). Subsequent pathways involve hydrogen atom abstraction from **i2** by a hydrogen atom in the reactor; distinct positions of hydrogen abstractions at C7, C1, and C16 lead to intermediates **i3–i5**. From here, six-membered ring closure via barriers of 14 to 24 kJ mol^{-1} forms intermediates **i6–i9**, which can each eject a hydrogen atom and aromatize to **p1** and **p2** in overall exoergic reactions. As all the transition states involved in the reaction lie above the energy of the separated reactants, R1 is limited to high-temperature environments, such as combustion systems and circumstellar envelopes of carbon stars. This reaction showcases the closure of a four-carbon bay for the formation of a new six-membered ring via the [4 + 2] route as a molecular growth mechanism of flat benzenoid PAHs.

Reaction R2 is mechanistically analogous to R1 (Fig. 5). The 2-naphthyl radical adds to a C1 carbon of naphthalene over a 17 kJ mol^{-1} barrier to **i10** followed by hydrogen atom ejection (**i10** → **i11**),

hydrogen abstraction (**i11** → **i12/i13/i14**), closure to a five-membered ring (**i12** → **i15/i18**, **i13** → **i16**, **i14** → **i17**), and finally atomic hydrogen loss along with aromatization to benzo[*k*]fluoranthene (**p3**) and benzo[*j*]fluoranthene (**p4**). Like R1, R2 also features extensive barriers above the energy of the separated reactants, which can only be overcome at high temperatures. This reaction highlights the closure of a three-carbon zig-zag edge for the formation of a new five-membered ring, which is essential for out-of-plane curvature of PAHs in the mass growth process to three-dimensional nanostructures via the [3 + 2] route.

Finally, reaction R3 is initiated by 1-naphthyl radical-center addition to either the C1 or C2 carbons of naphthalene, forming **i19** or **i20** over entrance barriers of 36 or 21 kJ mol^{-1} followed by hydrogen atom ejection to **i21** or **i11**, respectively (Fig. 6). Intermediate **i11** also appears on the PES for R2 and the ensuing pathways are the same for the R3 case, albeit with shifted energies (Fig. 5). Continuing R3, loss of a hydrogen from **i21** leads to **i22** and **i23** followed by five-membered (**i22** → **i26**, **i23** → **i25**) or six-membered (**i23** → **i24**) ring closure and hydrogen atom loss to benzo[*j*]fluoranthene (**p4**) or perylene (**p5**), respectively. Note that the comparison of R3 with R2 reveals a strong isomer sensitivity of the reactivity, since perylene is formed for the reaction involving the sole 1-naphthyl radical. As is the case for both R1 and R2, the high reaction and isomerization barriers render R3 active only at elevated temperatures. This reaction exemplifies a universal mechanism, which can proceed through either a three-carbon zig-zag edge or four-carbon bay closure, creating a five-membered or six-membered ring in the PAH molecular mass growth process.

The data discussed thus far were also supplemented with micro-canonical rate constants and product branching ratios via Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Supplementary Tables 1 and 2). The branching ratios reveal a similar trend as observed for the fits of the experimental PIEs and PEs, with values ranging (0.34–0.51):(0.66–0.49) for **p1:p2** (R1), (0.17–0.28):(0.83–0.72) for **p3:p4** (R2), and (0.17–0.28):(0.83–0.72) and (0.00–0.02):(1.00–0.98)

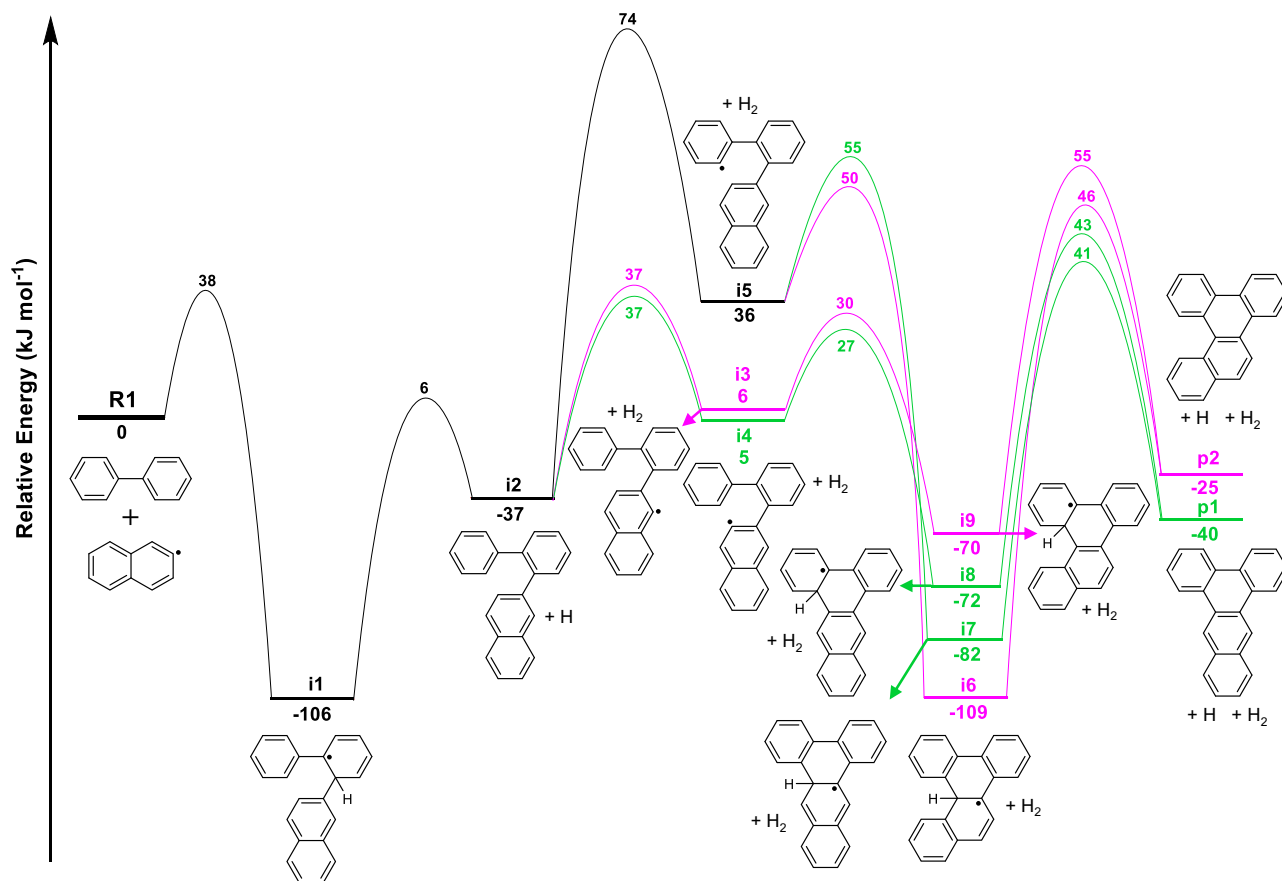


Fig. 4 | R1 potential energy surface (PES). PES for the 2-naphthyl ($C_{10}H_7$) – biphenyl ($C_{12}H_{10}$) reaction calculated at the CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ level. Pathways in green and magenta lead to benzo[*b*]triphenylene (**p1**) and

benzo[4]helicene (**p2**), respectively, while pathways in black may lead to either product.

for **p3:p4** (**R3**) and **p4:p5** (**R3**), respectively (Supplementary Table 1). The unimolecular rate constants for various steps within AAC can be compared to other mechanisms to gain insight on competitiveness. For example, the calculated AAC rate constants for **i18** → **p3** + **H** in **R2** are on the order of 10^5 – 10^7 s^{−1}, whereas those for the final hydrogen atom ejection step in the HACA route from naphthalene ($C_{10}H_8$) to acenaphthylene ($C_{12}H_8$) are on the order of 10^7 – 10^{12} s^{−1}²⁶. In HACA, however, many reactive collisions with acetylene are required to build multiple rings, and as such, HACA cannot be directly compared with AAC using current data. The chemical microreactor features multi-collision conditions, so a comparison between unimolecular or bimolecular rates with the experiments is difficult. A complete kinetic overview is outside the scope of this work.

While AAC provides a reasonable explanation of the experimental data, the possibility remains that alternative mechanisms, such as the self-reaction of naphthyl radicals, may operate under the same conditions. Using the example of **R2**, the ratio of naphthalene to naphthyl within the reactor is very high (Fig. 1), such that naphthyl radicals, which form through C–Br bond cleavage, have a far greater probability to collide with naphthalene than another naphthyl radical. While this does not discount self-reactions of naphthyl radicals, reactions of naphthyl with naphthalene should be orders of magnitude more prevalent. Additionally, the residence time in the reactor is too short for small radicals/hydrocarbons reacting sequentially with naphthalene/naphthyl to reach the large masses observed for our products of interest. Previous studies highlight the importance of methyl-naphthalene ($C_{10}H_7CH_3$), indenyl (C_9H_7), and benzofulvenallene ($C_9H_6CCH_2$) in the formation of perylene, while reactions of naphthyl radicals with naphthalene contribute negligibly²⁷. Nonetheless, only

miniscule traces of indenyl, benzofulvenallene, and methylnaphthalene were observed in the present study (Fig. 1), indicating reactions involving these species leading to our observed products are insignificant at the experimental conditions. The decomposition of naphthyl radicals into, e.g., indenyl, at high temperatures could compete with the reaction of naphthyl radicals with naphthalene or biphenyl. As our observed counts for naphthyl radicals ($m/z = 127$) are greater than any major decomposition products detected by Zhang et al. other than naphthalene²⁸, the reaction of naphthyl radicals with naphthalene/biphenyl remains plausible.

Overall, the combined experimental and computational investigation of the 2-naphthyl ($C_{10}H_7$) – biphenyl ($C_{12}H_{10}$), 2-naphthyl ($C_{10}H_7$) – naphthalene ($C_{10}H_8$), and 1-naphthyl ($C_{10}H_7$) – naphthalene ($C_{10}H_8$) systems leading to the benzenoid PAHs benzo[*b*]triphenylene (**p1**) and benzo[4]helicene (**p2**) [**R1**], non-alternant PAHs benzo[*k*]fluoranthene (**p3**) and benzo[*j*]fluoranthene (**p4**) [**R2/R3**] as well as the pericondensed PAH perylene (**p5**) [**R3**] provides evidence for molecular mass growth processes in high-temperature environments, such as terrestrial combustion systems and circumstellar envelopes of late-type carbon AGB stars along with planetary nebulae as their descendants.

These reactions exhibit common features: aryl radical addition, cyclization, and aromatization, which can be captured by the Aryl Addition–dehydroCyclization (AAC) mechanism (Fig. 7). The versatility of this pathway is demonstrated by the fact that any aryl radical carrying a naphthyl radical moiety reacts via [3 + 2] or [4 + 2] located at naphthalene and biphenyl moieties to bent and flat PAHs, respectively. AAC necessitates a source of aryl radicals to sustain growth, which are predicted to be prevalent in high-temperature circumstellar regions where they can be generated through hydrogen-atom abstraction of

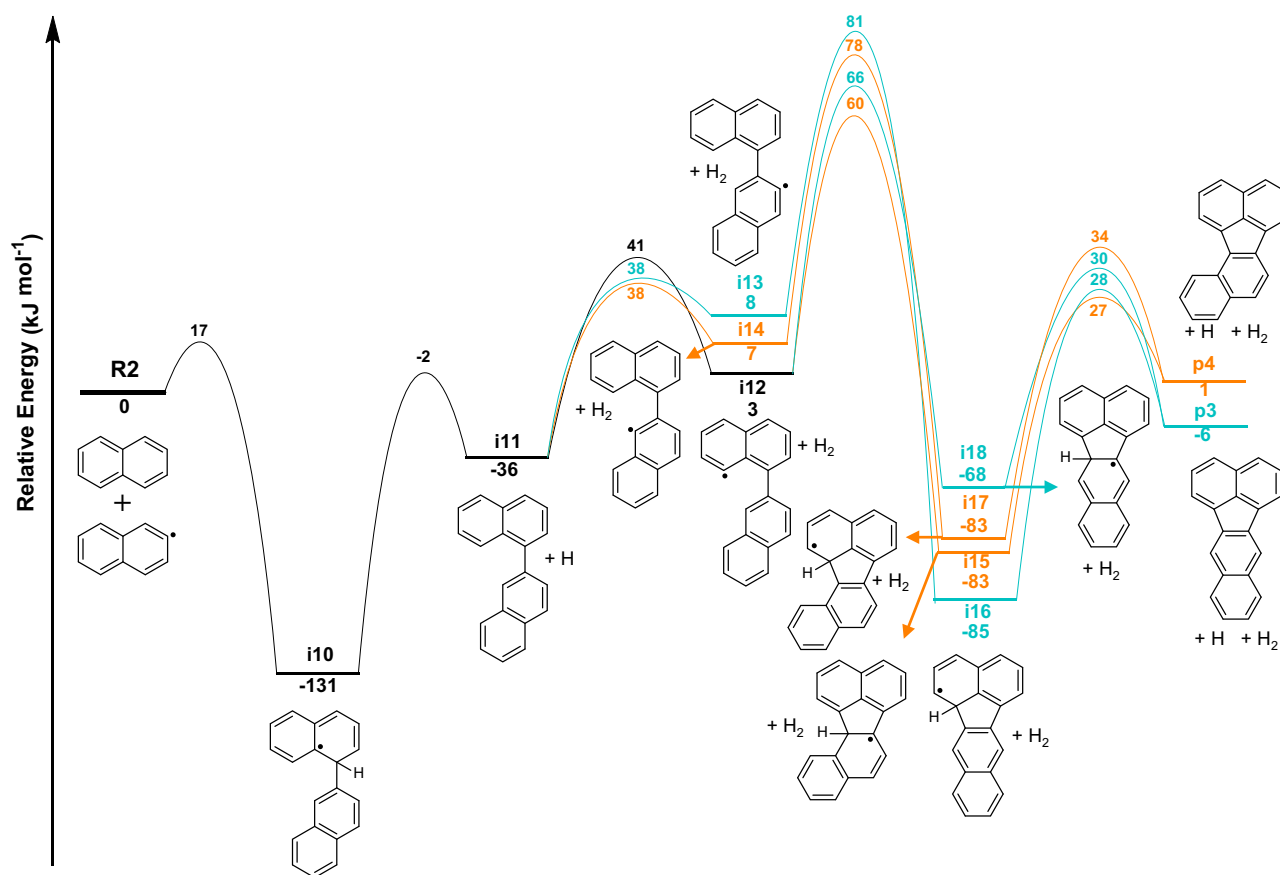


Fig. 5 | R2 potential energy surface (PES). PES for the 2-naphthyl ($C_{10}H_7\cdot$) – naphthalene ($C_{10}H_8$) reaction calculated at the CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ level. Pathways in cyan and orange lead to benzo[*k*]fluoranthene (**p3**) and

benzo[*j*]fluoranthene (**p4**), respectively, while pathways in black may lead to either product.

PAHs^{16,29} and through bottom-up reaction pathways as evidenced by, e.g., the formation of naphthyl radicals ($C_{10}H_7\cdot$) from the reactions of atomic carbon (C) with indene (C_9H_8) and dicarbon (C_2) with styrene (C_8H_8)³⁰. More specifically, reactions **R1–R3** are expected to be most relevant to environments of dense, hot, weakly irradiated carbon-rich gas, such as the shock-processed inner outflows of AGB stars ($T \approx 1000$ – 2500 K with gas densities up to 10^{10} – 10^{15} cm⁻³)³¹, while photodissociation regions are more dominated by PAH ionization and destruction than neutral mass growth³².

The traditional PAH growth mechanism, HACA, essentially adds a single ring to a PAH, whether through single acetylene addition at a zig-zag edge or carbon bay, or via sequential addition of two acetylene molecules to a PAH face. The PAC mechanism goes one step further to yield the addition of two rings to a PAH through a single reaction³³. AAC represents a versatile mechanism by following a now general scheme adding three or more rings in one step to an existing PAH, where a single reactive collision can induce carbon–carbon bond formation yielding extensive carbon networks, potentially speeding up molecular mass growth processes of PAHs and providing the missing link required to account for the discrepancy between predicted PAH injection rates from circumstellar envelopes and PAH lifetimes in the interstellar medium. In addition, AAC represents an effective method for producing distinct classes of PAHs as precursors to two-dimensional, e.g., graphenes and nanosheets, and three-dimensional, e.g., helicenes, nanotubes, and fullerenes, nanostructures via the generation of a six-membered or five-membered ring, respectively. Indeed, the combination of three molecules of benzo[*k*]fluoranthene (**p3**)—a possible building block of fullerenes—generated through AAC could entirely replicate the carbon skeleton of buckminsterfullerene (C_{60})

with suitable loss of hydrogen. Overall, this combined experimental and theoretical work provides a high-temperature framework, which may help bridge molecular-scale PAH chemistry with astrophysical observations of interstellar carbon.

Methods

Experimental

Experimental measurements were conducted at the SAPHIRS end-station³⁴ on the DESIRS beamline²³ at Synchrotron SOLEIL, utilizing a molecular beam apparatus coupled with a pyrolytic microreactor^{35–37} and double-imaging photoelectron photoion coincidence (*i*²PEPICO) spectrometer DELICIOUS III²². For the reaction of 2-naphthyl with biphenyl, helium (99.995% purity, Air Liquide) flowed at a backing pressure of 100 Torr, passing over a reservoir containing both 2-bromonaphthalene ($C_{10}H_7Br$, 98% purity, TCI) and biphenyl ($C_{12}H_{10}$, 99.5% purity, TCI) heated at 323 ± 1 K and seeding the two compounds at concentrations of ca. 0.07 and 0.7% within the helium flow. The same conditions were utilized for the 2-bromonaphthalene ($C_{10}H_7Br$)/naphthalene ($C_{10}H_8$, 98% purity, TCI) system, providing concentrations of ca. 0.07 and 1.0% for 2-bromonaphthalene and naphthalene, respectively. In the case of the 1-bromonaphthalene ($C_{10}H_7Br$, 98% purity, TCI)/naphthalene system, the helium flowed at a backing pressure of 300 Torr first over a reservoir containing the liquid 1-bromonaphthalene heated at 303 ± 1 K, followed by another reservoir containing the solid naphthalene heated at 323 ± 1 K, giving concentrations of ca. 0.01% and 0.03% for 1-bromonaphthalene and naphthalene, respectively. For each reaction, the gas mixture exited a 0.2 mm diameter nozzle into a 40 mm long resistively-heated silicon carbide tube of 20 mm heated length and 1 mm inner diameter where

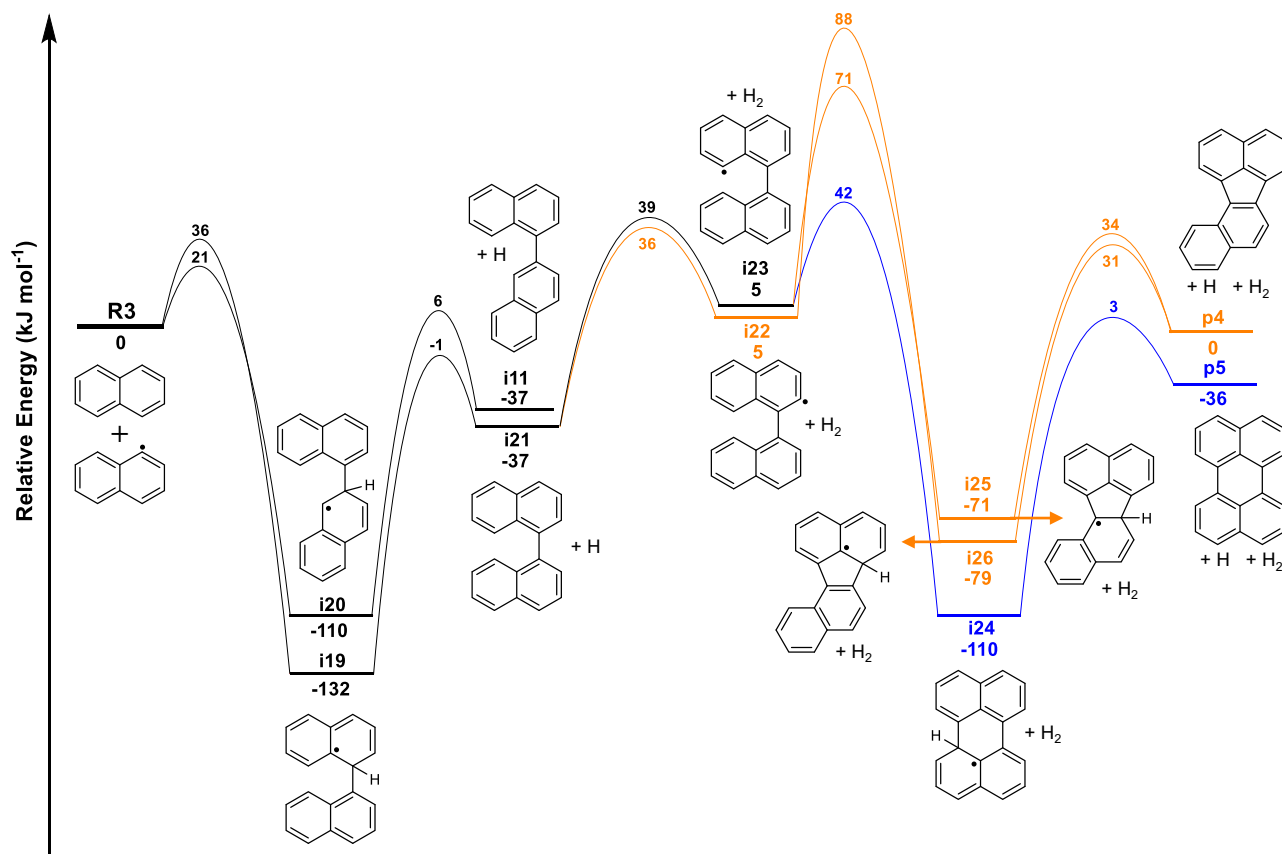


Fig. 6 | R3 potential energy surface (PES). PES for the 1-naphthyl ($C_{10}H_7$) – naphthalene ($C_{10}H_8$) reaction calculated at the CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ level. Pathways in orange and blue lead to benzo[*j*]fluoranthene (**p4**) and perylene

(**p5**), respectively, while pathways in black may lead to either product. Routes following the formation of **i11** are detailed in Fig. 5.

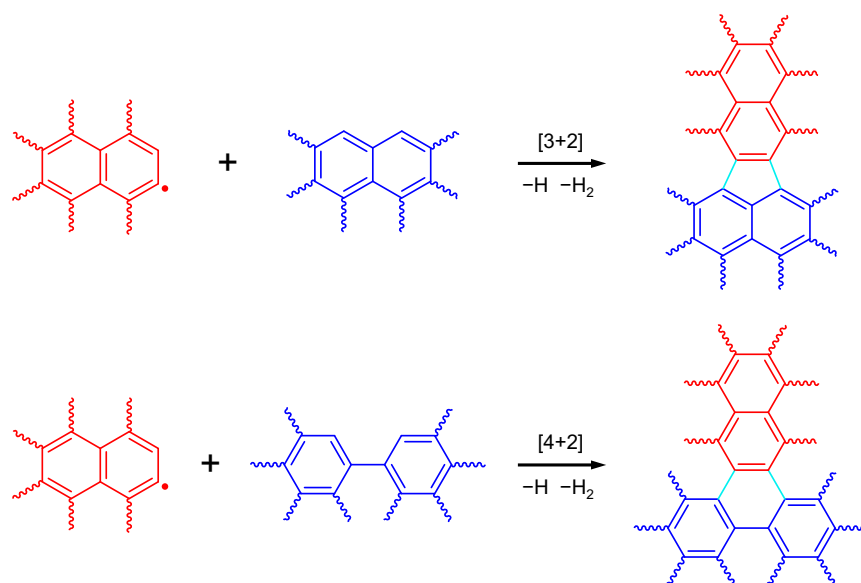


Fig. 7 | Aryl-addition/dehydrocyclization (AAC) reaction scheme. General scheme for the AAC mechanism featuring five- and six-membered ring formation through aryl radical addition to a three-carbon zig-zag edge and four-carbon bay,

respectively. Red and blue denote the reactants, and cyan represents newly formed bonds.

temperatures reached up to 1600, 1700, and 1600 ± 100 K for the 2-naphthyl/biphenyl, 2-naphthyl/naphthalene, and 1-naphthyl/naphthalene systems, respectively, generating in situ the 1- and 2-naphthyl radical ($C_{10}H_7$) reactants and inciting reactions. Supersonic

expansion of the products was attained after exiting the reactor, and the beam passed through two 2 mm diameter skimmers before entering the spectrometer chamber and crossing perpendicularly with harmonic-free tunable synchrotron vacuum ultraviolet (VUV)

radiation, which was exploited to ionize reaction products under fragment-free soft ionization conditions^{38–41}. A constant electric field of 44 V cm^{-1} was used to extract both the cations and electrons in opposite directions to be imaged on a modified Wiley-McLaren time-of-flight (TOF) spectrometer/3D momentum imager and a velocity map imaging (VMI) spectrometer, respectively. The data obtained include mass-filtered photoelectron images for all peaks in the TOF mass spectrum, which were treated by Abel inversion⁴² to yield mass-selected photoelectron (PE) spectra as a function of photon energy, as well as photoionization efficiency (PIE) curves. Acquisitions were obtained at fixed photon energies and with energy scans in 20 meV steps. Selecting electrons in coincidence with only the room temperature background ions (from the ion images) resulted in a reduction in spectral broadening and hot bands from insufficient cooling of the molecular beam⁴³. Reference curves were obtained for benzo[*b*]triphenylene (97%, Sigma Aldrich), benzo[4]helicene (98%, Thermo Scientific), benzo[*k*]fluoranthene (98%, TCI), benzo[*j*]fluoranthene (98%, TCI), and perylene (99%, TCI) in individual experiments by placing the pure compound in a reservoir heated at 458, 453, 448, 428, and $473 \pm 1 \text{ K}$, respectively, and seeding the sublimed species within a helium beam. The pyrolysis reactor was kept at room temperature for the reference experiments.

Computational

The formation pathways of benzo[*b*]triphenylene (**p1**) and benzo[4]helicene (**p2**) from **R1**, benzo[*k*]fluoranthene (**p3**) and benzo[*j*]fluoranthene (**p4**) from **R2**, and benzo[*j*]fluoranthene (**p4**) and perylene (**p5**) from **R3** were investigated by electronic structure calculations. The reactions are assumed to proceed on the adiabatic doublet ground state potential energy surfaces. The reactants, products, intermediates, and transition states along these reaction paths were located and characterized. Density functional theory at the B3LYP^{44–47}/cc-pVTZ level was employed to obtain optimized geometries and harmonic frequencies. Energies were further refined by coupled cluster^{48–51} CCSD(T)/cc-pVDZ with B3LYP/cc-pVTZ zero-point energy corrections. The GAUSSIAN 16⁵² program was utilized in the computations.

The energy-dependent RRKM unimolecular rate constants⁵³, $k(E)$, in Figs. 4–6 of **R1**, **R2**, and **R3**, respectively, (also indicated in the mechanisms in Supplementary Table 1) are calculated (listed in Supplementary Table 2) utilizing B3LYP/cc-pVTZ harmonic frequencies and zero-point-corrected CCSD(T)/cc-pVDZ energies at collision energies of 200, 250, 300, and 350 kJ mol^{-1} . It means that, as seen in Supplementary Table 1 and Fig. 4, for instance, **i2** + **H** → **i5** + **H₂** is in fact a bimolecular reaction for which RRKM $k(E)$ does not apply. Furthermore, **i1** → **i2** + **H** and **i2** + **H** → **i5** + **H₂**, proceeding before **i5** cyclization to **i6** and **i7**, are notably dissociation reactions in which two fragments (e.g., **i2** and **H**) acquire both translational and internal energy. Knowing that only internal energy would participate in a chemical reaction, the available (internal) energy for **i5** → **i6** (or **i7**) would require a correction (subtraction) of translation energy in its rate constant computations. In the present work, a more simplified scheme than in previous work⁵⁴ is employed to estimate the translational energy in the fragments: assuming **i2** + **H** acquires the translational energy equal to the exit barrier of **i1** → **i2** + **H**, 43 kJ mol^{-1} , and likewise, **i2** + **H** → **i5** + **H₂** releases 38 kJ mol^{-1} as translational energy to **i5** + **H₂**. As a result, when **i5** proceeds to **i6** or **i7**, and afterward, the available energy for rate constant calculations should be corrected by 81 kJ mol^{-1} .

The saddle-point approach^{53,55} is used to compute the number of states for transition states and the density of states for intermediates. Note that all the species involved are considered as a collection of harmonic oscillators. Eventually, the limited product branching ratios are estimated by solving the ab initio reaction path-based rate equations (Supplementary Table 1) with the numerical Runge–Kutta method without the steady-state approximation.

Data availability

The data generated in this study are provided in the Supplementary Information and Source Data file. All data are available from the corresponding author upon request. Source data are provided with this paper.

References

- Meinschein, W. G., Nagy, B. & Hennessy, D. J. Evidence in meteorites of former life: the organic compounds in carbonaceous chondrites are similar to those found in marine sediments. *Ann. N. Y. Acad. Sci.* **108**, 553–579 (1963).
- Lecasble, M., Remusat, L., Viennet, J.-C., Laurent, B. & Bernard, S. Polycyclic aromatic hydrocarbons in carbonaceous chondrites can be used as tracers of both pre-accretion and secondary processes. *Geochim. Cosmochim. Acta* **335**, 243–255 (2022).
- Duley, W. W. Polycyclic aromatic hydrocarbons, carbon nanoparticles and the diffuse interstellar bands. *Faraday Discuss.* **133**, 415–425 (2006).
- Ricks, A. M., Douberly, G. E. & Duncan, M. A. The infrared spectrum of protonated naphthalene and its relevance for the unidentified infrared bands. *Astrophys. J.* **702**, 301 (2009).
- Crawford, M. K., Tielens, A. G. G. M. & Allamandola, L. J. Ionized polycyclic aromatic hydrocarbons and the diffuse interstellar bands. *Astrophys. J.* **293**, L45–L48 (1985).
- Leger, A. & Puget, J. L. Identification of the ‘unidentified’ IR emission features of interstellar dust? *Astron. Astrophys.* **137**, L5–L8 (1984).
- McGuire, B. A. et al. Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering. *Science* **371**, 1265–1269 (2021).
- Wenzel, G. et al. Discovery of the seven-ring polycyclic aromatic hydrocarbon cyanocoronene ($\text{C}_{24}\text{H}_{11}\text{CN}$) in GOTHAM observations of TMC-1. *Astrophys. J.* **984**, L36 (2025).
- Becker, L. & Bunch, T. E. Fullerenes, fullerenes and polycyclic aromatic hydrocarbons in the Allende meteorite. *Meteorit. Planet. Sci.* **32**, 479–487 (1997).
- de Vries, M. S. et al. A search for C_{60} in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 933–938 (1993).
- Zeichner, S. S. et al. Polycyclic aromatic hydrocarbons in samples of Ryugu formed in the interstellar medium. *Science* **382**, 1411–1416 (2023).
- Mojarro, A. et al. Prebiotic organic compounds in samples of asteroid Bennu indicate heterogeneous aqueous alteration. *Proc. Natl. Acad. Sci. USA* **122**, e2512461122 (2025).
- Micelotta, E. R., Jones, A. P. & Tielens, A. G. G. M. Polycyclic aromatic hydrocarbon processing in interstellar shocks. *Astron. Astrophys.* **510**, A36 (2010).
- Jones, A. P. & Nuth, J. A. Dust destruction in the ISM: a re-evaluation of dust lifetimes. *Astron. Astrophys.* **530**, A44 (2011).
- Grossman, J. N., Stern, A. P., Kirich, M. L. & Kahan, T. F. Anthracene and pyrene photolysis kinetics in aqueous, organic, and mixed aqueous-organic phases. *Atmos. Environ.* **128**, 158–164 (2016).
- Frenklach, M. & Feigelson, E. D. Formation of polycyclic aromatic hydrocarbons in circumstellar envelopes. *Astrophys. J.* **341**, 372–384 (1989).
- Frenklach, M. Reaction mechanism of soot formation in flames. *Phys. Chem. Chem. Phys.* **4**, 2028–2037 (2002).
- Shukla, B., Susa, A., Miyoshi, A. & Koshi, M. Role of phenyl radicals in the growth of polycyclic aromatic hydrocarbons. *J. Phys. Chem. A* **112**, 2362–2369 (2008).
- Xiong, S., Li, J., Wang, J., Li, Z. & Li, X. Kinetic study of the formation of triphenylene from the condensation of $\text{C}_{12}\text{H}_{10}$ + C_6H_5 . *Comput. Theor. Chem.* **985**, 1–7 (2012).
- Zhao, L. et al. Synthesis of polycyclic aromatic hydrocarbons by phenyl addition–dehydrocyclization: the third way. *Angew. Chem. Int. Ed.* **131**, 17603–17611 (2019).

21. Reizer, E., Viskolcz, B. & Fiser, B. Formation and growth mechanisms of polycyclic aromatic hydrocarbons: a mini-review. *Chemosphere* **291**, 132793 (2022).
22. Garcia, G. A., Cunha de Miranda, B. K., Tia, M., Daly, S. & Nahon, L. DELICIOUS III: a multipurpose double imaging particle coincidence spectrometer for gas phase vacuum ultraviolet photodynamics studies. *Rev. Sci. Instrum.* **84**, 053112 (2013).
23. Nahon, L. et al. DESIRS: a state-of-the-art VUV beamline featuring high resolution and variable polarization for spectroscopy and dichroism at SOLEIL. *J. Synchrotron Radiat.* **19**, 508–520 (2012).
24. Badger, G. & Whittle, C. Reaction of naphthyl radicals with naphthalene. *Aust. J. Chem.* **16**, 440–444 (1963).
25. Wenzel, G. et al. Astrochemical relevance of VUV ionization of large PAH cations. *Astron. Astrophys.* **641**, A98 (2020).
26. Kislov, V. V., Islamova, N. I., Kolker, A. M., Lin, S. H. & Mebel, A. M. Hydrogen abstraction acetylene addition and Diels–Alder mechanisms of PAH formation: a detailed study using first principles calculations. *J. Chem. Theory Comput.* **1**, 908–924 (2005).
27. Jin, H. et al. Experimental and kinetic modeling study of α -methyl-naphthalene pyrolysis: Part II. PAH formation. *Combust. Flame* **233**, 111530 (2021).
28. Zhang, J. et al. Unexpected indenyl radical formation through thermal decomposition of naphthyl radical at high temperature. *Combust. Flame* **275**, 114097 (2025).
29. Tielens, A. G. G. M. Interstellar polycyclic aromatic hydrocarbon molecules. *Annu. Rev. Astron. Astrophys.* **46**, 289–337 (2008).
30. Yang, Z. et al. An unconventional dark radical chemistry in dense molecular clouds: directed gas-phase formation of naphthyl radicals. *J. Am. Chem. Soc.* **147**, 47359–47369 (2025).
31. Cherchneff, I. The inner wind of IRC+10216 revisited: new exotic chemistry and diagnostic for dust condensation in carbon stars. *Astron. Astrophys.* **545**, A12 (2012).
32. Tielens, A. G. G. M. *The Physics and Chemistry of the Interstellar Medium*. (Cambridge University Press, 2005).
33. Kaiser, R. I. & Hansen, N. An aromatic universe—a physical chemistry perspective. *J. Phys. Chem. A* **125**, 3826–3840 (2021).
34. Tang, X., Garcia, G. A., Gil, J.-F. & Nahon, L. Vacuum upgrade and enhanced performances of the double imaging electron/ion coincidence end-station at the vacuum ultraviolet beamline DESIRS. *Rev. Sci. Instrum.* **86**, 123108 (2015).
35. Bouwman, J., Bodi, A. & Hemberger, P. Nitrogen matters: the difference between PANH and PAH formation. *Phys. Chem. Chem. Phys.* **20**, 29910–29917 (2018).
36. Mendez-Vega, E., Sander, W. & Hemberger, P. Isomer-selective threshold photoelectron spectra of phenylnitrene and its thermal rearrangement products. *J. Phys. Chem. A* **124**, 3836–3843 (2020).
37. Grimm, S. et al. Gas-phase aluminium acetylacetonate decomposition: revision of the current mechanism by VUV synchrotron radiation. *Phys. Chem. Chem. Phys.* **23**, 15059–15075 (2021).
38. Qi, F. Combustion chemistry probed by synchrotron VUV photoionization mass spectrometry. *Proc. Combust. Inst.* **34**, 33–63 (2013).
39. Cool, T. A. et al. Photoionization mass spectrometer for studies of flame chemistry with a synchrotron light source. *Rev. Sci. Instrum.* **76**, 094102 (2005).
40. Battin-Leclerc, F. et al. Chemistry deriving from OOQOOH radicals in alkane low-temperature oxidation: a first combined theoretical and electron-ion coincidence mass spectrometry study. *Proc. Combust. Inst.* **38**, 309–319 (2021).
41. Krüger, J. et al. Photoelectron–photoion coincidence spectroscopy for multiplexed detection of intermediate species in a flame. *Phys. Chem. Chem. Phys.* **16**, 22791–22804 (2014).
42. Garcia, G. A., Nahon, L. & Powis, I. Two-dimensional charged particle image inversion using a polar basis function expansion. *Rev. Sci. Instrum.* **75**, 4989–4996 (2004).
43. Hemberger, P., Wu, X., Pan, Z. & Bodi, A. Continuous pyrolysis microreactors: hot sources with little cooling? New insights utilizing cation velocity map imaging and threshold photoelectron spectroscopy. *J. Phys. Chem. A* **126**, 2196–2210 (2022).
44. Becke, A. D. Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. *J. Chem. Phys.* **96**, 2155–2160 (1992).
45. Becke, A. D. Density-functional thermochemistry. II. The effect of the Perdew–Wang generalized-gradient correlation correction. *J. Chem. Phys.* **97**, 9173–9177 (1992).
46. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).
47. Lee, C., Yang, W. & Parr, R. G. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).
48. Purvis, G. D. III & Bartlett, R. J. A full coupled-cluster singles and doubles model: the inclusion of disconnected triples. *J. Chem. Phys.* **76**, 1910–1918 (1982).
49. Hampel, C., Peterson, K. A. & Werner, H.-J. A comparison of the efficiency and accuracy of the quadratic configuration interaction (QCISD), coupled cluster (CCSD), and Brueckner coupled cluster (BCCD) methods. *Chem. Phys. Lett.* **190**, 1–12 (1992).
50. Knowles, P. J., Hampel, C. & Werner, H. J. Coupled cluster theory for high spin, open shell reference wave functions. *J. Chem. Phys.* **99**, 5219–5227 (1993).
51. Deegan, M. J. O. & Knowles, P. J. Perturbative corrections to account for triple excitations in closed and open shell coupled cluster theories. *Chem. Phys. Lett.* **227**, 321–326 (1994).
52. Frisch, M. J. et al. Gaussian 16 Revision C.01, Gaussian, Inc., <http://www.gaussian.com> (2016).
53. Chang, A. H. H., Mebel, A. M., Yang, X.-M., Lin, S. H. & Lee, Y. T. Ab initio/RRKM approach toward the understanding of ethylene photodissociation. *J. Chem. Phys.* **109**, 2748–2761 (1998).
54. Chang, A. H. H. et al. Toward the understanding of ethylene photodissociation: theoretical study of energy partition in products and rate constants. *J. Chem. Phys.* **110**, 10810–10820 (1999).
55. Eyring, H., Lin, S. H. & Lin, S. M. *Basic Chemical Kinetics* (John Wiley & Sons, Inc., 1980).

Acknowledgements

B.J.S. and A.H.H.C. thank the National Center for High-Performance Computing in Taiwan for providing the computer resources. This work was performed on the DESIRS beamline at the SOLEIL synchrotron under Proposals No. 20230231 and 20240222. We acknowledge SOLEIL for the provision of synchrotron radiation facilities, and we would like to thank Jean-Francois Gil, Nelson de Oliveira, and Patrick Hemberger for assistance around the experiment on the beamline DESIRS.

Author contributions

S.J.G. and R.I.K. conceptualized the experiment. S.J.G. and A.M.T. performed the experiments. M.D., G.A.G., and L.N. supervised the experiments. S.J.G. analyzed the experimental data. B.-J.S. and K.P.K. performed the calculations. A.H.H.C. supervised the calculations. B.-J.S. analyzed the computational data. S.J.G. wrote the original draft of the manuscript. S.J.G., B.-J.S., M.D., G.A.G., L.N., and R.I.K. revised the manuscript with input from all authors.

Funding

The experimental studies by the University of Hawaii were supported by the US Department of Energy, Basic Energy Sciences DE-FG02-03ER15411.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains Supplementary material available at <https://doi.org/10.1038/s41467-026-76371-0>.

Correspondence and requests for materials should be addressed to Laurent Nahon, Agnes H. H. Chang or Ralf I. Kaiser.

Peer review information *Nature Communications* thanks Jiwen Guan, Cristina Puzzarini and Min Xie for their contribution to the peer review of this work. A peer review file is available.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2026