**Title: Low Temperature Gas Phase Formation of Indene in the Interstellar Medium**

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**One Sentence Summary:** Low temperature gas phase synthesis of indene-a fundamental molecular building block of non-planar polycyclic aromatics.

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**Abstract:**

Poly­cyclic aromatic hydrocarbons (PAHs) are fundamental molecular building blocks of fullerenes and carbonaceous nano­struc­tures in the interstellar medium and in combustion systems. However, an under­standing of the formation of aromatic molecules carrying five membered rings - the essential building block of non-planar PAHs - is still in its infancy. Ex­plo­it­ing crossed mole­cular beam experi­ments augmented by electronic structure cal­cu­­lations and astrochemical modeling, we re­veal an unu­sual pathway leading to the formation of indene (C9H8) - the prototype aromatic molecule with a five-mem­­bered ring - via a barrierless bimo­le­cu­lar reac­tion invol­ving the si­m­­p­­lest organic radical -methylidyne (CH)-and sty­rene (C6H5C2H3) through the hi­ther­to elu­sive **M**e­thyli­dyne **A**ddition – **C**yc­li­zation – **A**romatization (MACA) mechanism. Through extensive structural reorganization of the carbon backbone, the incorporation of a fi­­ve-mem­­bered ring may eventually le­ad to three-dimensional PAHs such as cor­annu­lene (C20H10) along with fullerenes (C60, C70) thus offe­ring a new concept on the low temperature che­mi­stry of carbon in our Galaxy.

**Introduction.**

Since Léger’s and Puget’s very first hypothesis of polycyclic aromatic hydrocarbons (PAHs) - organic molecules composed of fused benzene rings - as the missing link between small carbon molecules and carbonaceous nanoparticles (interstellar grains) ([*1*](#_ENREF_1)), PAHs ([*2*](#_ENREF_2)) along with their (de)hy­dro­­­­genated ([*3*](#_ENREF_3)), alkylated ([*4*](#_ENREF_4)*,* [*5*](#_ENREF_5)), protonated ([*6*](#_ENREF_6)), and ionized ([*7*](#_ENREF_7)) counterparts have been associated with the dif­fu­se interstellar bands (DIBs) ([*8*](#_ENREF_8)) - discrete absorption features superimposed on the interstellar ex­tinc­t­ion curve ranging from the visible (400 nm) to the near-infrared (1.2 µm) - and the unidentified infrared (UIR) emission bands ([*9*](#_ENREF_9)*,* [*10*](#_ENREF_10)) in the 3–14 µm range. Encompassing up to 20 % of the carbon budget in our Galaxy ([*11*](#_ENREF_11)*,* [*12*](#_ENREF_12)), the identification of PAHs in carbonaceous chondrites such as Murchison, Allende, and Orgueil ([*13*](#_ENREF_13)*,* [*14*](#_ENREF_14)) along with 13C/12C and D/H isotopic analyses ([*15*](#_ENREF_15)) advocate a circumstellar origin of aromatics in carbon rich Asymptotic Giant Branch (AGB) stars and planetary nebulae as the descendants of AGB stars at elevated temperatures of a few 1,000 K through molecular mass growth processes involving (H)ydrogen (A)bstraction (C)arbon (A)ddition (HACA) sequences ([*16*](#_ENREF_16)).

Tielens et al. revealed that once formed, interstellar PAHs are swiftly destroyed by galactic cosmic rays, photo­lysis, and shock waves causing lifetimes of only a few 108 years ([*17*](#_ENREF_17)*,* [*18*](#_ENREF_18)). These time scales are substantially shorter than those for the injection of PAHs from carbon-rich circum­stel­lar enve­lopes into the interstellar medium of 2×109 years ([*19-22*](#_ENREF_19)). Conse­quent­ly, PAHs should neither exist in the interstellar medium nor in meteorites, and the ubi­qui­tous pre­­sen­ce of PAHs repre­sents a key paradox in astrophysics. This inconsistency could be resolved by infer­ring the existence of hither­to elusive low temperature routes to a rapid growth of PAHs in the interstellar medium to offset their destruction ([*23*](#_ENREF_23)). An identification of these low-tempe­ra­ture pathways is of particular importance to untangle the origin of PAHs carrying five-mem­be­red rings such as indene which represents an essential molecular building block of non-planar PAHs like corannu­lene (Fig. 1). Non-planar PAHs – potential precursors to fullerenes ([*24*](#_ENREF_24)*,* [*25*](#_ENREF_25)) - require five-mem­bered rings in the carbon backbone to bend PAHs out of the plane and to ultimately form three dimensional carbonaceous nanostructures ([*26*](#_ENREF_26)). However, the low temperature formation mecha­ni­sms of even the simplest prototype of a PAH carrying a five-membered ring – indene (C9H8) – from astro­che­mically relevant precursor molecules are still unknown. This requires an intimate un­der­standing of the elementary reactions and dynamics of reactions leading to indene on the most funda­mental, microscopic level ([*27*](#_ENREF_27)).

Here, we reveal that the indene molecule (C9H8) can be synthesized barrierlessly via the elementary reaction of the simplest organic radical - methylidyne (CH) - with styrene (C6H5 C2H3) under single collision conditions. Combining crossed molecular beam reactive scattering experiments with elec­tronic structure calcu­lations and astrochemical modeling, our study implicates an unexpected gas phase che­mistry initiated by a single collision event, which operates even at temperature as low as 10 K present in cold mole­cular clo­u­ds like the Taurus Molecular Cloud (TMC-1) and the Orion Molecular Cloud (OMC-1). The reaction of me­thy­lidyne with styrene involves a hitherto elusive low temperature **M**e­thyli­dyne **A**ddi­tion – **C**yc­li­zation – **A**roma­ti­zation (MACA) mechanism and may exemplify the prototype of a barrierless path­way to in­dene in those molecular clouds, where a rapid gas phase che­mistry fol­lows ice man­t­le subli­ma­tion. MACA operates at ultralow temperatures and eventually transforms a vinyl (C2H3) side group of aromatic molecules to a fused pentacycle involving an extensive reorga­ni­zation of the carbon skeleton. These findings dispute established paradigms that mole­cu­lar mass growth processes to non-planar PAHs operate only at high temperatures such as in circum­stellar envelopes of carbon stars and in combustion systems ([*28*](#_ENREF_28)) and suggest that a low tem­perature chemistry can initiate the formation of the very first aromatic molecules in the in­ter­stellar me­di­um carrying a five membered ring: indene. The carbon back­bone of in­dene – the simp­lest repre­sen­tative of an aromatic mo­le­cule carrying a six membered benzene ring fused with a five mem­bered cyclopen­tadiene moi­ety – represents a fundamental molecular building block of non-planar PAHs like corannu­lene (C20H10) and may signify an essential reac­tion in­ter­mediate in the mole­cu­lar mass growth pro­ces­ses leading ultimately to interstellar fullerenes (C60, C70) ([*24*](#_ENREF_24)*,* [*25*](#_ENREF_25)).

**Results - Crossed Molecular Beams Studies - Laboratory Frame.**

     The reactive scat­te­ring ex­peri­ments were carried out exploiting a crossed molecular beam apparatus (Mate­ri­als and Methods). For the reaction of the methylidyne radical (CH; 13 amu) with styrene (C8H8; 104 amu), reactively scattered products were observed at mass-to-charge (m/z) of m/z 117 (C9H9+), 116 (C9H8+), and 115 (C9H7+) with relative intensities of 10 ± 2 %, 100 %, and 200 ± 10 %, respectively. The scattering signal was relatively weak; hence at each angle up to 5 × 106 time-of-flight (TOF) spectra had to be averaged over 50 hours to obtain reasonable signal-to-noise ra­tios. After scaling, the TOF spectra at all three m/z values were found to be superimposable. These findings propose that signal at m/z = 116 arises from the hydrogen atom loss channel ac­com­­panied by the formation of a molecule with the molecular formula C9H8 formed via the reac­tion CH (13 amu) + C8H8 (104 amu) → C9H8 (116 amu) + H (1 amu). Signal at m/z= 117 (13CC8H8+) arises from the natural abundance of 13C isotope of carbon, whereas ion counts at m/z = 115 are connected to dissociative electron impact ionization of the neutral reaction products in the detector. Therefore, having evidenced the formation of molecule(s) with the formula C9H8, TOF spectra of the nascent C9H8 reaction product were collected at m/z= 116 at distinct la­bo­ratory angles from 36˚ to 66˚ in 5˚ intervals. The TOFs were then normalized with respect to the TOF at the center-of-mass (ΘCM) and integrated to yield the laboratory angular distribution (LAD) (Fig. 2). Notable features of the LAD of the C9H8 product(s) are the symmetry around the CM angle and the angular spread of at least 30˚ in the scattering plane suggesting indirect scattering dynamics via the formation of C9H9 complexes.

**Results - Crossed Molecular Beams Studies - Center-of-Mass Frame.**

     To unravel the under­ly­ing reaction mechanism(s) along with the nature of the C9H8 isomer(s), the experimental data were transformed from the laboratory to the CM reference frame ([*29*](#_ENREF_29)*,* [*30*](#_ENREF_30)). This for­ward convolution approach yields the center-of-mass translational *P(ET)* and angular flux *T(θ)* distri­bution as depicted in Fig. 3. Best fits of the laboratory data are accomplished with a single-channel fit forming products with a mass combination of 116 amu (C9H8) and 1 amu (H). A detailed inspection of the CM functions delivers critical information on the pertinent reaction channel(s) and dynamics. First, the *P(ET)* assists in the identification of the product isomer(s). Accounting for the conservation of energy, for those products formed without internal excitation, the high energy cutoff of 376 ± 38 kJmol-1 denotes the sum of the absolute value of the reaction exoergicity plus the collision energy EC (20.6 ± 0.2 kJ mol-1). The subtraction of the collision energy reveals that the reaction is highly exoergic by -355 ± 38 kJ mol-1. This value agrees nicely with the NIST reaction energy of -364 ±12 kJ mol-1 to form the indene isomer along with atomic hydrogen ([*31*](#_ENREF_31)). Further, the *P(ET)* function holds a distribution maximum at 25 ± 3 kJ mol-1 indi­cating a tight exit transition state. Finally, the *T(θ)* distribution depicts flux over the complete an­gular range along with a forward-backward symmetry. This finding proposes indirect scat­te­ring dynamics via the formation of C9H9 complex(es) having a lifetime(s) longer than the(ir) ro­ta­tional period. The pronounced distribution maximum at 90˚ suggests geometrical cons­tr­aints of the decomposing complex(es), i.e. a preferential emission of the hydrogen atom in the exit tran­si­ti­on state perpendicular to the rotational plane of the decomposing intermediate nearly parallel to the total angular momentum vector ([*32*](#_ENREF_32)*,* [*33*](#_ENREF_33)).

**Results – Electronic Structure Calculations & Formation Mechanism.**

     The present study reveals that at least the indene molecule – the prototype aromatic molecule carrying one five- and one six membered ring - can be formed via the elementary reactions of the methylidyne radi­cal with styrene in the gas phase. We are combining these findings with computational and statis­tical results to propose the underlying reaction mechanism(s) (Fig. 4; Fig. S1). The computations reveal that the methylidyne radical can add barrierlessly either to the π electron density of the carbon-carbon double bond of the vinyl moiety (C2H3) (Fig. 4A) or to the aromatic ring (Fig. 4B and 4C). In analogy to the stem compounds ethylene (C2H4) ([*34*](#_ENREF_34)) and benzene (C6H6) ([*35*](#_ENREF_35)), methylidyne is unlikely to insert into any carbon – hydrogen bond of the phenyl or vinyl functional groups. The addition of methylidyne to the vinyl moiety leads to a phenyl-substituted cyclopropanyl intermediate (**i1**), which ring-opens to the thermodynamically prefer­red phenyl-substituted allylic radical intermediate (**i2**). The later undergoes cis-trans isomerization to **i3** followed by cyclization to **i4**; this reaction sequence is terminated by a hydrogen atom emission from the bridging C4 carbon atom accompanied by aromatization and formation of indene (**p1**) in an overall exoergic (-356 ± 8 kJ mol-1) reaction through a tight exit transition state.

     The addition of methylidyne to the benzene moiety is more complex since six chemically non-equivalent ’aromatic’ carbon-carbon bonds exist. The barrier-less addition leading to inter­me­diate **i5**, which undergoes a facile ring-opening via a barrier of only 8 kJ mol-1 to the vinyl-tropylium radical intermediate **i6**, is exemplified in Fig. 4B and 4C. Note the addition process to any ’aromatic’ carbon-carbon bond followed by ring opening results in the formation of the doublet radical intermediate **i6** (Fig. S2). This intermediate isomerizes via ring contraction to the bicyclic intermediate (**i7**) followed by the four-membered ring opening to an open shell di-substituted cyclopentadiene derivative (**i8**). Three distinct reaction pathways lead ultimately to the 1H-inden-6-yl-1,5-dihydro intermediate (**i11**) which eventually fragments via a hydrogen atom loss from the CH2 moiety located at the six-membered ring complemented by aromatization and synthesis of indene (**p1**) once again via a tight exit transition state. These isomerization sequences involve rotations of the side chains – one of them representing the vinyl side chain of the styrene reactant – around the C-C bonds connecting them with the five-membered ring (**i8** → **i9**, **i8** → **i15** → **i16**, or **i12** → **i13** → **i14**), which may be preceded by hydrogen migration in the five-membered ring (**i8** → **i12**). The rotations are followed by ring closures (**i9** → **i10** or **i14** → **i11**), in which the six-membered ring is re-formed from two exocyclic C2 moieties; the bicyclic intermediate **i10** is linked to **i11** via H migration in the five-membered ring. Alternatively, intermediate **i6** could isomerize in one or two steps involving (multiple) hydrogen migration steps eventually leading to **i18**. A sequence of ring contraction (**i19**) – hydrogen shift (**i20**) – ring opening (**i21**) – and cyclization (**i22**). The 1-indanyl radical represents the global minimum of the C**9**H**9** potential energy surface and undergoes unimolecular decomposition via atomic hydrogen from the methylidyne moiety at the C2 carbon loss through a tight exit transition state accompanied by aromatization and formation of indene (**p1**).

          Having identified six feasible reaction pathways leading eventually to indene plus atomic hydrogen, we are exploiting now a Rice–Ramsperger–Kassel–Marcus (RRKM) Master Equation analysis (Mate­ri­als and Methods) to predict the dominating reaction pathway(s) to indene. First, we evaluate the probability of methylidyne addition to the C=C double bond in the vinyl side chain versus the addition to the benzene ring. The rate constant for methylidyne addition to the double bond in the side chain is expected to be close to that for the prototype methylidyne – ethylene reaction, which, according to the literature data, is in the range of 3-5×10-10 cm3 molecule-1 s-1 for 23-300 K ([*36*](#_ENREF_36)*,* [*37*](#_ENREF_37)) and 2-3×10-10 cm3 molecule-1 s-1 for 300-700 K. ([*38*](#_ENREF_38)) While for the methylidyne – benzene system, experimental kinetic data are available for 25 K (2.7 ×10-10 cm3 molecule-1 s-1) ([*39*](#_ENREF_39)) and from 297 K to 674 K ([*40*](#_ENREF_40)) with nearly temperature independent rates of 4 ×10-10 cm3 molecule-1 s-1, ([*36*](#_ENREF_36)) our present variable reaction coordinate transition state theory (VRC-TST) calculations of methylidyne addition to the aromatic ring in benzene and to the double C=C bond in ethylene revealed that the rate constants for the former are by a factor of typically 1.5 higher than those for the latter in the same temperature interval (Supplementary Materials). The temperature dependence of the calculated rate constant for methylidyne – benzene is similar to that for the experimental rate constant for methylidyne – ethylene and the computed values for both reactions reproduce the experimental measurements within 20% or better. Based on this comparison, we can anticipate that methylidyne addition to the benzene ring should be approximately 1.5 times more likely than methylidyne addition to the vinyl side chain. Next, according to RRKM calculations of product branching ratios at the experimental collision energy, the addition to the side chain nearly exclusively produces indene via hydrogen atom loss from the benzene ring (96 + 2 % versus 4 + 2 % **p2**). Alternatively, methylidyne addition to the benzene ring is predicted to result in the production of 63 + 6 % indene (by hydrogen atom loss from the vinyl chain), 33 + 6 % vinylcyclopentadienyl plus acetylene (**p5**), and 5 + 3 % other C9H8 isomers with the indene core (**p3** and **p4**, Fig. S1), which might be formed via hydrogen atom losses both from the ring and the vinyl chain. Note that the error bars in the computed branching ratios were assessed by varying the heights of the critical barriers for different product channels by +4 kJ mol-1, which is the typical expected accuracy for relative energies computed in this study. Neglecting the small contribution from the alternative C9H8 isomers **p3** and **p4**, we evaluate the relative yields of hydrogen atom losses from the side chain and the benzene ring as 1.5×0.63/1 or nearly 1:1. Thus, the pathways to indene initiating with methylidyne addition to the ring, predominantly via intermediates **i6**, **i7**, **i8**, and **i11** are as likely as the **i1**→**i2**→**i3**→**i4**→**p1** route initiating with methylidyne addition to the side chain.Interestingly, according to the predicted reaction mechanism indene cannot be formed by elimination of the hydrogen atom originating from the methylidyne reactant.

**Results – Astrochemical Modeling**

     Having provided compelling evidence on the formation of indene under single collision con­di­ti­ons via the **M**e­thyli­dyne **A**ddition – **C**yc­li­zation – **A**romatization (MACA) mechanism, we are examining through astrochemical modeling how these findings can be transferred from the laboratory to the interstellar me­di­um. This is central since crossed molecular beam experiments along with computations cannot simulate the chemical complexity in molecular clouds. The computations predict that the elementary reaction of methylidyne with styrene has no entrance barrier to addition, all barriers implicated in the formation of indene are situated below the ener­gy of the separated reactants, and the overall reaction to indene is exoergic. These fin­dings sig­nify vital criteria for this reaction to be open in low-temperature environments such as in mo­le­cular clouds holding temperatures as low as 10 K. Any barrier would block these reac­tions in low-temperature interstellar environments. Therefore, our results can be applied to any cold en­vironment in deep space such as molecular clouds, where both the methylidyne and styrene reac­tants exist. Methylidyne radicals can be generated in the gas phase photolysis of methane (CH4) ([*41*](#_ENREF_41)) by Lyman α even present within the internal ultraviolet (UV) pho­ton field deep inside mo­le­­cular clouds ([*42*](#_ENREF_42)). Styrene can be formed either via the barrierless, bimolecular reaction of a me­thy­lidyne radical with toluene (C6H5CH3) (Fig. S3 ([*43*](#_ENREF_43))) or via UV and galactic cosmic ray in­du­ced (reactive) desorption along with grain-grain colli­sions and removal of ice mantles of grains containing styrene ([*44*](#_ENREF_44)*,* [*45*](#_ENREF_45)). Toluene itself can be produced barrierlessly from acyclic species in bimolecular ethynyl (C2H) plus isoprene (C5H8) ([*46*](#_ENREF_46)) and 1-propynyl (CH3CC) plus 1,3-buta­diene (C4H6) ([*47*](#_ENREF_47)) reactions. To explore the overall efficiency of MACA on the formation of in­dene in the interstellar medium, astrochemical simulations were run for the cold mo­le­cular cloud TMC-1 using the Nautilus v1.1 code([*48*](#_ENREF_48)). Physical parameters and initial fractional abundances of the reactive species were adopted from Hincelin et al. ([*49*](#_ENREF_49)) and are described in more detail in the Supple­men­tary Material. This reaction network was updated to include chemistries leading even­tually to the indene molecule as elucidated in the present work.

     These modeling studies reveal exciting findings (Fig. 5). The left-hand panel shows the results of the simulation with the standard cosmic ray ionization rate of ζ = 1.3 × 10-17 s-1, while the right-hand panel depicts results using a value of ζ=1.3 ×10-16 s-1, which is in line with data recently derived by Ivlev et al. for L1544, another source in Taurus. ([*50*](#_ENREF_50)) The astrochemical models disclose significant amounts of indene formed via MACA in the gas phase at fractional abundances of up to a few 10-12. The dipole moment of indene (C9H8) of 0.50 Debye is slightly higher than the dipole moment of propylene (C3H6), which has been detected recently in TMC-1, of 0.36 Debye([*51*](#_ENREF_51)) suggesting that an astronomical detection of indene toward TMC-1 is challenging, but tech­no­logically feasible in the context of a high-spectral resolution, high-sensitivity survey using, e.g. the Robert C. Byrd 100 m Green Bank Telescope (GBT) or the Atacama Large Millimeter/submillimeter Array (ALMA). Cyanoindene isomers (C9H7CN; Fig S5), which may form via rapid, barrier­less neutral – neutral reactions of indene with the cyano radical (CN), ([*52*](#_ENREF_52)) hold sig­ni­ficantly higher di­­­po­­le moments between 4.03 and 5.70 Debye thus classifying ‘cyano-tagged’ indene viable candidates to be searched for. This strategy has been exploited successfully by Chin et al. ([*53*](#_ENREF_53)) and Lo­vas et al. ([*54*](#_ENREF_54)) along with McGuire et al. ([*55*](#_ENREF_55)) to detect cyanoallene (H2CCCH(CN)) and cyano­ben­zene (C6H5CN) formed via bimolecular gas phase reactions of cyano radi­cals with microwave in­ac­tive allene (H2CCCH2) ([*56*](#_ENREF_56)) and benzene (C6H6), ([*57*](#_ENREF_57)) respectively. Our astro­chemical models pre­dict cyanoindene isomers to be present with fractional abundances of up to 10-11 with respect to molecular hydrogen – levels which are comfortably in the realm of the GBT or ALMA - with the larger va­lue of ζ revealing an even stronger effect on the abundances of cyanoindene compared to indene.

**Discussion & Conclusions**

     Our combined crossed molecular beams, electronic structure, and astrochemical modeling study reveals that indene may form not only in hot circumstellar envelopes of carbon-rich stars together with planetary nebulae as thought previously, but also in cold molecular clouds via facile, barrierless reactions involving the simplest organic radical (methylidyne) with styrene. Since indene carries a five-membered ring, the low temperature pathway may deliver a popu­lation of indene, which could provide a struc­tural motif for the generation of non-planar PAHs such as corannulene and even fullerenes (Fig. 1). These five-membered rings are critical to bent PAHs out-of-plane; as evident form kinetic Monte Carlo models of graphene-edge growth, the exclusion of reactions creating five-membered rings from the simulation lead only to planar PAHs ([*23*](#_ENREF_23)*,* [*58*](#_ENREF_58)). It is worth mentioning that PAH formation might also involve nucleation, where reactive surfaces provided by seed particles such as silicon carbides initiate grain growth processes through deposition of aromatic molecules. After ejection to the interstellar medium, the upper layers of these grains, which may contain aromatic molecules, might be desorbed by ultraviolet radiation, sputtering, or shuttering by grain-grain collision ([*59*](#_ENREF_59)). Further, in solar nebula, the abstraction of a hydrogen atom followed by the addition of acetylene molecules may form significant quantities of PAHs by considering the higher initial concentration based on the astronomical observational results; these processes involve entrance barriers and only operate at elevated temperatures of typically 1,000 K and beyond ([*60*](#_ENREF_60)). Thus, the present investigation of barrierless, low temperature pathways to indene may bring us closer to unraveling the paradox of the injection and destruct­ion timescales of aromatics.

     The work reported here represents an important step toward a systematic understanding of the fundamental chemical processes leading to the formation of indene and non-planar PAHs in low temperature environments in deep space. Whereas indene has been shown to be the product in high temperature processes involving reactions of phenyl radicals (C6H5) with allene (H2CCCH2) and methylacetylene (CH3CCH) ([*61*](#_ENREF_61)*,* [*62*](#_ENREF_62)) along with the benzyl radical (C7H7) – acetylene (C2H2) system ([*63*](#_ENREF_63)), the **M**e­thyli­dyne **A**ddition – **C**yc­li­zation – **A**romatization (MACA) mechanism opera­tes at low temperatures such as in molecular clouds. The only other barrierless reaction, which has been recently shown to form indene, is *o*-benzyne (C6H4) plus allyl (C3H5), ([*64*](#_ENREF_64)) but it involves two unstable species not detected in deep space. MACA has the potential to convert *any* vinyl group (C2H3) linked to an aromatic, six-membered ring eventually to a cyclopentadiene moiety via reaction of a methylidyne radical (Fig. 6). MACA can compete with the ethynyl addition mechanism (EAM), ([*65*](#_ENREF_65)*,* [*66*](#_ENREF_66)) which is predicted to convert the vinyl group attached to a PAH molecule to a six-membered ring. Whereas the carbon backbone of the benzene ring stays intact as long as the methylidyne radical adds to the vinyl moiety (Fig. 7), an addition to the benzene ring leads to a complete structural reorganization of the benzene moiety leading to a newly formed six-membered ring incorporating the vinyl functional group. The complete reorganization of the carbon skeleton of a ‘stable’ aromatic system even at temperatures as low as 10 K leads to a complete ‘loss of memory’ of the molecular structure and is rather unprecedented as traditional molecular mass growth processes to aromatic systems merely ‘add’ rings to an existing aromatic structure. Considering the crucial role of non-planar PAHs in the formation of fullerenes and carbonaceous dust particles – commonly referred to as interstellar grains – and in the chemical evolution of the universe, with grains acting as vital molecular factories to synthesize biorelevant organics like amino acids and sugars, the elucidation of the elementary steps leading to dust particles in our galaxy is fundamental to enhance our knowledge of the chemistry of carbonaceous matter in our Galaxy.

**Mate­ri­als and Methods**

**Crossed Molecular Beam Experiments.**

The reaction of the methylidyne (CH; X2Π) radical with styrene (C8H8; X1A′) was performed in gas phase under single collision conditions exploiting a crossed molecular beam machine ([*67*](#_ENREF_67)). A pulsed supersonic beam of methylidyne radicals was produced by photodissociation of helium (99.9999 %; Air Gas) seeded bromoform (CHBr3, Aldrich Chemistry, ≥ 99 %) held in a stainless-steel bubbler at a stagnation pressure of 2.2 atm and 283 K. This mixture was introduced into a pulsed piezoelectric valve operating at a repe­ti­tion rate of 60 Hz, pulse widths of 80 µs, and a peak voltages of -400 V. The 248 nm output of excimer laser (COMPex 110, Coherent, Inc.; 30 Hz) intersected molecular beam 1 mm downstream of the nozzle ([*68*](#_ENREF_68)). A chopper wheel rotating at 120 Hz selected a section of the pulse defined by a peak velocity of 1850 ± 11 ms-1 and speed ratio of 11.7 ± 0.7. The rotational temperature was characterized by laser induced fluorescence (LIF) to be 14 ± 1 K ([*69*](#_ENREF_69)). This segment crossed a pulsed supersonic beam of styrene (C8H8, TCI America, >99.0 %) seeded in xenon (99.999 %; Matheson) at a fraction of 1% at 550 Torr perpendicularly. The section of the supersonic styrene beam crossing the methylidyne radical beam has a peak velocity and speed ratio of 386 ± 4 ms-1 and ratio 28.0 ± 0.4, respectively resulting in a collision energy of 20.6 ± 0.2 and center-of-mass (CM) angle 59.1 ± 0.3˚. The beam characteristics are defined in Table S1. The reactive-scattering products were ionized by an electron-impact ionizer operating at 80 eV and 2 mA emission current, before they entered a quadrupole mass spectrometer (QMS, Extrel QC 150) operating in the time-of-flight (TOF) mode ([*70*](#_ENREF_70)*,* [*71*](#_ENREF_71)). The designated ion species filtered by the QMS at a specific *m/z* travelled towards a stainless steel target coated with a thin layer of aluminum biased at -22.5 kV and a cascade-of-electron pulse was initiated upon impact. The electrons were then expelled from the stainless steel target and flew towards an organic scintillator to generate a photon pulse, prior to be detected by a Burle photomultiplier tube (PMT, Model 8850) operating at -1.35 kV. The signal was filtered by a discriminator (Advanced Research Instruments, Model F-100TD) at a level of 1.6 mV and fed into a Stanford Research System SR430 multichannel scaler. The rotatable detector allows the collection of angular resolved time-of-flight (TOF) spectra at discrete angles, integrate and normalize them with respect to the intensity at the CM angle, and then derive the product laboratory angular distribution at a specific mass-to-charge ratio (m/z). In order to obtain information on the reaction dynamics, we employed a forward-convolution routine to convert the data from the laboratory frame into the center-of-mass reference frame ([*29*](#_ENREF_29)*,* [*30*](#_ENREF_30)). Considering the barrierless reaction, the collision energy (Ec) dependence of the cross section σ was obtained from the line-of-center model as σ ~ EC-1/3 ([*32*](#_ENREF_32)). The flux contour map, *I(θ,u)* = *P(u)* × *T(θ)*, which presents the flux of the reactively scattered products as a function of the CM scattering angle (*θ*) and product velocity (*u*), contains all information of the reactive scattering process.

**Electronic Structure and RRKM Calculations.**

Geometries of the reactants, products, intermediates, and transition states involved in the methylidyne - styrene reaction on the C9H9 potential energy surface were optimized at the B3LYP/6-311G(d,p) level of theory, ([*72*](#_ENREF_72)*,* [*73*](#_ENREF_73)) with vibrational frequencies computed using the same method. Single-point energies were further improved using the composite G3(MP2,CC) model chemistry scheme ([*74-76*](#_ENREF_74)). The G3(MP2,CC)//B3LYP theoretical approach is capable of providing the energetic parameters with ‘chemical accuracy’ within 3-6 kJ mol-1 for hydrocarbons in terms of average absolute deviations. The GAUSSIAN 09 ([*77*](#_ENREF_77)) and MOLPRO 2010 ([*78*](#_ENREF_78))program packages were employed for the ab initio calculations. Rice-Ramsperger-Kassel-Marcus (RRKM) theory, ([*79-82*](#_ENREF_79)) was used to compute energy-dependent rate constants of all unimolecular reaction steps on the C9H9 surface following the initial addition of the methylidyne radical to styrene and to obtain product branching ratios under single-collision conditions using our in-house Unimol code ([*83*](#_ENREF_83)).

**VRC-TST calculations of rate constants for methylidine addition to C6H6 and C2H4.**

Rate constants for the barierrless CH + benzene and CH + ethylene addition reactions were computed using Variable Reaction Coordinate-Transition State Theory (VRC-TST) ([*84-86*](#_ENREF_84)). A multifaceted spherical dividing surface ([*84*](#_ENREF_84)) used in the calculations was built as the equidistant surface between the pivot points assigned to the associating/dissociating fragments. At short-range distances (less than 5 Å) the pivot points placement was varied along the symmetry axis of the π-orbitals of benzene/ethylene. The centers of mass of the reacting fragments served as the pivot points at long-range distances ([*84*](#_ENREF_84)). A complex of interacting fragments on a dividing surface was generated using the geometries of CH and benzene/ethylene optimized as separate fragments at the B3LYP/6-311G(d,p) ([*72*](#_ENREF_72)*,* [*73*](#_ENREF_73)) level of theory. The notation “rigid” is used here to denote the lack of geometrical relaxation in a complex on a dividing surface. The single-point energies of “rigid” structures were probed at the at CCSD(T)/cc-pvdz ([*87*](#_ENREF_87)) level of theory. The single-point energies of the “rigid” structures were further amended with the one-dimensional geometry relaxation correction ([*84*](#_ENREF_84)) and the complete basis set (CBS) correction ([*88*](#_ENREF_88)). The one-dimensional geometry relaxation correction was calculated for the minimum energy path (MEP) “rigid” structures relaxed using B3LYP/6-311G(d,p) geometry optimization. The CBS correction was calculated using the CCSD(T)/cc-pV*n*Z (*n* = D, T, Q) energies of the “rigid” MEP structures. To summarize, in the VRC-TST reactive flux calculations, the energies of the “rigid” structures sampled on a dividing surface were first probed at the CCSD(T)/cc-pVDZ level of theory followed by the *ad hoc* one-dimensional relaxation and CBS corrections:

E = Erigid[CCSD(T)/cc-pVDZ] + ΔE[geom] + ΔE[CBS],

where Erigid is the single-point energy of the interacting “rigid” fragments, ΔE[geom] is the geometry relaxation correction computed as the difference of CCSD(T)/cc-pVDZ energy of the optimized MEP structure corresponding to a particular value of the RCC distance and the “rigid” structure at the same R. ΔE[CBS] was calculated as follows:

ΔE[pVTZ] = Erigid[CCSD(T)/cc-VTZ] – Erigid[CCSD(T)/cc-VDZ]

ΔE[pVQZ] = Erigid[CCSD(T)/cc-VQZ] – Erigid[CCSD(T)/cc-VTZ]

ΔE[CBS] = ΔE[pVQZ] + 0.69377×(ΔE[pVQZ] - ΔE[pVTZ])

The temperature dependent high-pressure-limit (HP) rate constants for the CH + benzene and CH + ethylene addition reactions are shown in Figure S4 and the computed ratios of these rate constants at different temperatures are presented in Table S3.

**Astrochemical Modeling.**

For this work, the three-phase astrochemical code, Nautilus v1.1, was used. ([*48*](#_ENREF_48)) In addition to running models using the standard cosmic ray ionization rate of ζ=1.3x10-17 s-1, we carried out additional simulations with a value of ζ=1.3x10-16 s-1. This latter value is based on the recent study by Ivlev and coworkers ([*50*](#_ENREF_50)) of gas and dust temperatures toward L1544, which is another source in Taurus fairly close to TMC-1. It has previously been suggested in a number of recent works that the cosmic ray ionization is higher than the standard value towards the Galactic Center, ([*89-91*](#_ENREF_89)) however, the study by Ivlev and coworkers is remarkable, in part, since it similarly suggests that the standard value is similarly too low even for regions outside the Galactic Center. To account for cosmic ray-driven reactions, the method of Shingledecker & Herbst is exploited. ([*92*](#_ENREF_92) *,* [*93*](#_ENREF_93)) The physical conditions and elemental abundances appropriate for TMC-1 are listed in Tables S5 and S6; an initial carbo-to-oxygen ratio of 1.2 was utilized ([*49*](#_ENREF_49)). Our chemical network is based on that used by Shingledecker et al. ([*94*](#_ENREF_94)) To it, we added reactions related to the formation of indene (C9H8) and similar polycyclic species. New gas phase reactions are given in Table S7 with rates taken from the literature where available or computed via equation (2) and (3); ζ is the cosmic ray ionization rate and α describes the efficiency of photodissociation by internally generated ultraviolet photons.

(1)

(2)

To objectively explore the effects of the formation of indene on the icy grains followed by desorption into the gas phase, we also explored (a) neutral-neutral reactions between ground state species, (b) the cosmic ray-driven radiolysis of the new species, and (c) reactions involving one ground state species and one suprathermal species in a higher electronic state. Suprathermal reactions occur quickly ([*95*](#_ENREF_95)*,* [*96*](#_ENREF_96)) with rate coefficients incorporated based on the attempt-frequency. ([*94*](#_ENREF_94)) Whenever experimental production rates in the ices were not available, we computed the rate coefficients using expression (3) where, α is the branching fraction, and γ is the G-value of formation, which gives the number of molecules produced per 100 eV deposited in the system.

(3)

Though we have included this grain-surface analogue system of the MACA route in our network, its contribution to the overall abundance of gas-phase indene was found to be negligible at levels of less than 1 %. The main destruction routes for indene include reactions with carbon atoms at model times less than ca. 105 yr, and with cyano radicals thereafter. Depletion onto the 10 K grains represents another destruction mechanism for gas phase indene and the dominant destruction route for cyanoindenes.

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**Competing Interests**

The authors declare that they have no competing interests.

**Author contributions**

R.I.K. designed research and managed the overall project; S.D., G.R.G., H.W., A.M.T., C.H., Z.Y., A.N.M., C.N.S., A.M.M., and R.I.K. performed research; S.D., G.R.G., H.W., C.N.S., A.M.M., and R.I.K analyzed data and wrote the paper.

**Data availability**

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials

**Supplementary Materials**

Figures S1-S5

Tables S1-S7

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**Figure 1.** Simplest representatives of two-ring PAHs carrying two six membered (naphthalene; C10H8; **1**) and one six- along with one five-membered ring (indene; C9H8; **2**). Whereas the **H**ydrogen-**A**bstraction-**V**inylacetylene-**A**ddition (HAVA) mechanism can lead to the formation of naphthalene at 10 K, a low temperature pathway to indene – a fundamental molecular building block of bent PAHs like corannulene (C20H10; **3**) and buckminsterfullerene (C60; **4**) – is still elusive. Carbon and hydrogen atoms are color coded in gray and white, respectively, with the carbon backbone of indene highlighted in black.

**Figure 2.** Laboratory angular distribution and the associated time-of-flight spectra. Labora­tory angular distribution at mass-to-charge ratio of 116 (C9H8+) recorded in the reaction of the methylidyne radical (CH; X2Π) with styrene (C8H8; X1A′) (a) and the time-of-flight spectra collected at distinct laboratory angles overlaid with the best fits (b). The solid circles with their error bars indicate the normalized experimental distribution with ±1σ uncertainty, and the open circles indicate the experimental data points of the time-of-flight spectra. The red lines represent the best fits obtained from the optimized center-of-mass (CM) functions, as depicted in Fig. 3.

**Figure 3.** Center-of-Mass (CM) distributions and the associated flux contour map. CM translational energy flux distribution (a), CM angular flux distribution (b), and the top view of the corresponding flux contour map (c) leading to the formation of indene plus atomic hydrogen in the reaction of methylidyne radical with styrene. Shaded areas indicate the error limits of the best fits accounting for the uncertainties of the laboratory angular distribution and TOF spectra, with the red solid lines defining the best-fit functions. The flux contour map represents the flux intensity of the reactive scattering products as a function of the CM scattering angle (θ) and product velocity (u). The color bar indicates the flux gradient from high (H) intensity to low (L) intensity. Atoms are color coded in gray (carbon) and white (hydrogen).

**Figure 4.** Potential Energy Surface.Thepotential energy surface for the reaction of the methyli­dyne radical with styrene including reaction pathways energetically accessible in the crossed molecular beam experiments via addition to the vinyl (Path A) and benzene moiety (Paths B and C). The route in red highlights the reaction pathway leading to the formation of indene plus atomic hydrogen. Relative energies are given in units of kJ mol-1. Atoms are color coded in gray (carbon) and white (hydrogen).

**Figure 5.** Modeled fractional abundances of indene (C9H8) and cyanoindene (C9H7CN) in cold molecular clouds. Left: Simulation with a cosmic ray ionization rate of ζ = 1.3 × 10-17 s-1. Right: Simulation with a cosmic ray ionization rate of ζ = 1.3 ×10-16 s-1. The solid and dashed lines depict upper and lower limits of the fractional abundances (Supplementary Material).

**Figure 6.** Versatile conversion of a methyl (CH3) functional group of a PAH to the indene moiety via methylidyne radical reactions through vinyl (C2H3) substituted PAHs involving the novel **M**e­thyli­dyne **A**ddition – **C**yc­li­zation – **A**romatization (MACA) mechanism. The waved lines indicate the incorporation within a PAH.

**Figure 7.** Indene Carbon Skeleton.Location of the carbon atoms within the styrene and methylidyne reactants and for the indene reaction product following addition to the vinyl (Path A) and benzene moieties (Path B and C).