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A Free-Radical Pathway to Hydrogenated Phenanthrene in Molecular Clouds—Low Temperature Growth of Polycyclic Aromatic Hydrocarbons

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The hydrogen-abstraction/acetylene-addition mechanism has been fundamental to unravelling the synthesis of polycyclic aromatic hydrocarbons (PAHs) detected in combustion flames and carbonaceous meteorites like Orgueil and Murchison. However, the fundamental reaction pathways accounting for the synthesis of complex PAHs, such as the tricyclic anthracene and phenanthrene along with their dihydrogenated counterparts, remain elusive to date. By investigating the hitherto unknown chemistry of the 1-naphthyl radical with 1,3-butadiene, we reveal a facile *barrierless* synthesis of dihydrophenanthrene adaptable to low temperatures. These aryl-type radical additions to conjugated hydrocarbons via resonantly stabilized free-radical intermediates defy conventional wisdom that PAH growth is predominantly a high-temperature phenomenon and thus may represent an overlooked path to PAHs as complex as coronene and corannulene in cold regions of the interstellar medium like in the Taurus Molecular Cloud.

The hydrogen-abstraction/acetylene-addition (HACA) mechanism[1] has been instrumental for rationalizing the synthesis of polycyclic aromatic hydrocarbons (PAHs)—organic molecules carrying fused benzene rings—in high temperature combustion systems[2–3] and in circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars.[3–4] The ubiquity of PAHs along with their (de)hydrogenated, ionized, and side-chain-substituted counterparts in the interstellar medium (ISM)[5–6] is surmised from the unidentified infrared (UIR) emission bands (3 to 20 μm)[7–8] and the UV-bump[9–11]—an absorption feature superimposed on the interstellar extinction curve near 217.5 nm—that correlate with laboratory spectra of aromatic hydrocarbons. Although individual PAHs have not been detected in the ISM yet, the explicit identification of PAHs like phenanthrene and anthracene ($C_{14}H_{10}$) in carbonaceous chondrites like Murchison and Orgueil bearing anomalous $^{13}C/^{12}C$ and D/H isotopic ratios[12–15] strongly suggests an inter-stellar origin with fashionable astrochemical reaction networks mainly loaned from the combustion chemistry community.

Here, under fuel rich conditions, acetylene (C_2H_2) has been proposed to react with aromatic hydrocarbons undergoing ring formation and expansion through a series of bimolecular reactions assembled in the HACA mechanism. Kinetic modeling[16–19] along with electronic structure calculations[20–24] suggest recurring progressions of hydrogen atom abstractions from the aromatic hydrocarbon followed by sequential addition of two acetylene molecules to the radical sites prior to cyclization and aromatization. Recent studies exploiting tunable vacuum ultraviolet (VUV) light exposed that the naphthalene molecule ($C_{10}H_8$) can be formed via the reaction of the phenyl radical ($C_6H_5^{\bullet}$) with two acetylene molecules (C_2H_2)[25] through key transients in the HACA framework—styrenyl ($C_8H_7^{\bullet}$) and *ortho*-vinylphenyl ($C_8H_7^{\bullet}$).[26] HACA-type reactions involving naphthyl ($C_{10}H_7^{\bullet}$) and of biphenylyl radicals ($C_6H_5C_6H_4^{\bullet}$) with acetylene also produced the three-membered ring PAHs acenaphthylene ($C_{12}H_8$)[27] and phenanthrene ($C_{14}H_{10}$),[28] respectively, under combustion-relevant conditions.

High temperatures along with acetylene enrichment near the photospheres of carbon-rich AGB stars underscore HACA's applicability to describing soot production in these outflows. Aromatic species [benzene (C_6H_6) or phenyl (C_6H_5)] likely form within the envelope and undergo processing into polycyclic compounds via HACA[4] before exiting to the ISM as "free" PAHs, or condensed as carbonaceous grains or fullerenes.[4,29–30] Carbonaceous grains comprising aromatic interiors[31] could contribute to the interstellar PAH budget through shattering facilitated by turbulence or supernova-induced shockwaves that release aromatic content to the ISM.[32–33] However, in recent years, astronomical models combined with observations revealed that the destruction of interstellar PAHs and carbonaceous grains by, for example, high velocity shockwaves, limit their lifetime to a few 10^8 years.[34–35] This time span is much shorter than the PAH injection time from stellar sources, including C-rich AGB stars such as CW Leo (IRC+10216), of some 10^9 years, and thus the ubiquitous distribution of PAH-like species in the interstellar medium coupled with the less-than-expected production of PAHs in circumstellar envelopes suggests that crucial routes for the fast chemical growth of PAHs are missing. These routes may involve low temperature interstellar environments such as cold molecular clouds that hold temperatures down to 10 K. Considering the barriers of

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acetylene addition to aromatic radicals of typically 10 to 20 kJ mol^{-1},[20] HACA cannot operate in cold molecular clouds since these entrance barriers cannot be overcome. Therefore, key production routes to PAH-like species in the interstellar medium associated with molecular growth processes are clearly missing.

Herein, we report the reaction dynamics of the aromatic 1-naphthyl radical [$C_{10}H_7^{\bullet}$ (X^2A')] with 1,3-butadiene [C_4H_6 (X^1A_g)] under single collision conditions in a crossed molecular beam experiment (Experimental Methods; Supporting Information) as a prototype system of a barrier-less ring expansion in PAHs via aryl radical reactions with conjugated hydrocarbons.[36] A recent combined experimental, computational, and modeling study suggests that 1,3-butadiene can be synthesized in the gas phase via the reaction of the methylidyne radical (CH) with propylene (C_3H_6),[37] which are known constituents of the ISM. Combined with electronic structure calculations, our study exposes the first *barrierless* synthesis of a tricyclic PAH—1,4-dihydrophenanthrene ($C_{14}H_{12}$)—via ring expansion involving resonantly stabilized free radical (RSFR) intermediates that underscore PAH mass growth processes in the cold interstellar medium beyond the classical HACA framework. This system is also interesting from the viewpoint of a physical-organic chemist as a benchmark to unravel the chemical reactivity, bond breaking processes, and the synthesis of truly combustion and astrochemically relevant cyclic and aromatic hydrocarbons via bimolecular gas-phase reactions in single collision events.

In the crossed molecular beam reaction of the 1-naphthyl radical with 1,3-butadiene, scattering signal was probed for the adduct at *m/z* 181 ($C_{14}H_{13}^+$) and for the atomic and molecular hydrogen loss channels at *m/z* 180 ($C_{14}H_{12}^+$) and *m/z* 179 ($C_{14}H_{11}^+$), respectively. Considering that no signal was detectable at *m/z* 181 and that the time-of-flight spectra (TOF) at *m/z* 180 and *m/z* 179 are superimposable after scaling, only the atomic hydrogen loss channel leading to a hydrocarbon with the molecular formula $C_{14}H_{12}$ is open under the current experimental conditions. Therefore, TOF spectra were collected at *m/z* 180, then integrated and scaled to yield the laboratory angular distribution of $C_{14}H_{12}$, which depicts a relatively narrow spread of 10° holding a maximum close to the center-of-mass angle of 10.2 ± 1.1° (Figure 1). This shape proposes a complex forming reaction mechanism (indirect scattering dynamics) involving $C_{14}H_{13}$ reaction intermediate(s). However, considering that the hydrogen atom can be emitted from the 1-naphthyl radical and/or from the 1,3-butadiene reactant, the latter was substituted *ceteris paribus* by the isotopologue 1,3-butadiene-d_6 (C_4D_6). In this system, reactive scattering signal was probed at *m/z* 186 ($C_{14}H_6D_6^+$) and *m/z* 185 ($C_{14}H_7D_5^+$) at the center-of-mass angle 11.3 ± 1.1°. Signal was detected at *m/z* 186 and *m/z* 185. Within the signal-to-noise, the TOF of the *m* = 2 loss channel (*m/z* 185) overlays agreeably with that of the atomic hydrogen loss channel (*m/z* 186). Therefore, we can conclude that atomic hydrogen is emitted from the 1-naphthyl radical leading to signal at *m/z* 186, and that the signal observed at *m/z* 185 likely results from dissociative ionization of $C_{14}H_6D_6$. The corresponding TOF spectrum taken at *m/z* 186 at the center-of-mass is depicted in Figure 2. In summary, our laboratory data alone suggest that in the reaction of the 1-naphthyl radical with 1,3-butadiene, a hydrocarbon molecule of the formula $C_{14}H_{12}$ is formed via indirect reaction dynamics with the hydrogen atom displaced from the naphthyl moiety [Reaction (1)].

$$C_{10}H_7^{\bullet} + C_4H_6 \rightarrow C_{14}H_{12} + H \quad (1)$$

The goal of our investigation is not only to obtain the molecular formula of the reaction product ($C_{14}H_{12}$), but also to explore the structure(s) of the product isomer(s) together with the underlying reaction mechanism(s) and chemical dynamics possibly leading to PAH(s). This is accomplished through a forward-convolution routine that transforms the laboratory data into the center-of-mass reference frame.[38–39] The outcome is two 'best-fit" center-of-mass functions: the translational energy $P(E_T)$ and angular $T(\theta)$ flux distributions (Figure 3). It is important to highlight that the laboratory data could be fit with a single reaction channel leading to $C_{14}H_{12}$ plus atomic hydrogen via the 1-naphthyl radical and 1,3-butadiene reactants. The best fit center-of-mass (CM) angular flux distribution, $T(\theta)$, is isotropic and depicts flux over the complete scattering range. This finding is indicative of an indirect reaction mechanism that proceeds through the formation of rovibrationally excited $C_{14}H_{13}$ intermediate(s). Within the error limits, a slightly forward $T(\theta)$ distribution could fit the experimental data as well. The (nearly) isotropic distribution results from the inability of the light hydrogen atom to carry away a significant fraction of the initial total angular momentum.[40] Most important, the translational energy flux distribution, $P(E_T)$, reveals a maximum product translational energy (E_{max}) of 173 ± 25 kJ mol^{-1}. For molecules born without rovibrational excitation, E_{max} represents the sum of the collision energy plus the reaction exoergicity. Therefore, a subtraction of the collision energy from E_{max} reveals that the reaction to form $C_{14}H_{12}$ along with atomic hydrogen is exoergic by 104 ± 25 kJ mol^{-1}. Also, the $P(E_T)$ shows a distribution maximum at 14 ± 4 kJ mol^{-1}, which suggests that the unimolecular decomposition of the $C_{14}H_{13}$ complex involves a tight exit transition state. Therefore, the reverse reaction is characterized by an entrance barrier of hydrogen atom addition to a closed shell (unsaturated) hydrocarbon. Taken together, the center-of-mass functions $P(E_T)$ and $T(\theta)$ reveal that 1-naphthyl plus 1,3-butadiene reactively scatters forming a hydrogen atom plus the heavy $C_{14}H_{12}$ product via a (long-lived) $C_{14}H_{13}$ intermediate in an overall exoergic reaction.

We now merge these experimental results with the computational data to untangle the underlying reaction mechanism(s) and to evaluate to what extent reaction (1) can lead to the formation of a tricyclic PAH (Figure 4). The computations at the G3(MP2,CC)//B3LYP/6-311G** level of theory (Computational Methods; Supporting Information) reveal five exit channels leading to distinct $C_{14}H_{12}$ isomers, **p1** to **p5**, with overall exoergicities ranging from 16 to 106 kJ mol^{-1}. A comparison of these data with the experimental reaction energy of −104 ± 25 kJ mol^{-1} reveals that the formation of the thermodynamically most favorable isomer **p3** (1,4-dihydrophenanthrene) can account for the experimentally derived reaction energy; based

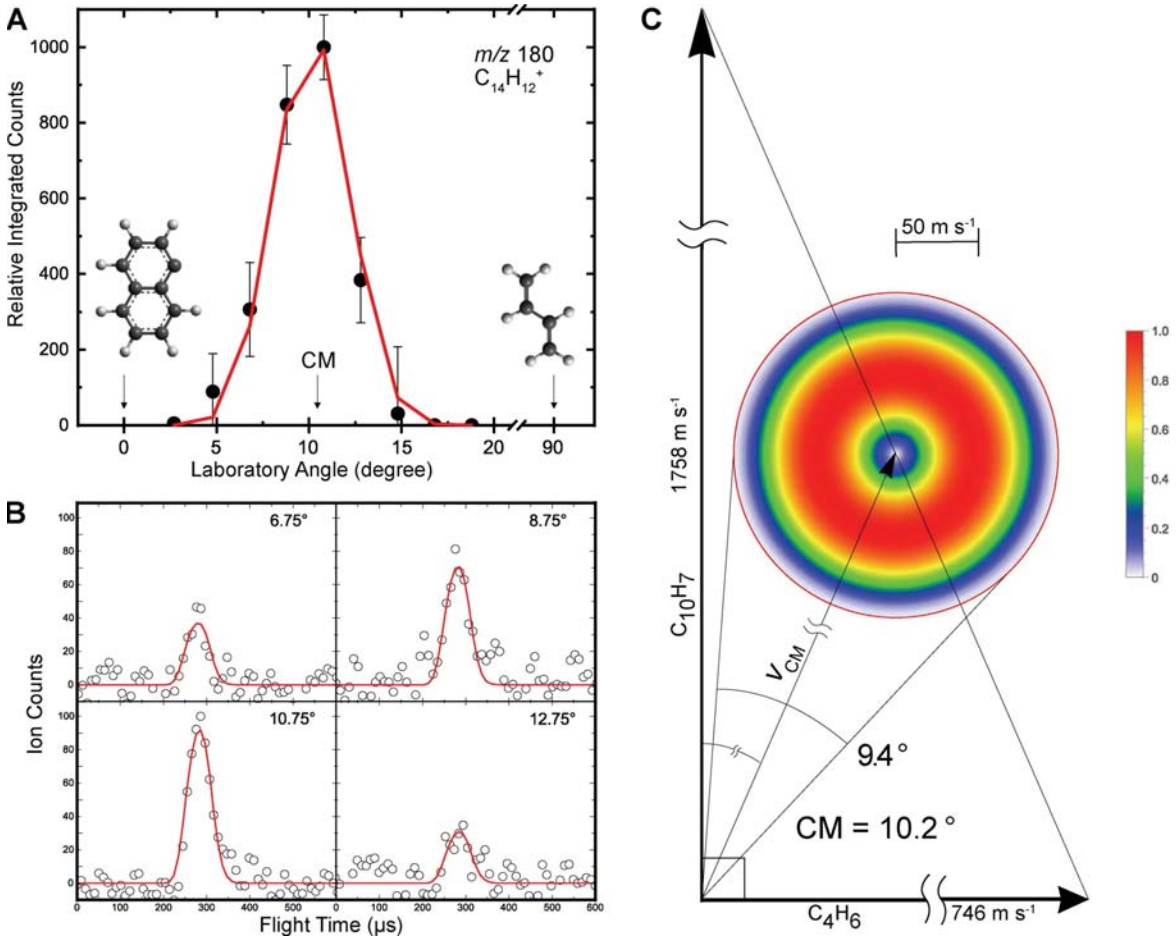


Figure 1. Laboratory angular distribution (A) and time-of-flight spectra (B) recorded at mass-to-charge 180 ($C_{14}H_{12}^+$) in the reaction of 1-naphthyl with 1,3-butadiene. The circles define the experimental data and the red lines represent the fitting based on the best-fit center-of-mass functions depicted in Figure 3. Error bars are standard error of the mean. The CM arrow indicates the center-of-mass angle. C) Newton diagram depicting the distribution of $C_{14}H_{12}$ produced in the crossed molecular beams reaction of 1-naphthyl + 1,3-butadiene. The differential cross section has a radius equal to the maximum center-of-mass velocity of $C_{14}H_{12}$.

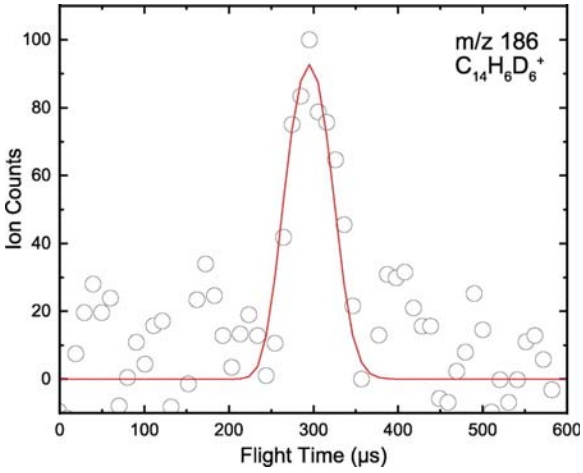


Figure 2. Time-of-flight spectrum taken at the center-of-mass angle for the reaction of 1-naphthyl with 1,3-butadiene-d_6 recorded at mass-to-charge ratio 186 ($C_{14}H_6D_6^+$). The circles define the experimental data and the red line represents the fitting based on the best-fit center-of-mass functions.

on the energetics alone, we cannot eliminate contributions of the thermodynamically less favorable isomers. The electronic structure calculations exposed a barrierless pathway to 1,4-dihydrophenanthrene initiated by the formation of a van-der-Waals complex **i0** from the separated reactants. This complex is weakly bound by 8 kJ mol^{-1} and isomerizes via a barrier of only 3 kJ mol^{-1} through addition of the radical center of the 1-naphthyl radical to the C1-carbon of 1,3-butadiene forming a resonantly stabilized intermediate **i1**. After a facile *cis-trans* isomerization from **i1** to **i2**, cyclization leads to intermediate **i3**, which is bound by 193 kJ mol^{-1} with respect to 1-naphthyl plus 1,3-butadiene. A hydrogen elimination from the bridging carbon atom leads to aromatization and formation of **p3** (1,4-dihydrophenanthrene) through a tight exit transition state that lies 25 kJ mol^{-1} above the separated products. This order of magnitude is in line with the experimental observation of an exit barrier close to 14 ± 4 kJ mol^{-1} with the hydrogen atom eliminated almost perpendicularly to the plane of the decomposing complex. It is important to recall that in the reaction of

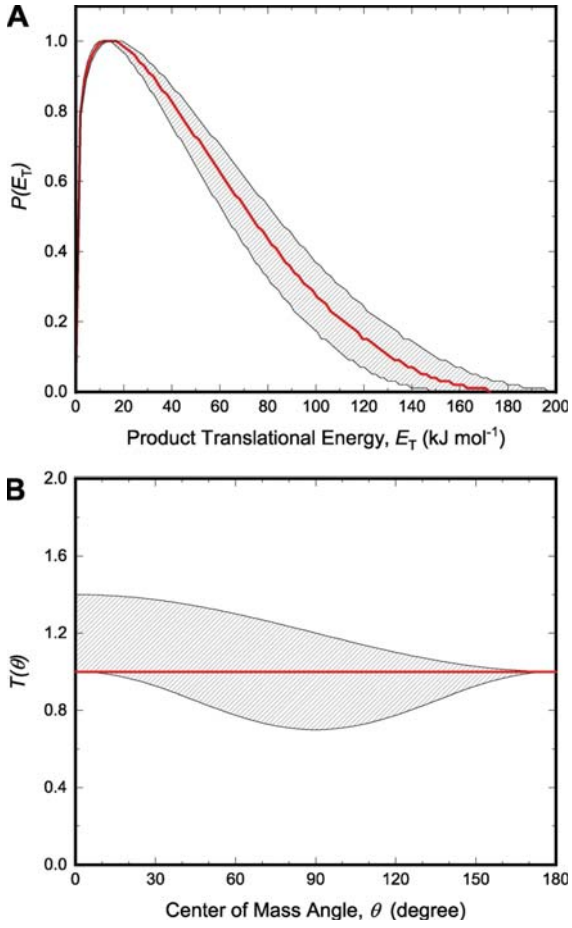


Figure 3. Center-of-mass translational energy flux distribution $P(E_T)$ (A) and angular flux distribution $T(\theta)$ (B) leading to the formation of the $C_{14}H_{12}$ molecule plus atomic hydrogen in the reaction of 1-naphthyl with 1,3-butadiene. Shaded areas indicate the acceptable upper and lower error limits of the fits. The red solid lines define the best-fit functions.

1-naphthyl with 1,3-butadiene-d_6, only the hydrogen atom loss was observed. Tracing the deuterium atoms in the 1,3-butadiene reactant supports this finding (Figure S1). Here, all deuterium atoms stay with the 1,3-butadiene moiety, and in the formation of 1,4-dihydrophenanthrene, the hydrogen atom is eliminated exclusively from the bridged carbon atom. Considering the energies of the barriers to isomerization, formation of **p1** (from **i1**), **p2** (from **i2**), **p4** (from **i1** via **i4**), and **p5** (from **i1** via **i5**) is unfavorable. At the low temperatures of the interstellar medium, alternative hydrogen abstraction pathways forming naphthalene plus C_4H_5 isomers along with the addition of the naphthyl radical to the C2 position of 1,3-butadiene are closed (Figure S2). However, these pathways may be open at elevated collision energies and equivalent higher temperatures.

Our experimental and computational investigation of the 1-naphthyl plus 1,3-butadiene reaction provides compelling evidence on the facile and barrierless formation of a three-ringed PAH—1,4-dihydrophenanthrene—under single collision conditions. The reaction follows indirect scattering dynamics and is initiated by the formation of a weakly-bound van-der-Waals complex, followed by the addition of the naphthyl radical to the C1-carbon of C_4H_6 yielding a resonantly stabilized free radical intermediate. The latter isomerized in two steps ultimately leading to 1,4-dihydrophenenthrene accompanied by hydrogen atom loss and aromatization. In the cold interstellar medium, due to the absence of an entrance barrier and location of all inherent barriers to isomerization residing below the energy of the separated reactants, this reaction leads *exclusively* to 1,4-dihydrophenanthrene. Indeed, statistical (Rice-Ramsperger-Kassel-Marcus; RRKM) calculations carried out for zero-pressure conditions corresponding to crossed molecular beam experiments as well as to cold molecular clouds showed that the relative yield of 1,4-dihydrophenanthrene changes only very slightly from 100% at zero collision energy to 99.5% at the collision energy of 100 kJ mol^{-1} if one considers the barrierless addition channels of 1-naphthyl to 1,3-butadiene. At the high collision energy, about 0.4% of the **p1** product is predicted to be formed. However, under combustion-relevant conditions at finite pressures, the reaction changes likely to a multichannel process that produces energetically less favorable $C_{14}H_{12}$ isomers along with potential hydrogen abstraction products. It is worth mentioning however that the difference in the exit barrier heights to form 1,4-dihydrophenanthrene and **p1** is 61 kJ mol^{-1}, that is 15 kJ mol^{-1} higher than the difference in the barrier heights to form 1,4-dihydronaphthalene and the one-ring analog of **p1** in the phenyl + 1,3-butadiene reaction.[41] This change originates from the additional aromatic stabilization due to the presence of the extra ring and results in a higher yield of 1,4-dihydrophenanthrene as compared to that of 1,4-dihydronaphthalene from $C_6H_5 + C_4H_6$.[41] Therefore, for larger PAHs, the analogous reactions of their radicals with 1,3-butadiene are anticipated to lead to a one-ring extension even more efficiently.

Considering that the related reactions of the phenyl radical with 1,3-butadiene[41] and vinylacetylene[42] synthesize 1,4-dihydronaphthalene and naphthalene, respectively, via submerged barriers, and that the 1-naphthyl-1,3-butadiene system leads solely to 1,4-dihydrophenanthrene at ultralow temperatures, our present works leads us to the prediction that the reaction of the 1-napthyl and 2-napthyl radicals with vinylacetylene is likely to result in the barrierless formation of phenanthrene and anthracene ($C_{14}H_{10}$) in the cold interstellar medium, such as in the Taurus Molecular Cloud TMC-1 (Scheme 1). Our recent RRKM—Master Equation calculations have shown that in the prototype phenyl plus vinylacetylene reaction naphthalene remains a major or significant low-temperature product up to the pressure of 10^{-7} bar.[43] This mechanism represents a hitherto overlooked low-energy (temperature) pathway to PAH growth—among them catacondensed $C_{14}H_{10}$ and $C_{14}H_{12}$ isomers—in the interstellar medium, and may resemble a key pathway for the addition of six-membered rings to existing PAHs that lack a bay-region. Once those pathways of 1- and 2-napthyl radicals with vinylacetylene have been unraveled, astrochemists and combustion scientists will be in the position to quantify the contribution of vinylacetylene and 1,3-buta-

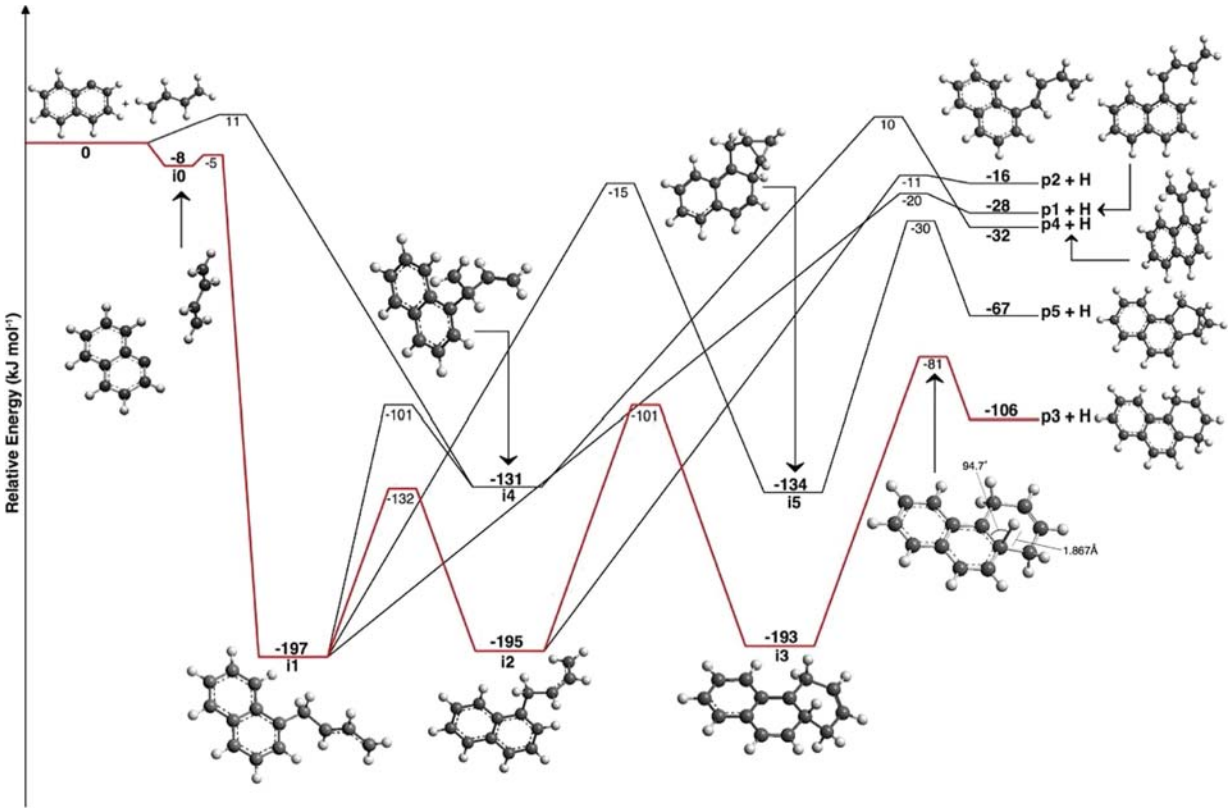
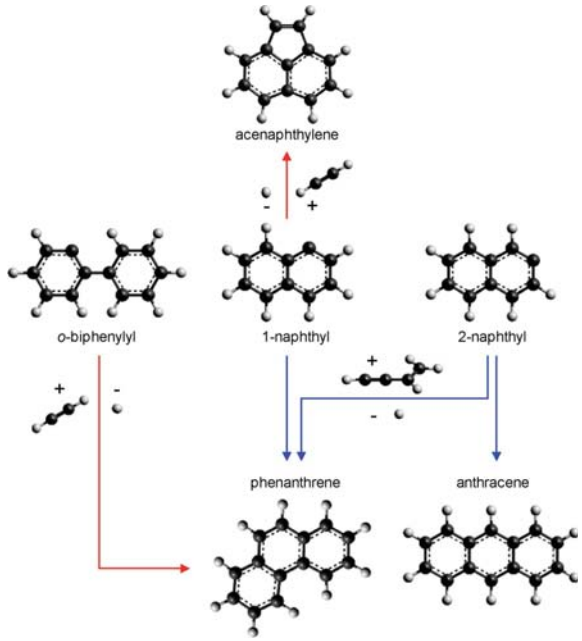


Figure 4. Potential energy surface for the reaction of 1-naphthyl [$C_{10}H_7^{\bullet}$ (X^2A')] plus 1,3-butadiene [C_4H_6 (X^1A_g)] depicting hydrogen-loss channels. Energies are relative to the separated reactants; energies are given in kJ mol^{-1}. The minimum energy path leading to the 1,4-dihydrophenanthrene ($C_{14}H_{12}$) plus atomic hydrogen products is highlighted in red. Details on the structures and vibrational frequencies are compiled in the Supporting Information.



Scheme 1. C_2H_2 addition to *o*-biphenylyl, 1-napthyl, and 2-naphthyl is inhibited by an entrance barrier (red), while that of C_4H_4 proceeds barrierlessly and is thus viable at extremely low temperatures (blue). All paths shown are exoergic overall.

diene mediated routes to PAHs in distinct extreme environments.

In conclusion, our study reveals the first low temperature pathway accounting for the barrierless formation of a tricyclic (polycyclic) aromatic hydrocarbon—1,4-dihydrophenanthrene ($C_{14}H_{12}$)—via the elementary bimolecular gas phase reaction of the 1-naphthyl radical ($C_{10}H_7^{\bullet}$) with 1,3-butadiene (C_4H_6). The reaction proceeds by a de-facto barrierless addition of the naphthyl radical with its radical center to the H_2C moiety of the 1,3-butadiene reactant—facilitated by a weakly bound van der Waals complex—followed by isomerization and atomic hydrogen loss accompanied by aromatization to form 1,4-dihydrophenanthrene. Statistical (RRKM) calculations confirm that the pathway leading to 1,4-dihydrophenanthrene plus atomic hydrogen accounts for 100% of all products in the limit of zero collision energy as closely present in cold molecular clouds such as TMC-1. This combination of experimental, ab initio, and statistical methodologies presented in this work reveals a novel reaction mechanism of aryl-type radical additions to conjugated hydrocarbon systems like 1,3-butadiene and vinylacetylene (C_4H_4), and changes how we think about molecular growth processes to PAHs in the cold regions of space.

Experimental Section

See the Supporting Information.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aryl radicals · astrochemistry · gas phase chemistry · mass spectrometry · polycyclic aromatic hydrocarbon

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