

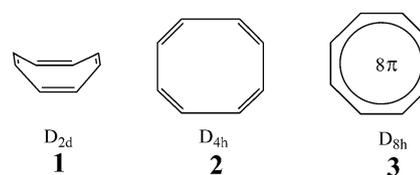
Gas-Phase Synthesis of the Elusive Cyclooctatetraenyl Radical (C_8H_7) via Triplet Aromatic Cyclooctatetraene (C_8H_8) and Non-Aromatic Cyclooctatriene (C_8H_8) Intermediates

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Abstract: The 1,2,4,7-cyclooctatetraenyl radical (C_8H_7) has been synthesized for the very first time via the bimolecular gas-phase reaction of ground-state carbon atoms with 1,3,5-cycloheptatriene (C_7H_8) on the triplet surface under single-collision conditions. The barrier-less route to the cyclic 1,2,4,7-cyclooctatetraenyl radical accesses exotic reaction intermediates on the triplet surface, which cannot be synthesized via classical organic chemistry methods: the triplet non-aromatic 2,4,6-cyclooctatriene (C_8H_8) and the triplet aromatic 1,3,5,7-cyclooctatetraene (C_8H_8). Our approach provides a clean gas-phase synthesis of this hitherto elusive cyclic radical species 1,2,4,7-cyclooctatetraenyl via a single-collision event and opens up a versatile, unconventional path to access this previously largely obscure class of cyclooctatetraenyl radicals, which have been impossible to access through classical synthetic methods.

Since Willstätter's pioneering synthesis of 1,3,5,7-cyclooctatetraene (C_8H_8 , COT) more than 100 years ago,^[1] 1,3,5,7-cyclooctatetraene along with the cyclooctatetraenyl radical (C_8H_7) have received considerable attention from the physical organic, theoretical, and synthetic organometallic chemistry communities from a fundamental point of view of electronic structure as a prototype of exotic ring inversion—bond shifting isomerization^[2,3] and as organic ligands.^[4–8] COT represents a benchmark of closed shell annulenes^[9]—conjugated monocyclic hydrocarbons with the general molecular formula C_nH_n and n being an even number. Annulenes can be

antiaromatic (C_8H_4 , [4]annulene, cyclobutadiene), aromatic (C_8H_6 , [6]annulene, benzene), and non-aromatic (C_8H_8 , [8]annulene, cyclooctatetraene). Although [8]annulene has 8π electrons and thus should be formally categorized as antiaromatic,^[10] the non-planar D_{2d} symmetric structure (**1**; Scheme 1) lies about 18 kJ mol^{-1} below the planar D_{8h} geometry (**3**),^[3] which represents a transition state for the bond shifting process in (**2**) (D_{4h});^[11] **2** defines the transition state in the ring inversion of the tub-like COT structure (Scheme 1). Addition of one or two electrons to the non-



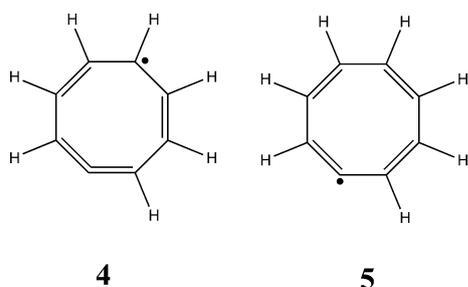
Scheme 1. Structures of 1,3,5,7-cyclooctatetraene (**1**) along with transition states for ring inversion (**2**) and bond-shifting isomerization processes (**3**). The point groups are also indicated.

bonding molecular orbitals changes the molecular structure of COT significantly: the 1,3,5,7-cyclooctatetraene radical anion ($COT^{\cdot-}$)^[12] and 1,3,5,7-cyclooctatetraene dianion (COT^{2-})^[13] are both planar and—in case of COT^{2-} — 10π Hückel aromatic.^[13] COT^{2-} has been recognized as a significant ligand in f-block chemistry. Since uranocene ($U(COT)_2$) was proposed by Fischer in 1963^[14] and first synthesized by Streitwieser and Müller-Westerhoff in 1968,^[4] extensive experimental^[7,8,15–17] and theoretical^[16,18–21] research has been conducted on uranocenes, actinocenes, and lanthanocenes including being identified as potential candidates for nanowires^[17] and single-molecular magnets.^[21]

However, despite the synthesis of 1,3,5,7-cyclooctatetraene more than a century ago, the cyclooctatetraenyl radical (C_8H_7), which can be formally derived by removing a hydrogen atom from any of the eight CH moieties in COT, has not been identified experimentally to date. Electronic structure calculations suggest enthalpies of formation at 0 K of 506 kJ mol^{-1} .^[22,23] Lin et al.^[22] and Mebel et al.^[23] proposed that this radical might represent a yet unobserved short lived intermediate in combustion processes via the reaction of the phenyl radical (C_6H_5) with acetylene (C_2H_2) formed after addition of phenyl to acetylene followed by the formation of a bicyclic doublet intermediate and a ring opening to cyclooctatetraenyl. Classically, the cyclooctatetraenyl radical might

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Scheme 2. Classical Lewis structures of the cyclooctatetraenyl radical (C_8H_7) depicting the C_2 symmetric 1,2,4,7- and C_1 symmetric 1,3,5,7-cyclooctatetraenyl forms (**4**) and (**5**), respectively.

hold two non-equivalent Lewis structures (Scheme 2): a 1,2-diene structure (**4**) representing a resonantly stabilized radical (1,2,4,7-cyclooctatetraenyl) and 1,3,5,7-cyclooctatetraenyl (**5**). A potential isomerization of (**5**) to (**4**) changes the hybridization of the carbon atom at the radical site from sp^2 to sp , while simultaneously transferring spin density of the unpaired electron across the ring to the sp^2 hybridized carbon atom. The 1,2-diene form (**4**) was found to be lower in energy by 10 to 13 kJ mol^{-1} compared to the classical structure (**5**); a shallow barrier of only 0.3 kJ mol^{-1} separates both structures.^[24] This barrier is too low to permit any bound vibrational states of 1,3,5,7-cyclooctatetraenyl, but as the location of the radical center effectively dictates the chemistry such as in a radical-radical recombination or oxidation,^[25–31] bimolecular reactions of the cyclooctatetraenyl might bifurcate via distinct reaction pathways. This classifies the elusive cyclooctatetraenyl radical as a prototype of an unsaturated π -conjugated radical depicting bond-shifting isomerization mechanisms.

Herein, we provide a unique glance into the chemistry of the cyclooctatetraenyl radical and report on its very first gas-phase synthesis under single-collision conditions via a bimolecular reaction of ground state atomic carbon (C , 3P_j) and 1,3,5-cycloheptatriene (C_7H_8) via two activated triplet C_8H_8 intermediates—the D_{8h} symmetric aromatic cyclooctatetraene ($^3A_{1g}$) and the C_1 symmetric non-aromatic cyclooctatriene (3A) species—utilizing the crossed-molecular-beams method. An investigation at the most fundamental, microscopic level delivers unique insights into the reaction mechanisms through which highly reactive molecules such as the cyclooctatetraenyl radical are formed. This eventually enables a clean gas-phase synthesis of this hitherto elusive cyclic species. This system is also exciting from the viewpoint of a physical-organic chemist as it represents a benchmark to unraveling the chemical reactivity, bond breaking processes, and the synthesis of a truly combustion related cyclic, resonantly stabilized free radicals (RSFR) in a single collision event, which cannot be obtained by traditional chemistry routes.

In the reaction of ground state atomic carbon (C ; 12 amu) with 1,3,5-cycloheptatriene (C_7H_8 ; 92 amu), the reactive scattering signal was detected at m/z 103 ($C_8H_7^+$) and 102 ($C_8H_6^+$) with data at m/z 103 illustrating the best signal-to-noise ratio. After scaling, the time-of-flight (TOF) spectra at both mass-to-charge ratios were superimposable signifying

that signal at m/z 102 stems from dissociative ionization of the C_8H_7 product in the electron impact ionizer of the detector with ions at lower m/z being fragments from m/z 103. Consequently, our experiments reveal that only the carbon versus hydrogen replacement pathway is open and that any molecular hydrogen loss mechanisms are closed. It should be highlighted that besides atomic carbon, the primary beam also contains dicarbon (C_2) and tricarbon molecules (C_3). At our experimental conditions, tricarbon is unreactive with unsaturated hydrocarbons (Supporting Information).^[32,33] The reactive scattering signal from dicarbon with 1,3,5-cycloheptatriene at m/z 115 or 114 was not observable either, and reactive scattering signal at m/z 103 could not be fit with a mass combination of the reactants of 24 amu (dicarbon) or 36 amu (tricarbon) plus 92 amu (1,3,5-cycloheptatriene). Figure 1 compiles selected TOF spectra recorded at various angles in the laboratory frame for the most intense ion at m/z 103 ($C_8H_7^+$). The laboratory angular distribution of the C_8H_7 product(s) is obtained by integrating the TOF spectra

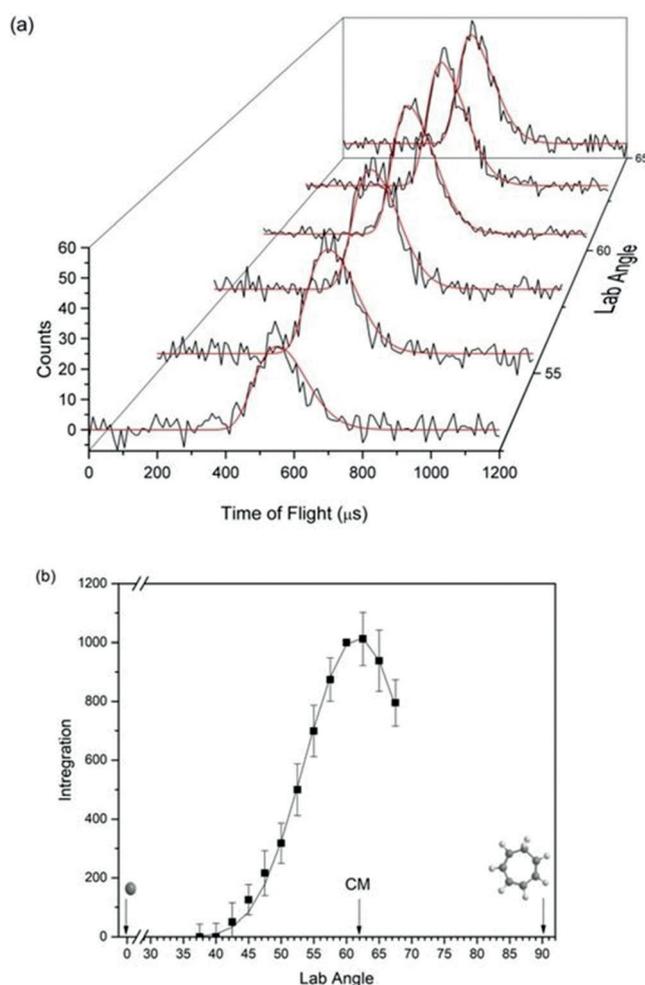


Figure 1. Time-of-flight data (a) and laboratory angular distribution (b) at m/z 103 ($C_8H_7^+$) for the reaction of ground state atomic carbon (C) with 1,3,5-cycloheptatriene (C_7H_8) forming $C_8H_7 + H$ product(s). The black line represents the experimental data and the red line represents the fit in (a) and the solid squares represent the experimental data, error bars present the standard deviation and the solid lines represent the fit in (b).

and peaks at the center of mass angle of $62.5 \pm 1.0^\circ$. To summarize, the raw data reveals the presence of a carbon versus hydrogen exchange channel along with the formation of C_8H_7 radicals under single collision conditions.

The goal of our study is to identify the C_8H_7 isomer formed in the elementary reaction of carbon with 1,3,5-cycloheptatriene. To achieve this, the data had to be transformed from the laboratory frame to the center-of-mass (CM) reference frame to extract the translational energy ($P(E_T)$) and angular ($T(\theta)$) distributions (Figure 2). The laboratory data could be fit with a single channel with the combination of the product masses of 103 amu (C_8H_7) and 1 amu (H). The $P(E_T)$ extends to a maximum translational energy release of 200 ± 34 kJ mol⁻¹. This data can be exploited to determine the reaction energy and—upon comparison with computed reaction energies—also the structural isomer formed. This can be achieved since the maximum of the translational energy of the $P(E_T)$ resembles the sum of the collision energy plus the reaction energy for those product molecules without internal excitation. Therefore, a subtraction of the collision energy of 32 ± 4 kJ mol⁻¹ reveals that the reaction to form C_8H_7 plus atomic hydrogen is exoergic by 168 ± 34 kJ mol⁻¹. Further, the $P(E_T)$ depicts a distribution maximum slightly away from zero translational energy spanning from about 5 to

35 kJ mol⁻¹. This finding indicates that at least one channel holds a tight exit transition state upon unimolecular decomposition of the C_8H_8 intermediate(s) with the hydrogen loss linked to a substantial electron rearrangement upon the formation of the C_8H_7 product; the broad plateau also suggests the existence of one channel with a rather loose exit transition state.^[33] Finally, the $T(\theta)$ distribution reveals a forward-backward symmetry with respect to 90° with flux distributed over the complete angular range of 0° to 180° . This outcome proposes indirect scattering dynamics of the reaction via the formation of C_8H_8 reaction intermediate, which can be characterized as a long-lived complex with a lifetime longer than its rotational period. The weak polarization of the center-of-mass angular distribution is the result of the inability of the light hydrogen atom to carry away a significant fraction of the total angular momentum. This is also reflected in the flux contour map, which represents an overall image of the reaction containing all the information of the reactive scattering process.

We are now elucidating the nature of the C_8H_7 isomer by comparing of the experimentally determined reaction exoergic (-168 ± 34 kJ mol⁻¹) with the reaction energies obtained from electronic structure calculations. The geometries of distinct C_8H_7 product isomers along with C_8H_8 intermediates were investigated via electronic structure calculations (Supporting Information). This study proposed the existence of two low-lying C_8H_7 product isomers 1,2,4,7-cyclooctatetraenyl (**p1**) and 2,4,6,7-cycloocta-tetraenyl (**p2**) in overall exoergic reactions of 176 and 54 kJ mol⁻¹. A comparison of the experimental reaction energy (-168 ± 34 kJ mol⁻¹) with our computed energetics reveals that at least the thermodynamically most stable 1,2,4,7-cyclooctatetraenyl isomer (**p1**) is formed (-176 ± 10 kJ mol⁻¹). Therefore, we can conclude that our experiments synthesized and observed the 1,2,4,7-cyclooctatetraenyl radical for the first time under single collision conditions in the gas phase.

With the identification of the 1,2,4,7-cyclooctatetraenyl radical (**p1**) as a reaction product, we would like to unravel the underlying reaction mechanism(s) to its formation and to quantify the contribution of the thermodynamically less stable isomer (**p2**) to the scattering signal. This is concluded by merging our experimental results with electronic structure calculations (Figure 3). Considering the structure of the 1,3,5-cycloheptatriene (C_7H_8) reactant, atomic carbon was found to add without entrance barrier to the C1=C2/C5=C6 and/or C3=C4 carbon-carbon double bonds leading to bicyclic triplet intermediate **i1** and a stationary structure **i0**, respectively. The computations reveal that **i1** can undergo a facile ring opening to **i2** via a barrier of only 28 kJ mol⁻¹. Structure **i0** is not a local minimum but rather a saddle point containing one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations initiated from **i0** lead to the identical structures **i3**, in which the attacking carbon atom completes its insertion into the C3-C4 bond and the seven-member ring extends to an eight-member ring. Since **i3** is non-planar, it has two enantiomers and the transition state **i0** connects the two enantiomers, that is, **i0** serves as a transition state for ring inversion in **i3**. Thus, from the reactants, the minimal energy reaction path leads to the vicinity of **i0** and then, the ring opens to **i3**. Both **i2** and **i3**

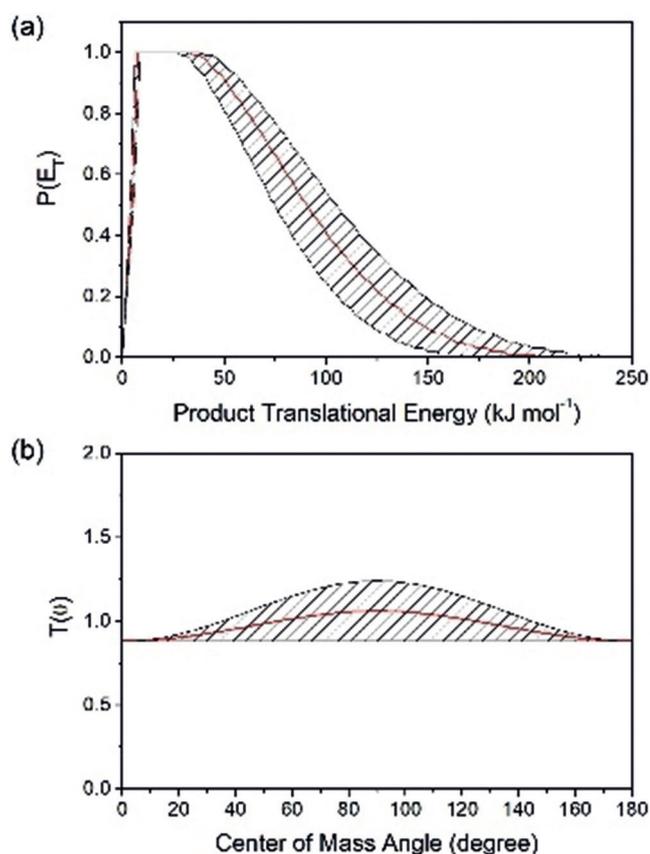


Figure 2. a) Center-of-mass translational-energy flux distribution $P(E_T)$ and b) angular distribution $T(\theta)$ for the atomic hydrogen loss channel in the reaction of carbon with 1,3,5-cycloheptatriene. Hatched areas indicate the acceptable upper and lower error limits of the fits and solid red lines define the best-fit functions.

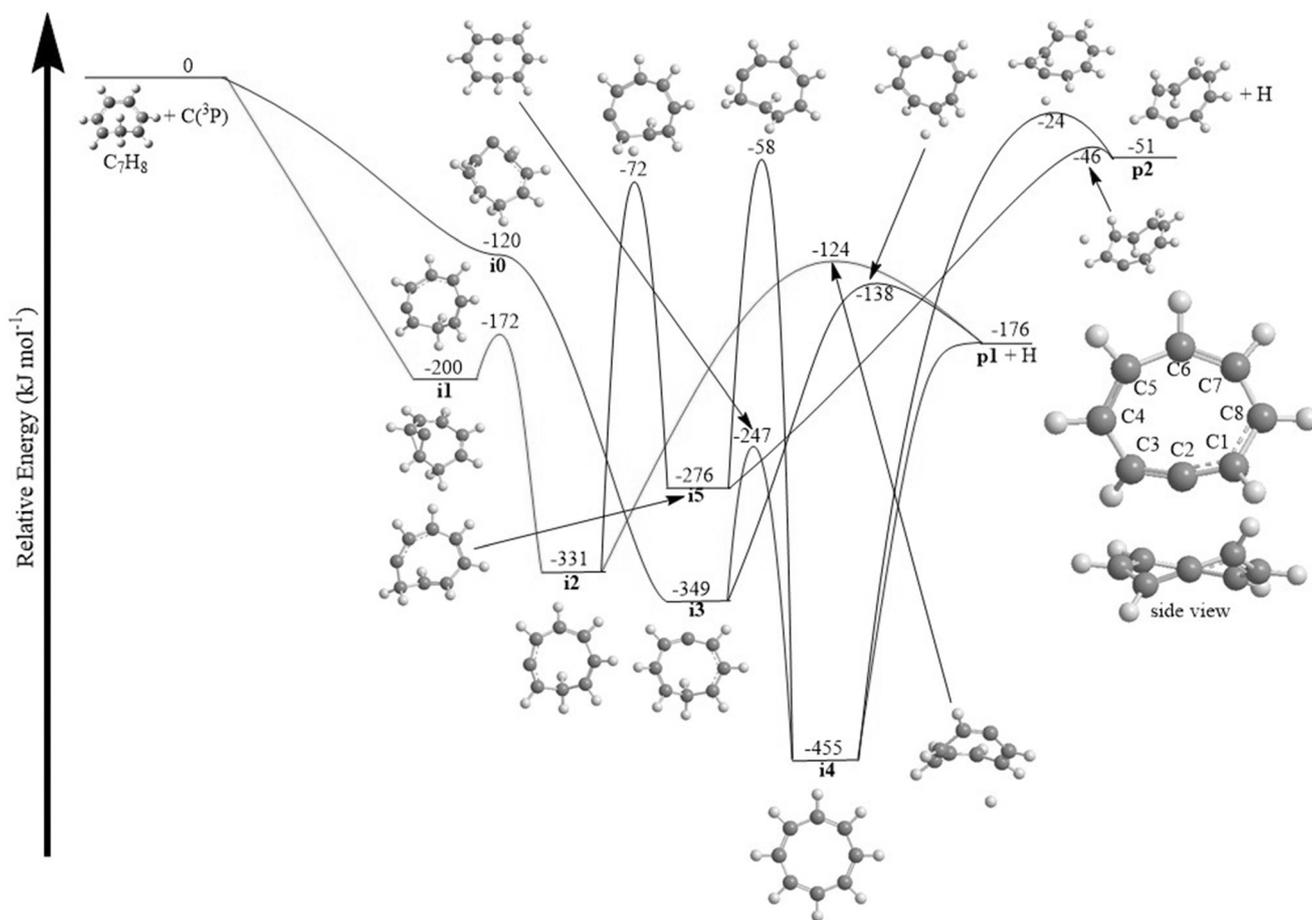


Figure 3. Low-energy paths for the reaction of triplet carbon with 1,3-cycloheptatriene (C_7H_8) leading to the 1,2,4,7-cyclooctatetraenyl radical (C_8H_7) under single-collision conditions. Intermediates are labeled as **iX**. The energies of intermediates and transition states relative to separated reactants are given in kJ mol^{-1} as calculated at the G3(MP2,CC)//B3LYP/6–311G** + ZPE (B3LYP/6–311G**) level of theory. The dominating pathways involving tight exit transition states are denoted in red and loose exit transition states are denoted in blue. See Supporting Information for bond lengths and bond angles.

can be classified as cyclic annulene derivatives on the triplet surface with the **i3** undergoing a hydrogen shift from the CH_2 moiety to the formally inserted carbon atom across the ring. This process leads to the D_{8h} symmetric triplet 1,3,5,7-cyclooctatetraene intermediate **i4**, which represents the global minimum of the triplet C_8H_8 potential energy surface (PES). Here, triplet 1,3,5,7-cyclooctatetraene (**i4**) represents a prototype of a system, which can be characterized as a $4n$ π triplet aromatic molecule.^[34] The carbon-carbon (140 pm) and carbon hydrogen (109 pm) bond lengths of triplet 1,3,5,7-cyclooctatetraene are almost identical to benzene of 139 pm and 108 pm (Supporting Information). Gogonea et al. characterized triplet 1,3,5,7-cyclooctatetraene as an aromatic molecule based on appreciable aromatic stabilization energy with respect to a triplet reference state—the lowest triplet state of the open-chain polyene with eight carbon atoms, negative nuclear-independent chemical shift, downfield ^1H NMR chemical shift, and a significant diamagnetic susceptibility exaltation (in the absence of the paramagnetic effects of unpaired electrons).^[34] Eventually, both triplet intermediates **i2** and **i4** undergo unimolecular decomposition via tight and loose exit transition states, respectively, leading to

the 1,2,4,7-cyclooctatetraenyl radical (**p1**). This radical (Figure 3) has a C_2 -symmetric structure and the 2B electronic term with the symmetry axis going through the bare atom C2 and the C6–H bond. The C2 atom is linked with its neighbors C1 and C3 by double bonds (131 pm) similar to those in allene. The C8–C1 and C3–C4 bonds have mostly a single character (146 pm), whereas the C4–C5/C7–C8 (138 pm) and C5–C6/C6–C7 (143 pm) bonds have an intermediate character between single and double reflecting delocalization of the unpaired electron between five carbon atoms C4, C6, C8, and C1–C3. The presence of the allene-like fragment centered at C2 makes the molecular structure puckered (Figure 3). Figure 4 illustrates key molecular orbital (MO) diagrams for the decomposing intermediates **i2** and **i4** and the product **p1**. One can see that in triplet aromatic **i4**, three bonding π orbitals are occupied (A_{2u} and E_{1g}), two unpaired electrons sit on the non-bonding E_{2u} molecular orbital (MO), and three antibonding π^* orbitals (E_{3g} and B_{2u}) are vacant. In the product, the symmetry is reduced to C_2 , but the singly occupied HOMO can be described as non-bonding π , whereas LUMO acquires an antibonding π^* character. Otherwise, due to the absence of the molecular plane, the doubly-occupied

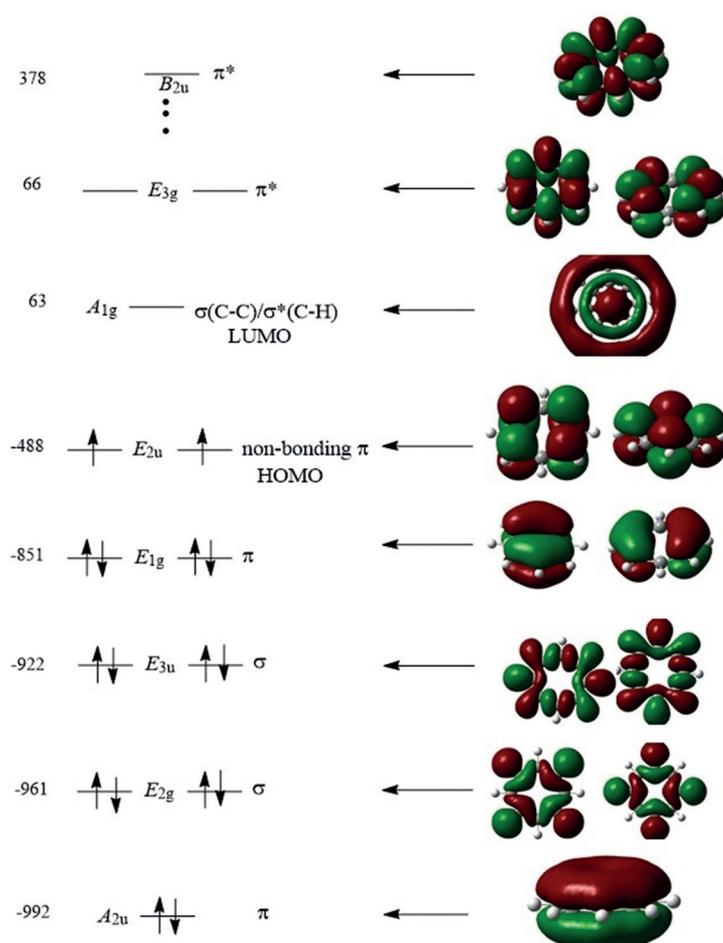


Figure 4. Molecular orbital diagram of the decomposing triplet aromatic intermediate **i4** (1,3,5,7-cyclooctatetraene, D_{8h}). Molecular orbital energy levels are shown in kJ mol^{-1} . Molecular orbital diagrams for the second decomposing intermediate **i2** (2,4,7-cyclooctatriene, C_1) and for the 1,2,4,7-cyclooctatetraenyl (C_8H_7 , C_2) radical product **p1** are given in the Supporting Information.

orbitals cannot be unambiguously assigned as π or σ . The same is also the case for the non-symmetric **i2** intermediate.

It is important to note that alternative reaction pathways involving **i5** may exist as well. However, considering the barrier of isomerization of **i2** to **i5** of 259 kJ mol^{-1} , this pathway does not compete with the decomposition of **i2** to form **p1** plus atomic hydrogen, which holds a barrier of only 207 kJ mol^{-1} with respect to **i2**. These findings are also confirmed by statistical calculations exploiting RRKM theory (Supporting Information). From the initial reaction intermediate **i1**, **p1** is formed almost exclusively (99.99%) from intermediate **i2** via a tight exit transition state located 52 kJ mol^{-1} above the energy of the separated products. On the other hand, if **i3** represents the initial collision complex, 1,2,4,7-cyclooctatetraenyl radical (**p1**) is formed predominantly from the triplet aromatic 1,3,5,7-cyclooctatetraene intermediate **i4** without an exit barrier (96%) and to a smaller amount from **i3**. Further, our statistical calculations indicate that **p1** is formed exclusively practically independent on the collision energy. Considering the symmetry of the 1,3,5-cycloheptatriene reactant, 2/3 of the reaction flux should lead

initially to **i1** and 1/3 to **i3**; hence, 67% of **p1** should originate from **i2**, 1% from **i3**, and 32% from **i4**.

The theoretically predicted reaction pathway to the 1,2,4,7-cyclooctatetraenyl radical is supported by our experimental findings. The indirect reaction pathway is contemplated from the center-of-mass angular distribution revealing intensity over the whole scattering range; likewise, the off-zero peaking of the center-of-mass translational distribution depicting a broad plateau from 5 to 35 kJ mol^{-1} proposed the existence of at least two reaction channels via a loose and tight exit transition states as verified experimentally (**i3** \rightarrow **i4** \rightarrow **p1** versus **i1** \rightarrow **i2** \rightarrow **p1**) which are corroborated by electronic structure calculations as well. The hydrogen loss via the tight exit transition state results in an ejection of the hydrogen atom nearly perpendicularly to the rotational plane of the decomposing complex leading to a best-fit center-of-mass angular distribution peaking at 90° as observed experimentally. As seen from the geometry of the exit transition state (Figure 3), the electronic structure calculations suggest an angle of hydrogen emission with respect to the principle axis of 85.5° thus confirming the aforementioned conclusion.

In summary, our combined experimental and theoretical investigation on the bimolecular gas-phase reaction of atomic carbon with 1,3,5-cycloheptatriene (C_7H_8) revealed a facile formation of the hitherto elusive 1,2,4,7-cyclooctatetraenyl radical (C_8H_7) under single-collision conditions via ring expansion exploiting the crossed molecular beams technique. The barrier-less route to form the cyclic 1,2,4,7-cyclooctatetraenyl radical opens up the involvement of exotic reaction intermediates on the triplet surface: non-aromatic 2,4,7-cyclooctatriene (**i2**) and aromatic 1,3,5,7-cyclooctatetraene (**i4**) reaction intermediates, which cannot be accessed by classical synthetic organic chemistry routes. Also, by replacing one or multiple hydrogen atoms in the 1,3,5-cycloheptatriene (C_7H_8) by side groups, substituted 1,2,4,7-cyclooctatetraenyl radicals along with triplet aromatic 1,3,5,7-cyclooctatetraenes can be synthesized. It should be noted that the structure of the 1,2,4,7-cyclooctatetraenyl radical (C_2 symmetry) is highly reminiscent of the structure of 1,2,4,6-cycloheptatetraene (C_2 symmetry). There has been considerable interest in the 1,2,4,6-cycloheptatetraene molecule as the apparent structure of the species generated upon reaction of benzene plus atomic carbon or upon ring-expansion of phenyl carbene.^[35] 1,2,4,7-cyclooctatetraenyl can be thought of as being derived from 1,2,4,6-cycloheptatetraene by the insertion of the methylidyne moiety (CH) into the C4–C5 bond. Consequently, future experimental and theoretical studies of these unusual triplet and doublet systems under single collision conditions are clearly warranted to systematically explore the unique unimolecular decomposition of triplet aromatic reaction intermediates to gain a comprehensive understanding of their electronic structures, chemical bonding, and stabilities.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: gas-phase chemistry · mass spectrometry · reaction dynamics · reaction intermediates · single-collision conditions

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