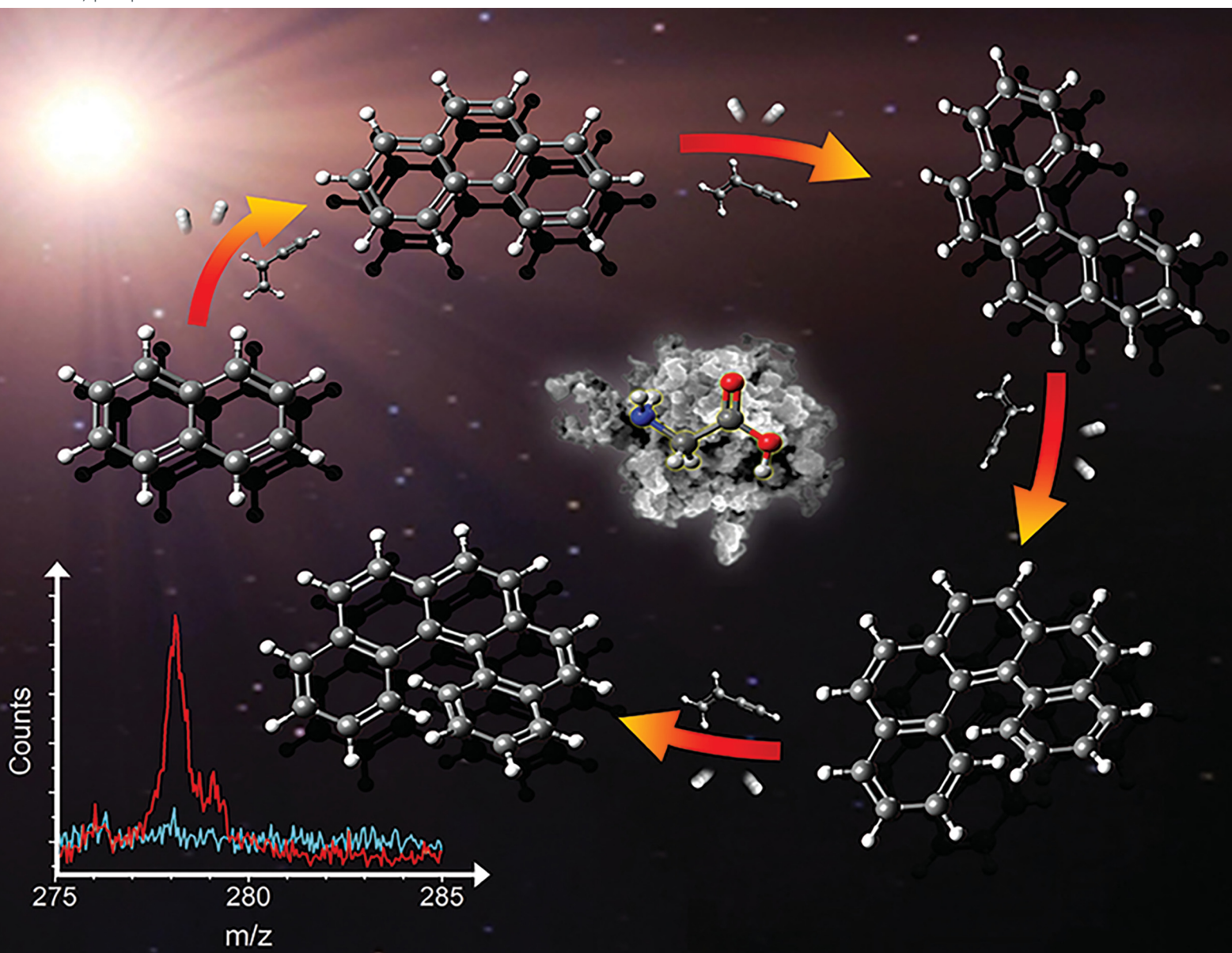


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PAPER

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Gas-phase synthesis of racemic helicenes and their potential role in the enantiomeric enrichment of sugars and amino acids in meteorites†

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The molecular origins of homochirality on Earth is not understood well, particularly how enantiomerically enriched molecules of astrobiological significance like sugars and amino acids might have been synthesized on icy grains in space preceding their delivery to Earth. Polycyclic aromatic hydrocarbons (PAHs) identified in carbonaceous chondrites could have been processed in molecular clouds by circularly polarized light prior to the depletion of enantiomerically enriched helicenes onto carbonaceous grains resulting in chiral islands. However, the fundamental low temperature reaction mechanisms leading to racemic helicenes are still unknown. Here, by exploiting synchrotron based molecular beam photoionization mass spectrometry combined with electronic structure calculations, we provide compelling testimony on barrierless, low temperature pathways leading to racemates of [5] and [6]helicene. Astrochemical modeling advocates that gas-phase reactions in molecular clouds lead to racemates of helicenes suggesting a pathway for future astronomical observation and providing a fundamental understanding for the origin of homochirality on early Earth.

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Introduction

The origin of biological homochirality – nature's selection of one specific enantiomer over the other – has remained a highly controversial topic^{1–5} since its discovery by Louis Pasteur in 1848. Chiral molecules exist in two mirror images which are not superimposable. On Earth, living organisms developed a strict

homochirality with D-sugars and L-amino acids incorporated in ribonucleic acids and polypeptides, respectively.⁶ Prevalent routes to homochirality implicate the propagation and amplification of primordial enantiomeric excesses such as the identification of D-enriched sugar alcohols and sugar acids like arabinonic acid⁷ along with the L-enriched amino acids isovaline, α -methyl norvaline, α -methyl valine, and α -methyl norleucine in the Murchison and Murray meteorites.^{8–10} These pathways might be initiated from racemic mixtures of chiral organic molecules like amino acids,^{11–15} sugars,¹⁶ and epoxides¹⁷ synthesized in the interstellar medium on ice-coated nanoparticles (interstellar grains) within molecular clouds, of which one enantiomer is preferentially destroyed through asymmetric beta-decay-related radiolysis^{18,19} or photolytically by ultraviolet circularly polarized light in star formation regions.^{20–23} Magnetars – white dwarfs with magnetic fields exceeding 10^{13} Tesla – may separate racemic mixtures of organic radicals,²⁴ these paramagnetic radicals may end up in spatially separated sections of the molecular clouds.^{24,25} If a primordial enantiomeric excess existed in the molecular cloud, this excess could be passed on *via* star forming regions to its descendants (planets, moons, comets, meteorites) leading to the homochirality of life on Earth as we know it. Compelling evidence for the delivery of enantiomerically enriched organics from meteorites such as Murchison and Murray to Earth exists,^{8,9}

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however, the question, how did *D*-sugars and *L*-amino acids outnumber *L*-sugars and *D*-amino acids is still unanswered. A fundamental understanding of the underlying pathways at the molecular, microscopic level is required to answer this question.

Here, molecular beam experiments with isomer-selective photoionization *via* a targeted, vinylacetylene-mediated gas-phase reaction of aromatic helicene radicals coupled with electronic structure calculations and astrochemical modeling reveal an elegant synthetic route to racemic helicenes – ortho-fused polycyclic aromatic hydrocarbons (PAHs),²⁶ in which benzene building blocks form helically-shaped molecules.²⁷ The simplest helicenes serve as benchmarks to unravel the exotic gas-phase chemistries leading to a facile low temperature formation of the 22- and 26- π -electron aromatic molecules [5] helicene (C₂₂H₁₄) and [6]helicene (C₂₆H₁₆) plus atomic hydrogen (1 amu) (reactions (1) and (2)), respectively. Combined with electronic structure calculations and astrochemical modeling, a molecular picture to barrierless, low temperature molecular mass growth processes of helicenes in cold molecular clouds such as TMC-1 and OMC-1 emerges through a stepwise ring annulation one ring at a time *via* bimolecular gas-phase reactions of an aromatic helicene radical with vinylacetylene.

These processes were previously conjectured to operate only at elevated temperatures of a few 1000 K prevailing in circumstellar envelopes of carbon rich stars and planetary nebulae as their descendants since entrance barriers equivalent to a few 100 K prohibit these reactions in cold molecular clouds.²⁸ Accounting for the handedness of the helix, clockwise and counterclockwise helices are non-superimposable causing an axial chirality (helical chirality) with left- and right-handed helices defined by *minus* (**M**) and *plus* (**P**) (Fig. 1).²⁹ Although the gas-phase mechanism unraveled here leads to *racemates* of [5] and [6]helicenes, *i.e.* mixtures of equal quantities of the **M** and **P** enantiomers, circularly polarized ultraviolet light³⁰ as detected toward the Orion Massive Star Forming Region³¹ may preferentially photolyze the **M** or **P** enantiomer in the gas-phase of the interstellar medium. This process may initiate the complex chain of reactions ultimately leading to an enantiomeric excess in biorelevant molecules such as *D*-sugars and *L*-amino acids and possibly homochirality in our Solar System (Fig. 1).

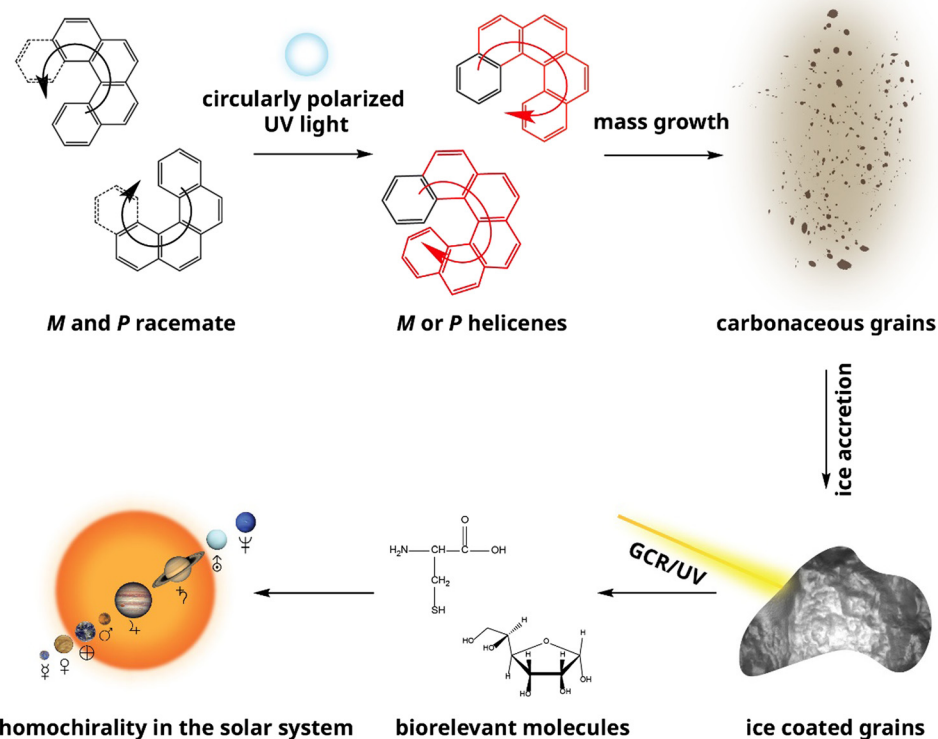
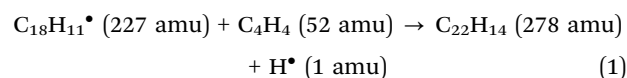
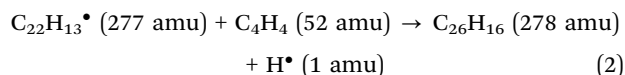


Fig. 1 Overview of the role of racemic helicenes in the enantiomeric of sugars and amino acids in meteorites. Racemic mixtures of [5] and [6]helicenes can form in the gas-phase of the interstellar medium at ultralow temperatures in the absence of reaction barriers *via* molecular mass growth processes. Ultraviolet circularly polarized light may then preferentially photolyze one of the enantiomers leading to an enrichment of one enantiomer over the other. Polycyclic aromatic hydrocarbons (PAHs) – including enantiomerically enriched helicenes – can be incorporated into carbonaceous grains through molecular mass growth resulting into chiral islands or chiral surfaces. Upon interaction with galactic cosmic rays and ultraviolet photons, enantiomerically enriched complex organic molecules of astrobiological significance like sugars and aminoacids may be synthesized on ice coated chiral grains. Enantiomerically enriched biorelevant molecules could have been eventually delivered to early Earth. This brings us closer to the understanding of the origin of homochirality. GCR: Galactic Cosmic Rays; UV: Ultra Violet.



Experimental

The experiments were carried out at the Chemical Dynamics Beamline (9.0.2) of the Advanced Light Source (ALS) with a resistively-heated silicon carbide (SiC) chemical reactor interfaced to a molecular beam apparatus operated with a Wiley–McLaren reflectron time-of-flight mass spectrometer (Re-TOF-MS).³² 2-Bromobenzo[*c*]phenanthrene and 9-bromodibenzo[*c,g*]phenanthrene were synthesized following literature procedures. The [4]helicenyl radicals were prepared *in situ via* pyrolysis of the corresponding brominated precursors. Note that the low vapor pressure of the heated [5]helicenyl precursor prohibited the collection of data at an adequate signal-to-noise ratio. Therefore, only a computational study was conducted for this system. The reactants were seeded at a level of less than 0.01% in a vinylacetylene (5%)–helium (95%) carrier gas at 150 Torr and introduced into a resistively heated silicon carbide tube (SiC) with the temperature of 1585 ± 85 K monitored using a Type-C thermocouple. The products formed in the reactor were expanded supersonically and passed through a 2 mm diameter skimmer located 10 mm downstream of the pyrolytic reactor and enter into the main chamber, which houses the Re-TOF-MS. Under the current experimental conditions, vinylacetylene does not pyrolyze.³³ The quasi-continuous tunable vacuum ultraviolet (VUV) light from the Advanced Light Source intercepted the neutral supersonic molecular beam perpendicularly to the extraction region of the Re-TOF-MS. VUV single photon ionization is essentially a fragment-free ionization technique and hence is characterized as a *soft ionization* method.³⁴ The ions formed *via* photoionization are extracted and detected by a multichannel plate detector. Photoionization efficiency (PIE) curves, which report ion counts as a function of photon energy ranged from 7.00 to 9.50 eV, with a step interval of 0.05 eV at a well-defined mass-to-charge ratio (*m/z*), were produced by integrating the signal recorded at the specific *m/z* for the species of interest.

Theoretical calculations

The geometric structures, vibrational frequencies, and energies of the local minima and transition states involved in the reactions of [4] and [5]helicenyl radicals with vinylacetylene were computed at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory.^{35–37} This dual-level computational approach involves geometry optimization and vibrational frequencies calculations at the density functional B3LYP level of theory with the 6-311G(d,p) basis set. Then, single-point energies of the optimized structures were refined within the framework of the G3(MP2,CC) model chemistry where the total energy of each species is computed as

$$E_0[\text{G3}(\text{MP2,CC})] = E[\text{CCSD}(\text{T})/6\text{-}31\text{G}(\text{d})] + \Delta E_{\text{MP2}} + E(\text{ZPE}),$$

where ΔE_{MP2} is a basis set correction, $\Delta E_{\text{MP2}} = E[\text{MP2}/\text{G3Large}] - E[\text{MP2}/6\text{-}31\text{G}(\text{d})]$, and $E(\text{ZPE})$ is the zero-point energy. Restricted RHF-RCCSD(T) and RMP2 energies were used for open-shell

species; RHF-RCCSD(T) stands for partially spin-adapted open-shell coupled cluster singles and doubles theory augmented with a perturbation correction for triple excitations starting from molecular orbitals obtained from restricted open shell Hartree–Fock calculations. For coupled cluster calculations, the degree of a multireference character of wave functions was monitored through T1 diagnostics. The theoretical method used is normally capable to provide a chemical accuracy of 3–6 kJ mol^{−1} for the relative energies and 0.01–0.02 Å for bond lengths as well as 1–2° for bond angles.³⁸ The GAUSSIAN 09³⁹ and MOLPRO 2021⁴⁰ program packages were used for the B3LYP and G3(MP2,CC) calculations, respectively. The Rice-Ramsperger-Kassel-Marcus (RRKM) theory,^{38,41,42} was used for the calculations of energy-dependent rate constants of all unimolecular steps in the [4]helicenyl + C₄H₄ and [5]helicenyl + C₄H₄ following the formation of the initial intermediates [i3] and [i12], respectively, at zero collision energy and in the limit of zero pressure corresponding to the conditions in cold molecular clouds. Note that under such conditions, only [i3] can be produced in the [4]helicenyl + C₄H₄ reaction where the vinylacetylene moiety adds to the radical site in the aromatic ring by its vinylic end. Alternatively, in the [5]helicenyl + C₄H₄ reaction, both additions by the vinylic and acetylenic ends feature submerged barriers and hence RRKM calculations began from the van der Waals complex [i12]. The computed rate constants were utilized to evaluate product branching ratios under cold molecular clouds conditions within steady-state approximation.⁴³

Astrochemical models

To study the chemistry of PAHs containing up to 6 six-membered rings in the cold molecular cloud TMC-1, we built the chemical model by expanding the RATE12 network⁴⁴ with barrierless neutral–neutral reactions leading to PAHs and their precursors. First, a fiducial time-dependent gas-phase model was operated⁴⁴ until the chemistry evolves to steady-state, *i.e.* after typically 10⁷ years. The molecular abundances at this point are then employed as the initial conditions for the next step. Second, the simulations were conducted over multiple runs with the ice mantle species injected into the gas phase through reactive desorption until it reaches the steady state; this strategy was exploited successfully to demonstrate the key role of neutral–neutral reactions in the formation of benzene in TMC-1.⁴⁵ These results were then benchmarked with astronomical observations for cyanobenzene (C₆H₅CN), and 1- and 2-cyanonaphthalene (C₁₀H₈CN) to verify the predictive capabilities of the chemical network (ESI[†]).

Results & discussion

Molecular beams experiments – identification of the molecular formula of the product

A chemical micro reactor was utilized to prepare [5]helicene *via* the gas phase reaction of the benzo[*c*]phenanthren-2-yl radical (C₁₈H₁₁[•]) with vinylacetylene (C₄H₄) (Fig. 2a inset). The reaction products were probed isomer-specifically in a molecular beam

via tunable vacuum ultraviolet (VUV) light followed by detection of the ionized molecules in a Re-TOF-MS (Methods). An illustrative mass spectrum recorded at a photoionization energy of 9.50 eV for the reaction of the benzo[*c*]phenanthren-2-yl radical ($C_{18}H_{11}^{\bullet}$) with vinylacetylene (C_4H_4) is shown in Fig. 2b; reference data were also collected by replacing the vinylacetylene reactant with non-reactive helium carrier gas (Fig. 2a). A detailed comparison of these data reveals compelling evidence for the preparation of a molecule with the molecular formula $C_{22}H_{14}$ (278 amu) along with its ^{13}C counterpart $^{13}CC_{21}H_{14}$ (279 amu) in the benzo[*c*]phenanthren-2-yl – vinylacetylene system (Fig. 2b, inset). Considering the molecular weight of the reactants and of the products, the $C_{22}H_{14}$ isomer(s) along with a light hydrogen atom represents the outcome of the reaction of the benzo[*c*]phenanthren-2-yl radical ($C_{18}H_{11}^{\bullet}$; 227 amu) with vinylacetylene (C_4H_4 ; 52 amu) (reaction (1)). Additional ion counts from $m/z = 226$ to 229 and 306–309 are observed in both the benzo[*c*]phenanthren-2-yl–vinylacetylene system *and* in the control experiment; this finding suggests that the generation of these species does not require molecular mass growth processes through the reaction of the benzo[*c*]phenanthren-2-yl radical with vinylacetylene (ESI;† Fig. S1).

Molecular beams experiments – identification of the structural isomers of the products

The nature of the structural isomer(s) at m/z of 278 ($C_{22}H_{14}^+$) prepared in the reaction of the benzo[*c*]phenanthren-2-yl radical with vinylacetylene is revealed by the detailed examination of the corresponding photoionization efficiency (PIE) curve, which

portrays the intensity of the ion as a function of the photon energy from 7.00 eV to 9.50 eV (Fig. 3a). The experimental PIE curve at $m/z = 278$ (Fig. 3, black line) can only be fit with a linear combination of known reference PIE curves of distinct isomers of $C_{22}H_{14}$ such as [5]helicene (Fig. 3, green line) and benzo[*a*]tetraphene (Fig. 3, blue line). The experimental and reference PIE curves for [5]helicene reveal an onset of the ion signal at 7.40 ± 0.05 eV. However, the PIE curve of [5]helicene alone cannot replicate the ion counts beyond 8.50 eV. Considering the error bars, the contribution of benzo[*a*]tetraphene is clearly required to account for the lack of ion counts from the range of 7.00 eV to 8.50 eV. The overall fit (red) consists of ion counts of [5]helicene ($82 \pm 5\%$) and of benzo[*a*]tetraphene ($18 \pm 4\%$). It is important to note that the actual branching ratios of [5]helicene *versus* benzo[*a*]tetraphene require the knowledge of their photoionization cross sections; these are unknown. Electronic structure theory has not advanced to such a level to accurately compute the photoionization cross sections of organic molecules as complex as [5]helicene and benzo[*a*]tetraphene. Nevertheless, our experiments reveal the proof-of-concept that the reaction of benzo[*c*]phenanthren-2-yl radical with vinylacetylene leads to two distinct product isomers *via* molecular mass growth processes: benzo[*a*]tetraphene (**p1**) and [5]helicene (**p2**). It is critical to highlight that the PIE curve recorded at $m/z = 279$ (Fig. 3b) can be associated with ^{13}C substituted isomer ($C_{17}^{13}CH_{12}$) of [5]helicene and benzo[*a*]tetraphene with an overall ion count intensities of $22 \pm 2\%$ as predicted from the 1.1% ^{13}C natural abundance along with 22 carbon atoms in the products.

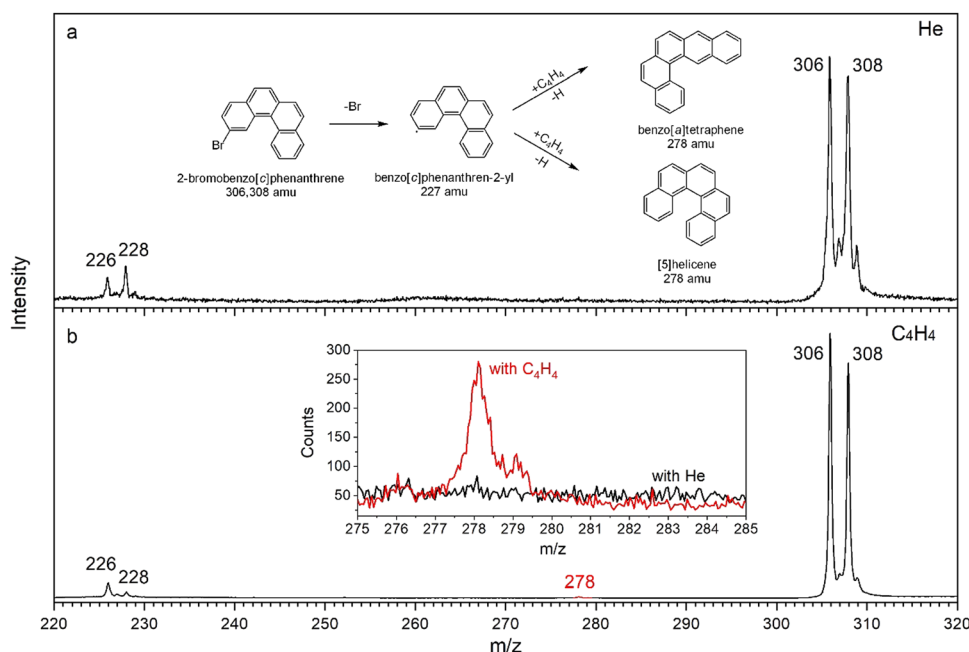


Fig. 2 Comparison of photoionization mass spectra recorded at a photon energy of 9.50 eV. (a) 2-bromobenzo[*c*]phenanthrene ($C_{18}H_{11}Br$)–helium (He) system; (b) 2-bromobenzo[*c*]phenanthrene ($C_{18}H_{11}Br$)–vinylacetylene (C_4H_4) system. The inset of (a) represents the formation of benzo[*a*]tetraphene ($C_{22}H_{14}$) and [5]helicene ($C_{22}H_{14}$) from the reaction of the benzo[*c*]phenanthren-2-yl radical ($C_{18}H_{11}^{\bullet}$) with vinylacetylene (C_4H_4). The benzo[*c*]phenanthren-2-yl radical is produced from the pyrolysis of 2-bromobenzo[*c*]phenanthrene ($C_{18}H_{11}Br$). The inset of (b) shows the mass peak in red of the newly formed species of interest along with the ^{13}C -counterparts.

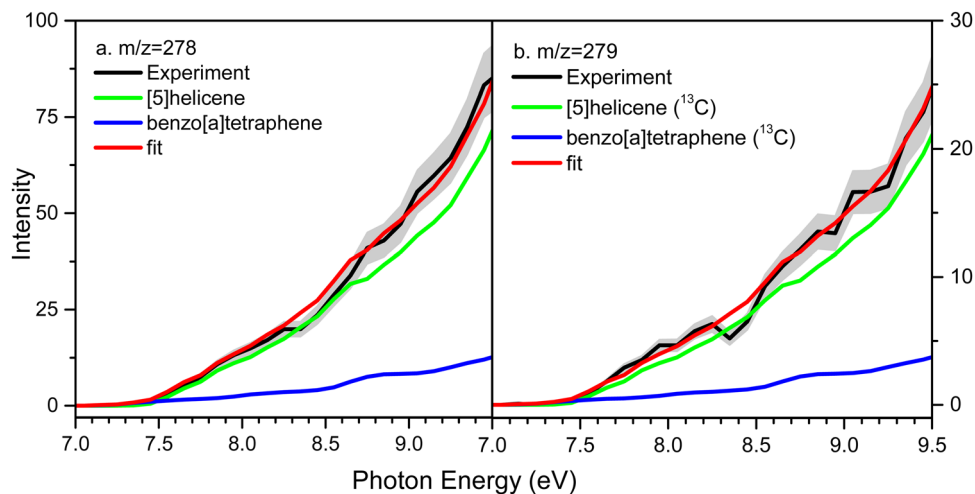


Fig. 3 Photoionization efficiency (PIE) curves of $m/z = 278$ and 279 for the reaction of 2-bromobenzo[*c*]phenanthrene ($C_{18}H_{11}Br$)-vinylacetylene (C_4H_4). Black: Experimentally derived PIE curves; colored lines (green and blue): reference PIE curves; red lines: overall fit. The overall error bars consist of two parts: $\pm 10\%$ based on the accuracy of the photodiode and a 1σ error of the PIE curve averaged over the individual scans.

Electronic structure calculations – [5]helicene and its isomers

With the experimental determination of distinct isomers [5]helicene and benzo[*a*]tetraphene ($C_{22}H_{14}$), we turn to electronic structure calculations to decipher the pathways that lead to their formation across complex potential energy surfaces. The computations were carried out at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory and reveal that the [4]helicenyl radical may approach the vinylacetylene reactant barrierlessly resulting in

the formation of two possible van der Waals complexes [i1] and [i2] (Fig. 4 and Table S1, ESI†). These complexes are stabilized by 9 and 14 kJ mol^{-1} with respect to the separated reactants and reveal a carbon-carbon distance between the radical center of the benzo[*c*]phenanthren-2-yl radical with the vinyl (C1) and acetylenic (C4) carbon atoms of vinylacetylene of 409 and 388 pm, respectively. The van der Waals complexes can isomerize through addition of the radical center to the vinyl (C1) and acetylenic (C4)

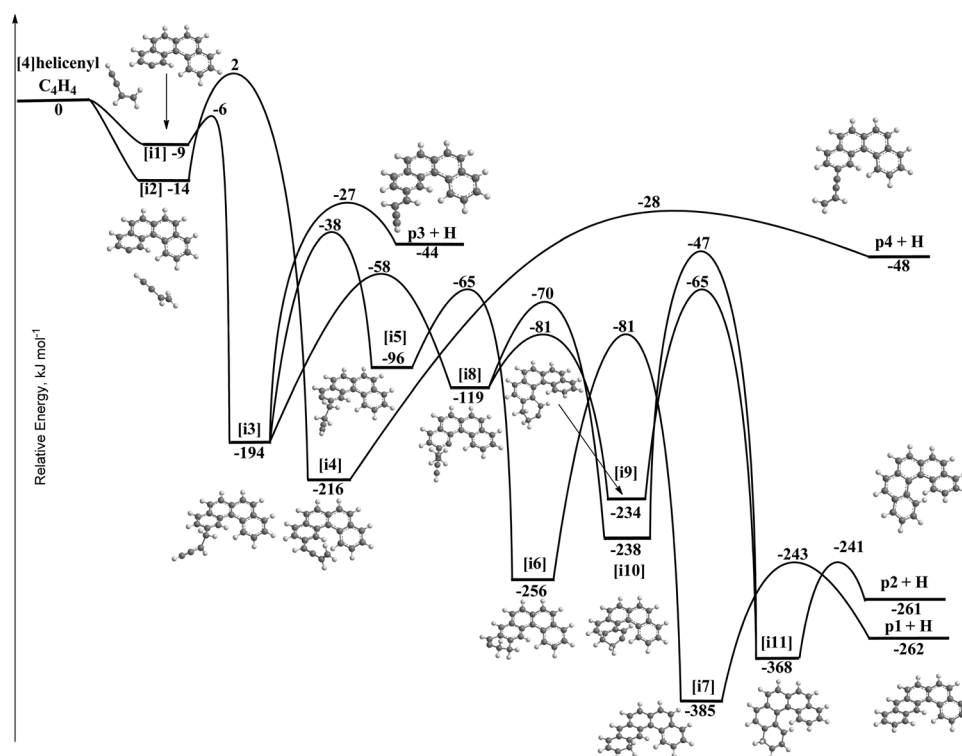


Fig. 4 Potential energy surface (PES) for the [4]helicenyl ($C_{18}H_{11}^*$) reaction with vinylacetylene (C_4H_4) leading to [5]helicene ($C_{22}H_{14}$). This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. The relative energies are given in kJ mol^{-1} .

moieties *via* barriers of 3 and 16 kJ mol⁻¹ yielding intermediates [i3] and [i4], respectively. A key feature of the addition to the C1 carbon atom is that the transition state to addition lies 6 kJ mol⁻¹ below the energy of the separated reactants. Therefore, an addition barrier exists, but is lower in energy than the separated reactants and hence is termed a submerged barrier.⁴⁶ Whereas [i3] and [i4] may undergo unimolecular decomposition *via* atomic hydrogen loss to 2-((*E*)-but-1-en-3-ynyl)[4]helicene (p3) and 2-(but-3-en-1-ynyl)[4]helicene (p4), respectively, the resonantly stabilized doublet radical intermediate [i3] is fundamental in the formation of [5]helicene (p2) and benzo[*a*]tetraphene (p1). Benzo[*a*]tetraphene (p1) can be accessed *via* the reaction sequence [i3] → [i5] → [i6] → [i7] → p1 + H, whereas [5]helicene (p2) can be prepared *via* [i3] → [i8] → [i9]/[i10] → [i11] → p2 + H involving hydrogen atom shifts and a six-membered ring closure terminated by hydrogen atom losses from the methylene (CH₂) moieties in [i7] and [i11] through tight transition states located 19 and 20 kJ mol⁻¹ above the energy of the separated products in overall exoergic reactions ($\Delta_{\text{R}}G(\text{p1} + \text{H}) = -262 \text{ kJ mol}^{-1}$; $\Delta_{\text{R}}G(\text{p2} + \text{H}) = -261 \text{ kJ mol}^{-1}$). A detailed analysis of the barriers of isomerization of [i3] suggests that [5]helicene (p2) is formed preferentially. This deduction gains full support from the theoretically predicted branching ratios of 0.002%: 99.8%: 0.2% for p3 *versus* p2 *versus* p1 for cold molecular clouds conditions at 10 K and nearly zero pressure thus amplifying the synthetic route to [5]helicene (p2) in low temperature conditions of deep space (10 K). The presence of the submerged barrier is critical since these low temperatures effectively block reactions proceeding *via* transitions states located above the energy of the separated

reactants such as the isomerization of [i2] to [i4] thus inhibiting the formation of 2-(but-3-en-1-ynyl)[4]helicene (p4). Recall that the thermodynamically less stable isomer p3 was not detected in our study. Consequently, isomerization of [i3] and formation of [5]helicene (p2) and benzo[*a*]tetraphene (p1) is preferred at the expense of unimolecular decomposition to 2-((*E*)-but-1-en-3-ynyl)[4]helicene (p3). It is interesting to note that in case of a chiral [4]helicenyl reactant, its reaction with vinylacetylene should form a racemic mixture of [5]helicene. The memory of a particular chirality of the reactant is lost in the intermediate [i8], which exhibits a planar geometry of the four aromatic rings due to the absence of an H atom in the most crowded position on one of the terminal rings. [i8] is still chiral due the presence of the CH₂CH₂CCH side chain but it can easily interconvert to its other enantiomer by facile rotation around the out-of-ring single C-CH₂ bond. Therefore, two different enantiomers of [i11] are predicted to be formed in nearly equal amounts and these enantiomers, after losing a hydrogen atom, would give rise to a racemic mixture of the product [5]helicene (p2). Alternatively, the particular chirality of the reactant is preserved along the entire reaction pathway toward p1; here, the chirality of benzo[*a*]tetraphene will coincide with that of the [4]helicenyl reactant.

Electronic structure calculations – [6]helicene and its isomers

The concept of a *de-facto* barrierless, vinylacetylene-mediated ring annulation to [4]helicenyl radicals leading to [5]helicene through resonantly stabilized free radical intermediates can be exported to [6]helicene. This mechanism provides a unified and versatile synthetic route to racemic helicenes *via* successive

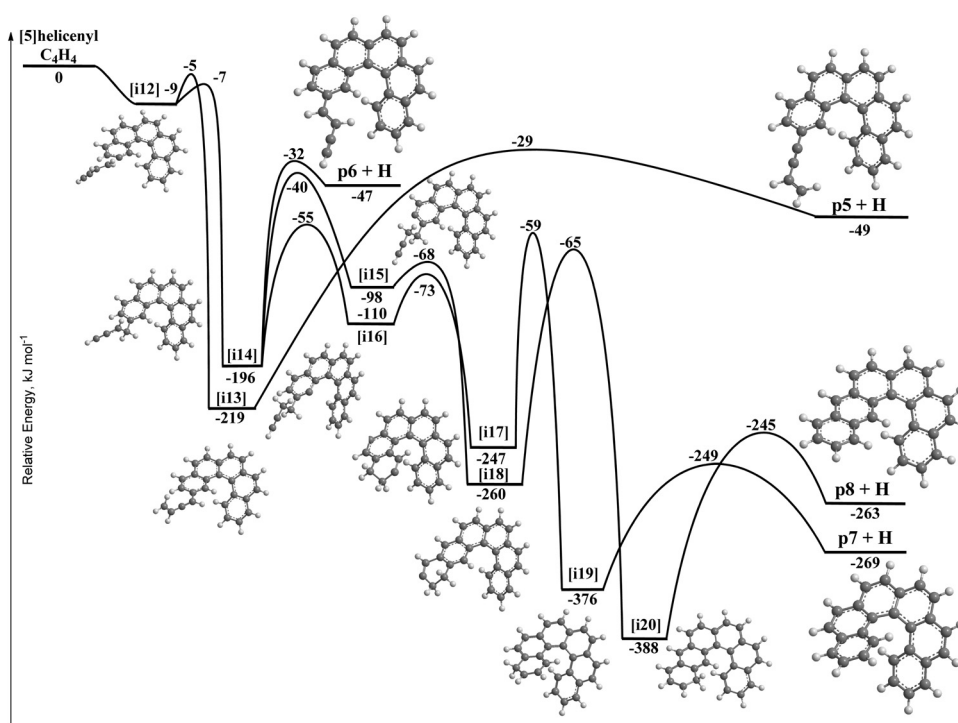


Fig. 5 Potential energy surface (PES) for the [5]helicenyl (C₂₂H₁₃^{*}) reaction with vinylacetylene (C₄H₄) leading to [6]helicene (C₂₆H₁₆). This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. The relative energies are given in kJ mol⁻¹.

molecular mass growth processes through bimolecular gas-phase reactions one ring at a time. The key features of the [5]helicenyl-vinylacetylene PES (Fig. 5 and Table S1, ESI†) fundamentally mirror the [4]helicenyl-vinylacetylene system (Fig. 4). The reaction is initiated through the formation of a van der Waals complex [i12]. Although two distinct long-range complexes could be located in the [4]-helicenyl-vinylacetylene system, despite an extensive search, only a single van der Waals complex was characterized in the reaction of [5]helicenyl with vinylacetylene with distances of at least 400 pm between the radical center and the vinyl and acetylene functional groups. This complex can isomerize through addition of the radical center of [5]helicenyl to the acetylenic or vinyl functional group forming [i13] or the resonantly stabilized free radical intermediate [i14], respectively. In both cases, the barriers to addition are located below the energy of the separated reactants; therefore, these can be once again be classified as submerged barriers. While [i13] may fragment *via* atomic hydrogen loss to 2-(but-3-en-1-ynyl)[5]helicene (p5), the chemistry of [i14] is more diverse. This intermediate either eliminates a hydrogen atom to form 2-((*E*)-but-1-en-3-ynyl)[5]helicene (p6) or undergoes hydrogen migration from the ortho or para position with respect to the side chain added to the benzene moiety yielding [i15] and [i16], respectively. These structures isomerize *via* ring closure to [i17] and [i18] followed by another hydrogen migration from the methylene group (CH₂) neighboring the carbene carbon atom to the latter; these shifts form intermediates [i19] and [i20], when then undergo hydrogen loss from the remaining methylene functional group accompanied by aromatization to [6]helicene (p7) and naphtho[1,2-*a*]tetraphene (p8) in overall exoergic reactions ($\Delta_{\text{R}}G(\text{p7} + \text{H}) = -269 \text{ kJ mol}^{-1}$; $\Delta_{\text{R}}G(\text{p8} + \text{H}) = -263 \text{ kJ mol}^{-1}$). The energies of the transition states for isomerization (or fragmentation) of [i14] along with the location of the barriers of the subsequent isomerization processes as discussed above advocate a favorable yield of [6]helicene (p7). Indeed, the computed branching ratios of 9.0%: 0.04%: 87.5%: 3.4% for p5 *versus* p6 *versus* p7 *versus* p8 for cold molecular clouds (10 K) are in line with our hypothesis. The chirality of the [5]-helicenyl reactant is maintained along all reaction pathways and hence will be the same in particular for the [6]helicene (p7) and naphtho[1,2-*a*]tetraphene (p8) products.

Astrochemical modeling

Having provided compelling evidence on the formation of [5] and [6]helicene through barrierless reactions of the helicenyl radicals with vinylacetylene (reactions (1) and (2)), we are applying these findings now to ‘real’ cold molecular clouds. It is important to highlight that both reactions have no entrance barriers, all barriers involved in the isomerization processes are below the energy of the separates reactants, and the overall reactions (1) and (2) to [5] and [6]helicene are exoergic. These findings denote key requirements for both reactions to proceed in low-temperature environments such as in molecular clouds (10 K). Any barrier located above the energy of the separated reactants would inhibit the reactions to [5] and [6]helicene in molecular clouds; likewise, the low

temperatures of the molecular clouds would prohibit endoergic reactions. In this context it is important to emphasize that although the reaction of the 4-phenanthrenyl radical (C₁₄H₉•) with vinylacetylene yields [4]helicene (C₁₈H₁₂),²⁸ the inherent barrier to addition in the entrance channel of 9 kJ mol⁻¹ – equivalent to about 800 K – cannot be overcome in cold molecular clouds. This barrier is essentially the result of the sterical hindrance and hence repulsion between the first aromatic ring of the 4-phenanthrenyl radical and the vinylacetylene molecule adding with the methyldene moiety (CH₂) to the aryl radical center. In our present study, the sterical hindrance for the reactions of the [4] and [5]helicenyl radicals with vinylacetylene is significantly reduced due to the positioning of the attacked radical site outside of the molecular “bay” thus lowering the barrier heights below the energy of the separated reactants hence resulting in a submerged barrier. In this sense, the features in the entrance channels of the reactions to [5] and [6]helicene are quite distinct from those of the reaction of the 4-phenanthrenyl radical (C₁₄H₉) with vinylacetylene (C₄H₄) leading to [4]helicene.²⁸ To explore the implications of our findings to the chemistry of aromatic hydrocarbons in cold molecular clouds, we explored the viability of the formation of polycyclic aromatic hydrocarbons *via* neutral–neutral reactions exploiting the University of Manchester Institute for Science and Technology (UMIST) Database (RATE2012).⁴⁴ The models were operated with physical parameters updated from ref. 44 and 47: a cosmic ray ionization rate of $1.3 \times 10^{-17} \text{ s}^{-1}$, a temperature of 10 K, a visual extinction of 10 Mag, and a number density of molecular hydrogen of 10^4 cm^{-3} . This network was updated with recently explored barrierless and rapid reactions related to the formation of benzene (C₆H₆),⁴⁵ naphthalene (C₁₀H₈),⁴⁶ phenanthrene (C₁₄H₁₀),⁴⁸ and [4]helicene⁴⁹ along with the channels to [5]helicene and [6]helicene elucidated in the present work (Fig. 6 and Table S2, ESI†). Reaction pathways to benzene (C₆H₆) were extracted from ref. 45 (Materials and methods; ESI†).

These modeling studies reveal fascinating conclusions. First, the performance of the astrochemical model for the cold molecular cloud TMC-1 can be benchmarked for the cyano derivatives of benzene (C₆H₆) and naphthalene (C₁₀H₈), *i.e.* cyanobenzene (C₆H₅CN), and 1- and 2-cyanonaphthalene (C₁₀H₈CN), which were recently observed at fractional abundances of $4 \pm 1.6 \times 10^{-11}$ ⁵⁰ as well as $7.35^{+3.32}_{-4.63} \times 10^{-11}$ and $7.05^{+3.32}_{-4.50} \times 10^{-11}$ toward TMC-1.⁵¹ Formed predominantly *via* the barrierless reactions of benzene and naphthalene with cyano radicals,^{52,53} the predicted peak fractional abundances at 2×10^5 years of cyanobenzene (C₆H₅CN) and both cyanonaphthalene (C₁₀H₈CN) isomers with respect to molecular hydrogen reproduce the astronomical observations exceptionally well (Fig. 7). Second, barrierless molecular mass growth processes *via* ring annulation lead from two-ring PAHs (C₁₀H₈; naphthalene) *via* three (C₁₄H₁₀; phenanthrene), four (C₁₈H₁₂; [4]helicene), five (C₂₂H₁₄; [5]helicene), and six-ring PAHs (C₂₆H₁₆; [6]helicene). With increasing complexity, the fractional abundances decrease from a few 10⁻⁸ for naphthalene *via* 2×10^{-9} for phenanthrene and 3×10^{-10} for [4]helicene to nearly 10⁻¹¹ for [5]helicene and 8×10^{-14} for [6]helicene. This implies

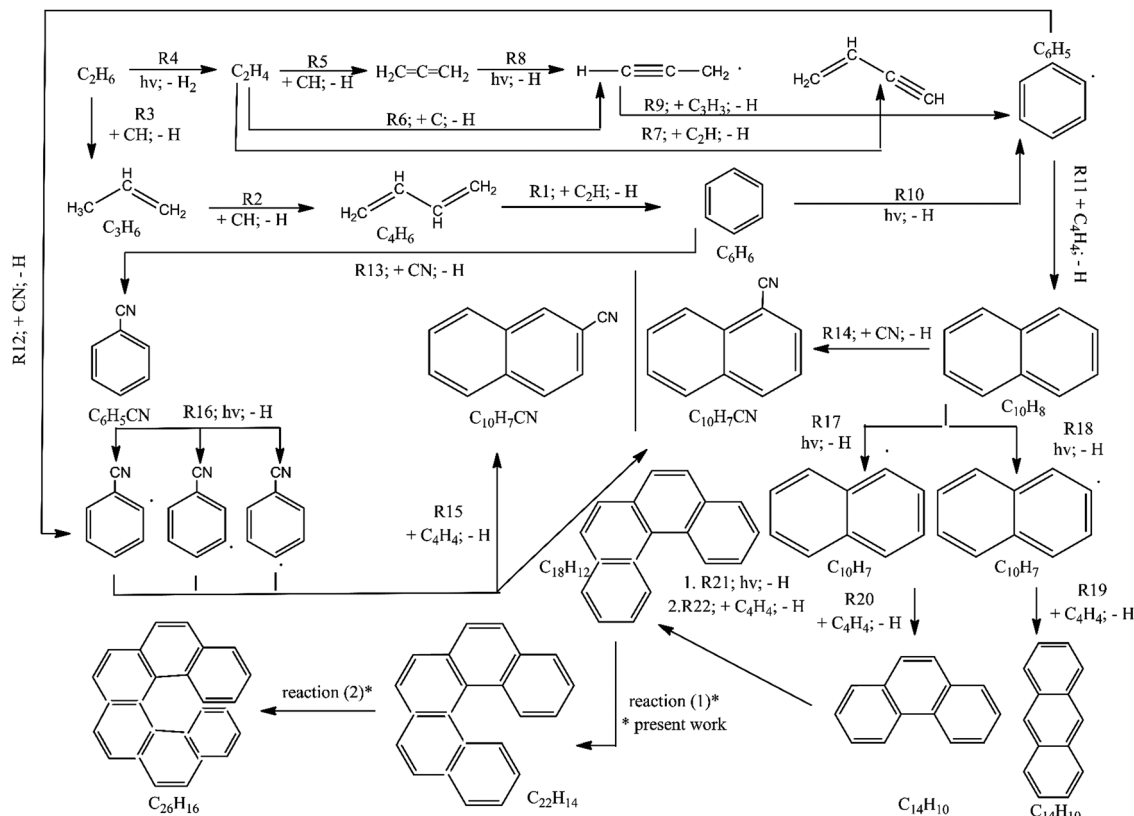


Fig. 6 Compilation of key bimolecular reactions leading to aromatic molecules as incorporated into the novel astrochemical models. The reactions R1–R22 are discussed in the ESI.†

that in future observations, at least three to five ringed PAHs including [4] and [5]helicenes might be detectable by radio telescopes.

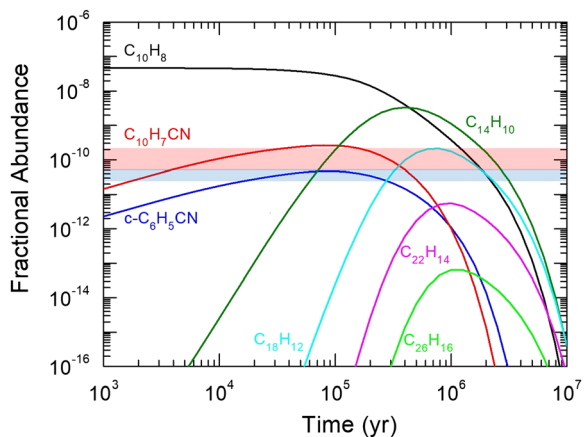
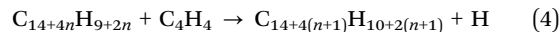
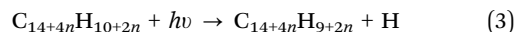


Fig. 7 Results of the astrochemical modeling for key pathways leading eventually to the formation of helicenes in TMC-1. The fractional abundances of the gas-phase species (C₁₀H₈; naphthalene), (C₁₄H₁₀; phenanthrene), (C₁₈H₁₂; [4]helicene), (C₂₂H₁₄; [5]helicene), and (C₂₆H₁₆; [6]helicene) are plotted versus time for the cold molecular cloud TMC-1. Astronomically observed fractional abundances along with the uncertainties of cyanobenzene (C₆H₅CN) and cyanonaphthalenes (C₁₀H₇CN) are visualized by the blue and red color-coded bars and agree nicely with the peak abundances predicted from the present models.

Conclusion

Our combined experimental, computational, and astrochemical modeling results provided compelling evidence on a versatile, barrierless molecular mass growth process to helicenes *via* ring annulation in cold molecular clouds (10 K) as the result of bimolecular reactions of helicenylyl radicals with vinylacetylene in the gas-phase. Commencing with the photolysis of an [*n*]helicene [C_{14+4*n*}H_{10+2*n*}] to an [*n*]helicenylyl radical [C_{14+4*n*}H_{9+2*n*}] through the internal ultraviolet field (reaction (3)),⁵⁴ this universal mechanism effectively converts an [*n*]helicene into an [*n* + 1]helicene [C_{14+4(*n*+1)}H_{10+2(*n*+1)}] (reaction (4)).



The gas-phase synthesis of helicenes may have profound implications for the origin of the chiral asymmetry of life and contemporary biorelevant molecules such as right-handed sugars and left-handed amino acids. Although the gas-phase processes unraveled here form racemates of [5] and [6]helicenes, in deep space, ultraviolet circularly polarized light may preferentially photolyze the **M** or **P** enantiomer; this process could lead to an enrichment of one enantiomer over the other (enantiomeric excess), which can be propagated by further growth. Since PAHs, to which helicene belongs, represent fundamental molecular building blocks of nanometer-sized

interstellar grains,^{55–60} a bottom-up formation of carbonaceous nanoparticles *via* PAHs leads to chiral carbonaceous nanostructures^{26,27,56,57,61} and may translate the enantiomeric excess of the helicenes from the gas-phase to the nanoparticles eventually resulting into chiral islands or chiral surfaces. Although there is no detailed description to date of how carbonaceous nanoparticles might form in deep space, PAHs are likely key contributors. Consequently, the work disseminated here signifies a critical advancement toward a systematic understanding of the fundamental chemical processes forming carbonaceous grains in the interstellar medium. At low temperatures of cold molecular clouds (10 K), these grains accrete nanometer thick icy layers of, *e.g.*, water, carbon monoxide, carbon dioxide, formaldehyde, methanol, methane, and ammonia. Interaction of interstellar ices with ionizing radiation such as galactic cosmic rays and the internal ultraviolet field⁶² revealed the synthesis of complex organic molecules of astrobiological significance such as amino acids,^{11–15} dipeptides,⁶³ and even sugars at 10 K.¹⁶ In the presence of chiral islands and chiral surfaces, a grain-surface-mediated synthesis may lead to an enantiomeric excess within the newly formed molecules like sugars and amino acids. Therefore, these biorelevant molecules, which have been enantiomerically enriched through a chiral surface-mediated low temperature ice-surface chemistry in molecular clouds, could have been eventually delivered to early Earth. This scenario gains strong support from the recent identification of D-enriched sugar alcohols and sugar acids like arabinonic acid⁷ along with L-enriched non-terrestrial amino acids such as isovaline, α -methyl norvaline, α -methyl valine, and α -methyl norleucine in Murchison and Murray carbonaceous meteorites⁸ thus bringing us closer to the understanding of the origin of homochirality.

Data availability

The datasets generated during this study are available upon request.

Author contributions

R. I. K. designed the experimental program and guided the astrochemical modeling; W. L. and L. Z. performed the experiments under the supervision of M. A.; M. M. E., V. N. A., and A. M. M. conducted the electronic structure and RRKM calculations; R. K. M. synthesized the precursors under supervision by F. R. F.; R. I. K. and M. A. wrote the manuscript. X. L. conducted the astrochemical modeling.

Conflicts of interest

The authors declare no competing interests.

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