

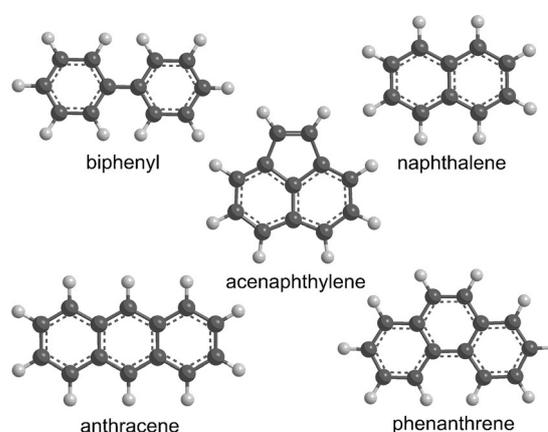
# HACA's Heritage: A Free-Radical Pathway to Phenanthrene in Circumstellar Envelopes of Asymptotic Giant Branch Stars

Tao Yang, Ralf I. Kaiser,\* Tyler P. Troy, Bo Xu, Oleg Kostko, Musahid Ahmed,\* Alexander M. Mebel,\* Marsel V. Zagidullin, and Valeriy N. Azyazov

**Abstract:** The hydrogen-abstraction/acetylene-addition (HACA) mechanism has been central for the last decades in attempting to rationalize the formation of polycyclic aromatic hydrocarbons (PAHs) as detected in carbonaceous meteorites such as in Murchison. Nevertheless, the basic reaction mechanisms leading to the formation of even the simplest tricyclic PAHs like anthracene and phenanthrene are still elusive. Here, by exploring the previously unknown chemistry of the *ortho*-biphenyl radical with acetylene, we deliver compelling evidence on the efficient synthesis of phenanthrene in carbon-rich circumstellar environments. However, the lack of formation of the anthracene isomer implies that HACA alone cannot be responsible for the formation of PAHs in extreme environments. Considering the overall picture, alternative pathways such as vinylacetylene-mediated reactions are required to play a crucial role in the synthesis of complex PAHs in circumstellar envelopes of dying carbon-rich stars.

The omnipresence of polycyclic aromatic hydrocarbons (PAHs)—organic molecules composed from fused benzene rings—as well as their ionized, (de)hydrogenated, and protonated counterparts in the interstellar medium<sup>[1–3]</sup> has been inferred from the diffuse interstellar bands (DIBs)<sup>[4,5]</sup>—discrete absorption features overlaid on the interstellar extinction curve from the blue part of the visible (400 nm) to the near-infrared (1.2  $\mu\text{m}$ )—and from unidentified infrared (UIR) emission bands in the 3–14  $\mu\text{m}$ <sup>[6]</sup> wavelength range. Also, a proposition has been made that PAHs represent the missing link between small carbon-containing molecules as

well as clusters and amorphous carbon particles in the interstellar medium, and potentially comprise up to 20% of the carbon budget.<sup>[7]</sup> This hypothesis links PAHs to the prebiotic evolution of the interstellar medium (Figure 1).<sup>[8–13]</sup> The explicit discovery of PAHs in carbonaceous chondrites suggests an interstellar origin<sup>[14,15]</sup> with contemporary astrochemical models on PAH formation “borrowed” from the combustion flame models.



**Figure 1.** Structures of biphenyl, naphthalene, acenaphthylene, anthracene, and phenanthrene.

Here, the hydrogen-abstraction/acetylene-addition (HACA) mechanism<sup>[16]</sup> has been instrumental in an attempt to explain the potential formation of PAHs in circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars and also in combustion systems.<sup>[17–20]</sup> Based on electronic structure calculations<sup>[19,21–24]</sup> and kinetic modeling,<sup>[16,25–29]</sup> HACA has been suggested to involve a repetitive sequence of atomic hydrogen abstraction from the reacting aromatic hydrocarbon followed by sequential addition of two acetylene molecules to the radical sites prior to cyclization and aromatization.<sup>[17,19,25,29]</sup> Very recently, it was revealed that the naphthalene molecule ( $\text{C}_{10}\text{H}_8$ ) can indeed be synthesized via the reaction of the phenyl radical ( $\text{C}_6\text{H}_5\cdot$ ) with two acetylene molecules ( $\text{C}_2\text{H}_2$ ) involving the HACA mechanism,<sup>[30]</sup> which was further proved via the reactions of styrenyl ( $\text{C}_8\text{H}_7\cdot$ ) and *ortho*-vinylphenyl ( $\text{C}_8\text{H}_7\cdot$ )—key transient species of HACA mechanism—with acetylene under combustion-like conditions, respectively.<sup>[31]</sup> However, the validity of HACA to form PAHs beyond naphthalene has remained conjectural, since not a single experiment could corroborate to what extent more complex PAHs like anthracene ( $\text{C}_{14}\text{H}_{10}$ ) and phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ) were formed.

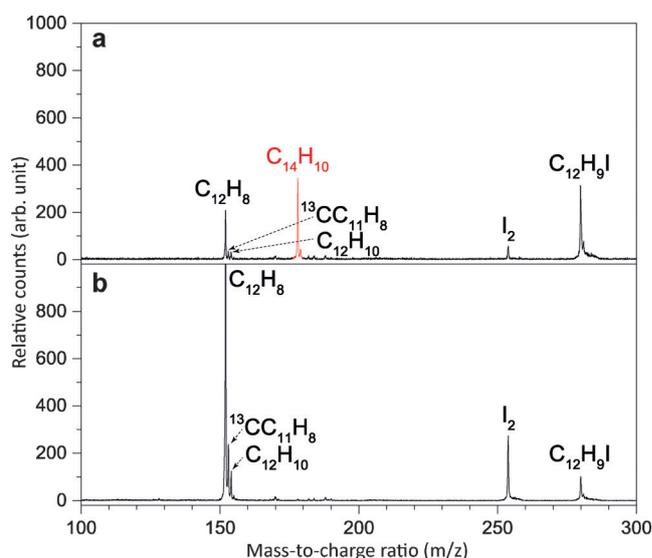
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A computational study by Mebel et al.<sup>[24]</sup> revealed that the ring growth involving HACA fails once expanded beyond two-membered ring PAHs and terminates with naphthalene and acenaphthylene ( $C_{12}H_8$ ).<sup>[19,21,32]</sup> These predictions were confirmed by Parker et al. revealing that the reaction of naphthyl radicals ( $C_{10}H_7^{\cdot}$ ) with acetylene ceases with the synthesis of acenaphthylene,<sup>[33]</sup> but does not lead to anthracene or phenanthrene as hypothesized.<sup>[25–29]</sup> Frenklach,<sup>[34]</sup> Mebel,<sup>[35]</sup> and Shukla<sup>[36]</sup> speculated that phenanthrene may be formed via reactions involving biphenyl ( $C_6H_5C_6H_4^{\cdot}$ ), but the reaction mechanism still remain ambiguous. Consequently, the potential ubiquitous presence of PAHs in the interstellar medium on one hand, and the unknown formation mechanism of PAHs on the other hand represents one of the greatest mysteries in astrochemistry.<sup>[37]</sup>

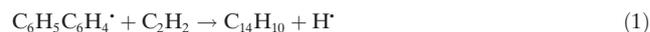
In this work, by exploring the reaction of the *ortho*-biphenyl radical (*o*-biphenyl) ( $C_6H_5C_6H_4^{\cdot}$ ;  $C_{12}H_9^{\cdot}$ ; 153 amu) with acetylene ( $C_2H_2$ ; 26 amu) under high temperature conditions, we untangle the hitherto unknown chemistry leading to the formation of the phenanthrene molecule ( $C_{14}H_{10}$ ; 178 amu) along with atomic hydrogen. Our study reveals compelling experimental evidence on the explicit synthesis of the prototype of a tricyclic PAH carrying three fused benzene rings—phenanthrene—via mass growth involving the elementary reaction of an aromatic radical—*o*-biphenyl—with a single acetylene molecule. In brief, phenanthrene was synthesized in a high temperature chemical reactor through a directed synthesis via the reaction of *o*-biphenyl with acetylene, and the isomer-specific products were probed by exploiting fragment-free photoionization of the products utilizing tunable vacuum ultraviolet (VUV) light in tandem with the detection of the ionized molecules by a high resolution reflectron time-of-flight mass spectrometer (Re-TOF-MS) (Supporting Information).

Figure 2 illustrates a typical mass spectrum recorded at a photoionization energy of 9.50 eV for the reaction of *o*-biphenyl with acetylene (Figure 2a); reference spectra were also recorded by replacing the acetylene reactant with the non-reactive helium carrier gas (Figure 2b). These data provide explicit evidence on the formation of a molecule with the molecular formula  $C_{14}H_{10}$  (178 amu) in the *o*-biphenyl–acetylene system (Figure 2a), which is absent in the control experiment exploiting helium carrier gas (Figure 2b). Therefore, considering the molecular weight of the reactants and the products, we conclude that the  $C_{14}H_{10}$  molecule(s) along with the atomic hydrogen is formed via the reaction of *o*-biphenyl with acetylene via reaction (1). Consequently, the interpretation of the mass spectra alone provides clear evidence that in the reaction of *o*-biphenyl with acetylene, a molecule with the formula  $C_{14}H_{10}$  is formed. Note that signal at mass-to-charge ratio ( $m/z$ ) 152 ( $C_{12}H_8^+$ ), 153 ( $^{13}CC_{11}H_8^+$ ), and 154 ( $C_{12}H_{10}^+$ ) along with  $m/z$  254 ( $I_2^+$ ) and 280 ( $C_{12}H_9I^+$ ) is observable in both the *o*-biphenyl–acetylene and the *o*-biphenyl–helium systems. Therefore, those masses do not stem from reactions between *o*-biphenyl and acetylene. Here, signal at  $m/z$  280 can be attributed to the parent ion of the non-pyrolyzed *ortho*-iodobiphenyl precursor ( $C_{12}H_9I$ ), whereas signal at  $m/z$  254 can be linked to the iodine molecule, formed via recombination of iodine

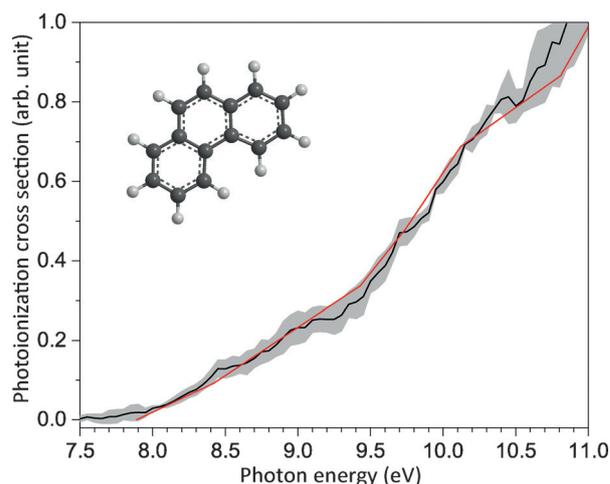


**Figure 2.** Comparison of photoionization mass spectra. Mass spectra of a) *o*-biphenyl–acetylene and b) *o*-biphenyl–helium systems were recorded at a photoionization energy of 9.50 eV. The mass peak of  $C_{14}H_{10}$  isomer(s) is colored red.

atoms as released via the pyrolysis of *ortho*-iodobiphenyl in the chemical reactor.



Having identified the molecular formula of the hydrocarbon molecule(s) synthesized in the reaction of *o*-biphenyl with acetylene as  $C_{14}H_{10}$ , we assign the structural isomer(s) formed. This required the analysis of the corresponding photoionization efficiency (PIE) curve, which reports the intensity of the ions at  $m/z$  178 ( $C_{14}H_{10}^+$ ) as a function of the photon energy from 7.50 eV and 11.00 eV (Figure 3). These data are compared with known reference



**Figure 3.** Comparison of the photoionization efficiency (PIE) curves. The black curve indicates the PIE curve recorded at  $m/z$  178 ( $C_{14}H_{10}^+$ ) in the *o*-biphenyl–acetylene system. The shaded area shows the  $1\sigma$  error limits of the experimental data. The red line represents the reference PIE curve for phenanthrene. The PIE curves are normalized.

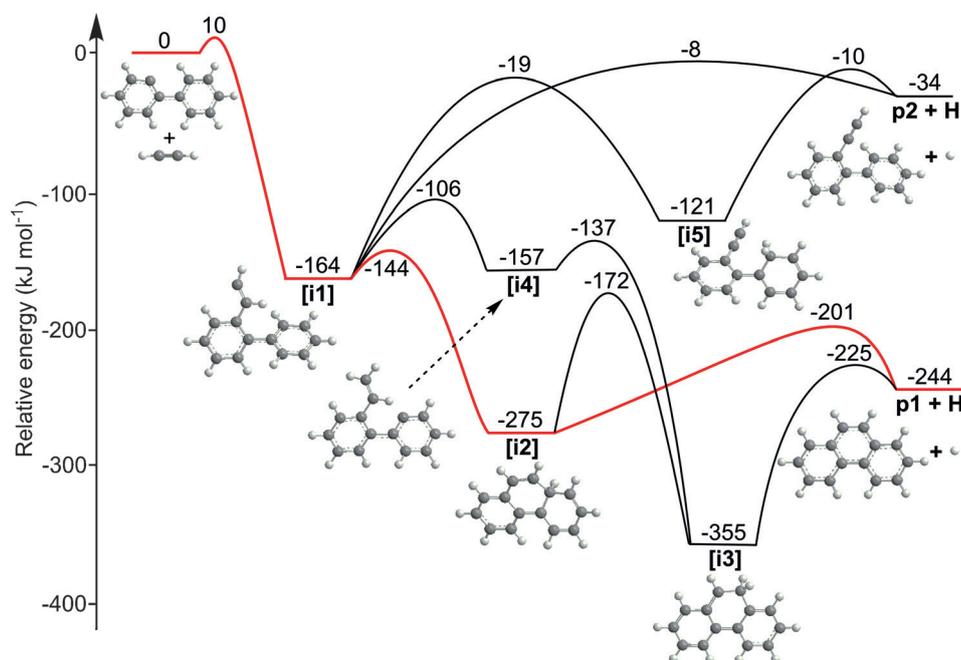
PIE curves for distinct  $C_{14}H_{10}$  isomers such as anthracene and phenanthrene. The experimental PIE curve at  $m/z$  178 can be reproduced well by the reference PIE curve of phenanthrene ( $C_{14}H_{10}$ )<sup>[38]</sup> superimposed in red; both the experimental and reference PIE curves depict onsets of the ion signal at  $7.89 \pm 0.04$  eV.<sup>[38–40]</sup> Note that the adiabatic ionization energy of the anthracene, whose PIE curve cannot reproduce the experimental data, was determined to be  $7.44 \pm 0.01$  eV; likewise, the adiabatic ionization energy of the ethynyl-biphenyl isomer was computed to be  $8.09 \pm 0.05$  eV.<sup>[38,40]</sup> The PIE identification of the product isomers at  $m/z$  152, 153 and 154 is illustrated in Supplementary Figure 1. It is important to point out that the PIE curves of  $C_{14}H_{10}$  isomers are distinctively correlated to each molecule stressing that the co-existence of alternative isomers in the molecular beam would alter the shape of the PIE considerably. Therefore, we conclude that phenanthrene exemplifies the only sole contributor to signal at  $m/z$  178 within our error limits.

Our experiments demonstrate that the prototype of a PAH carrying three fused benzene rings—phenanthrene—can be synthesized in the *o*-biphenyl-acetylene system. Supported by the G3(MP2,CC)//B3LYP calculations of the pertinent potential energy surface (PES) (Figure 4), we propose that this formation is dictated by the addition of the radical center of *o*-biphenyl to the acetylene molecule via a barrier of only  $10$  kJ mol<sup>-1</sup> followed by ring-closure of the  $C_{14}H_{11}$  collision complex [i1] by passing a transition state located  $20$  kJ mol<sup>-1</sup> above the complex leading to [i2]. The entrance barrier can be easily overcome in high temperature terrestrial and circumstellar environments. The tricyclic  $C_{14}H_{11}$  intermediate [i2] eventually eliminates atomic hydro-

gen and aromatizes via a tight transition state located  $43$  kJ mol<sup>-1</sup> above the energy of the separated products forming phenanthrene (p1) plus atomic hydrogen in an overall exoergic reaction ( $-244$  kJ mol<sup>-1</sup>). Alternative pathways involving intermediates [i3] and [i4] were found to be less competitive. The only other possible product is *ortho*-ethynylbiphenyl p2, which can be formed by the hydrogen loss from [i1] or by atomic hydrogen shift from the acetylene moiety to the opposite aromatic ring producing [i5] followed by hydrogen elimination from the newly formed  $CH_2$  group. The product p2 resides  $34$  kJ mol<sup>-1</sup> below the reactants and is much less exoergic than phenanthrene (p1). The critical transition states for the hydrogen atom losses lie at  $-8$  and  $-10$  kJ mol<sup>-1</sup> with respect to the reactant system. The pathways to p2 are clearly less favorable than the one to phenanthrene in terms of enthalpy, but may play a role at high temperatures because they are less entropically demanding.

To transfer our results from the laboratory to “real” circumstellar environments, a RRKM-Master Equation calculation provide critical temperature- and pressure-dependent rate constants for *o*-biphenyl plus acetylene reaction (Supplementary Information). The total reaction rate constant is practically independent of pressure up to 100 atm range and exhibits Arrhenius behavior steadily increasing from  $2.7 \times 10^{-14}$  to  $4.8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The fall-off from the high-pressure (HP) limit is noticeable above 1500 K and the  $k_{HP}/k_{finite}$  ratio reaches 1.95 at 2500 K. Phenanthrene is predicted to be the preferable product in the entire considered temperature range of 500–2500 K except at the high pressure of 100 atm and low temperatures up to 900 K where the combined yield of the stabilized intermediates [i1] and

[i2] is higher. While the branching ratios of the p2 product are insignificant below 1500 K, they grow steadily with temperature and slightly exceed that of phenanthrene at 2500 K. Nevertheless, the calculations clearly demonstrate, in synergism with our experimental observations, that phenanthrene is the major product of *o*-biphenyl plus acetylene in typical combustion and circumstellar envelopes such as of the carbon star IRC + 10216 holding temperatures up to 2000 K close to the central star. In the 1000–2500 K temperature interval, the rate constants to form phenanthrene depend on pressure within the 0.04–100 atm interval only slightly and vary in the range of  $4 \times 10^{-13}$ – $2.6 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, with a maximum at 2000 K. At the zero-pressure limit, the rate constants for the formation of phenanthrene are

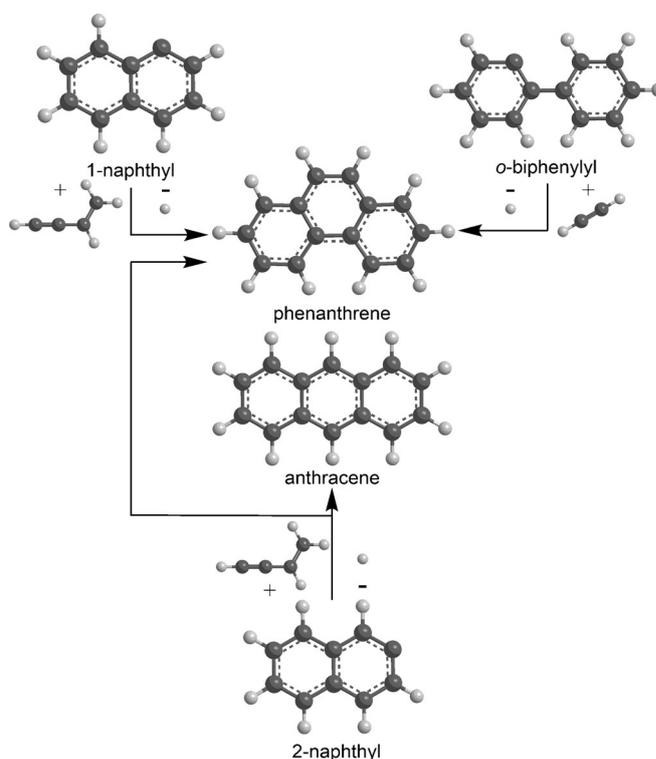


**Figure 4.** Potential energy surface (PES) for *o*-biphenyl reaction with acetylene. The surface is calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. The favorable pathway leading to phenanthrene is colored red. The relative energy is given in kJ mol<sup>-1</sup>.

in the range of  $2.7 \times 10^{-14}$ – $2.5 \times 10^{-12}$   $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with a maximum also achieved at 2000 K; the branching ratio of phenanthrene steadily decreases from 100 % at 500 K to 42 % at 2500 K considering the temperature relevant range of circumstellar envelopes close to the central star.

The proposed route to phenanthrene represents a prototype example of a HACA-type ring closure on an armchair edge of a PAH molecule and a strong alternative to a naphthyl radical-mediated formation of phenanthrene suggested within the framework of the HACA mechanisms.<sup>[35]</sup> The *o*-biphenyl-acetylene pathway to phenanthrene is initiated by abstraction of a hydrogen atom from the *ortho* position of a biphenyl molecule ( $\text{C}_6\text{H}_5\text{C}_6\text{H}_5$ ), which itself can be formed via the elementary reaction of benzene with the phenyl radical,<sup>[41]</sup> and is followed by acetylene addition. Thus, HACA-type pathways to phenanthrene require the reaction of *o*-biphenyl with acetylene, but not of a naphthyl radical with acetylene. Therefore, mass growth processes to more complex PAHs do not necessarily rely on PAH-type radicals such as naphthyl radicals, but can rather involve aromatic (non-PAH) radicals such as *o*-biphenyl. However, although detected in combustion flames and in meteorites, the HACA-type mechanisms still defy accessible pathways to the anthracene isomer.<sup>[33]</sup> Therefore, reaction mechanisms representing alternatives to HACA such as the recently revealed vinylacetylene-mediated formation of naphthalene<sup>[42]</sup> or recombination of two cyclopentadienyl radicals<sup>[43,44]</sup> or benzyl with propargyl<sup>[45,46]</sup> must be clearly involved in the formation of more complex PAHs such as anthracene and phenanthrene. If these pathways can be exported, the reaction of 1- and 2-naphthyl radicals with vinylacetylene (Figure 5) or recombination of indenyl with cyclopentadienyl or 1-/2-naphthalenyl-methyl radicals with propargyl should lead to the formation of anthracene and phenanthrene isomers.

In summary, the overall facile route to phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ) synthesis via the elementary reactions of the biphenyl radical ( $\text{C}_{12}\text{H}_9^\bullet$ ) with acetylene ( $\text{C}_2\text{H}_2$ ) provides a partial legitimacy of HACA-type mechanisms to PAH formation in circumstellar envelopes and also in combustion flames. However, structural isomers of PAHs such as anthracene and phenanthrene, as well as the hitherto unexplained synthesis of anthracene via HACA act as crucial tracers revealing the necessity of complementary reaction pathways to PAHs. Combined experimental and computational studies of the reaction of more complex aromatic radicals such as anthracenyl ( $\text{C}_{14}\text{H}_9^\bullet$ ) and phenanthrenyl ( $\text{C}_{14}\text{H}_9^\bullet$ ) with acetylene involving potential ring closure pathways eventually leading to a systematic PAH growth will be explored in the future. Once these pathways have been unraveled, combustion scientists and astrochemists will be in the position to quantify HACA versus alternative routes to PAHs based on the branching ratios of structural isomers of PAHs formed in distinct extreme environments.



**Figure 5.** Global picture of formation pathways to tricyclic PAHs. Naphthyl radicals can potentially lead to phenanthrene and anthracene via a vinylacetylene-mediated formation route, in which anthracene can act as a potential tracer of such mechanism.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** circumstellar envelopes · gas phase chemistry · hydrogen-abstraction/acetylene-addition (HACA) · mass spectrometry · polycyclic aromatic hydrocarbons

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