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Gas-Phase Optical Detection of 3-Ethynylcyclopentenyl: A Resonance-Stabilized C_7H_7 Radical with an Embedded 1-Vinylpropargyl Chromophore

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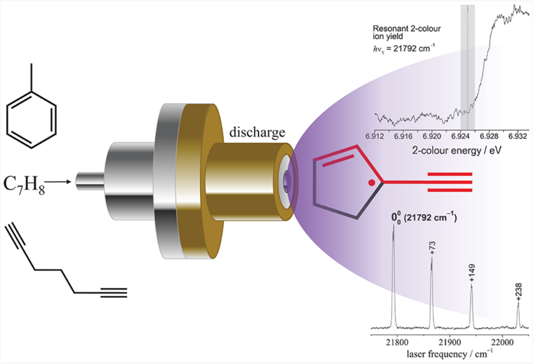
ABSTRACT: The 3-ethynylcyclopentenyl radical (3ecpr) has been identified as the carrier of an electronic spectrum with origin at 21792 cm^{-1} using resonant ionization and laser-induced fluorescence spectroscopies. The radical was first detected in a toluene discharge and is most efficiently produced from 1,6-heptadiyne. Overwhelming spectroscopic and chemical evidence support our diagnosis: (1) the observed (6.93 eV) and calculated (CCSD(T)/pVQZ) adiabatic ionization energies are the same; (2) the origin band rotational contour can be well simulated with calculated rotational constants; (3) convincing vibrational assignments can be made using computed frequencies; and (4) the same spectrum was observed in a discharge of 1-ethynylcyclopentanol, which contains the 3ecpr carbon framework. The π-chromophore is essentially that of *trans*-1-vinylpropargyl, a highly resonance-stabilized C_5H_5 radical that persists in conditions relevant to both combustion and circumstellar atmospheres. We suggest that 3ecpr may be a similarly important radical warranting inclusion in models of C_7H_7 chemistry. It is the second C_7H_7 isomer with a five-membered ring yet to be detected, the other being vinylcyclopentadienyl, a species crucially involved in a recently proposed mechanism of soot formation (*Science*, 2018, 361, 6406, 997−1000). We argue that 3ecpr should be a significant product of H addition to ethynylcyclopentadiene (C_7H_6), a known product of benzyl decomposition. Further, it is plausible that 3ecpr is the unidentified C_7H_7 product of sequential addition of acetylene to propargyl (*J. Phys. Chem. Lett.*, 2015, 6, 20, 4153−4158) in which 1-vinylpropargyl is an intermediate. As such, the $nC_2H_2 + C_3H_3$ cascade could represent a facile synthesis of a substituted five-membered ring in flames and stellar outflows.



1. INTRODUCTION

Resonance-stabilized radicals (RSRs), having an unpaired electron delocalized over a conjugated π-system, have long been recognized as key players in the earliest stages of molecular growth in hydrocarbon combustion and pyrolysis.[1,2] The stability conferred by radical delocalization ensures that RSRs are produced rapidly and consumed slowly, allowing them to become abundant in flames. Their recombination reactions are held to be of particular significance in the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion[3] and also in circumstellar atmospheres,[4] notable examples being the formation of benzene by self-reaction of propargyl (H_2CCCH)[5−7] and of naphthalene by reaction between propargyl and benzyl (C_7H_7).[8−10]

PAHs, in turn, are thought to be the molecular progenitors of soot,[11] posing significant risks to environmental and human health and contributing to climate change.[12−14] Uncovering a mechanism linking PAHs to soot has proved an enduring challenge. A significant recent advance was the detection by Johansson et al. of RSRs liberated from particles extracted from sooting flames.[15] The authors proposed a growth scheme beginning with small RSRs and driven by extension of radical delocalization, leading to covalently bound clusters with RSR character at the periphery. It would thus appear that RSR motifs are critically important throughout combustion and pyrolysis, from the formation of molecules to the inception of particles.

The elucidation of the RSR growth mechanism[15] was crucially underpinned by the spectroscopic diagnosis of a C_7H_7 product − the heaviest radical that could be unambiguously identified by VUV-photoionization mass spectrometry (VUV-PIMS). Surprisingly, the m/z = 91 photoionization (PI) spectrum showed no evidence of benzyl or tropyl, the two most stable C_7H_7

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isomers; instead, it was consistent only with vinylcyclopentadienyl radical (vcpr) (see Figure 1: benzyl, tropyl, and vcpr are isomers 1−3, respectively). This represents the first detection of vcpr, remarkably so given the importance of the C_7H_7 potential energy surface in combustion. The heightened significance of C_7H_7 PES is largely a consequence that transportation fuels comprise up to 30% toluene, which thermally decomposes to benzyl.[16,17] The decomposition and isomerization of benzyl have been investigated for several decades,[18−24] but only recently has a consensus been approached regarding the major pathways. Three channels have been identified from flash pyrolysis VUV-PIMS experiments,[23,24] of which the most important proceeds via the (unobserved) intermediate 4 (Figure 1) to produce H atoms and fulvenallene (C_5H_4=C=CH_2). However, computational studies that are broadly consistent with these findings also predict a plethora of C_7H_7 RSRs (isomers 5−10 in Figure 1) that remain undiscovered.[17,21,25−27]

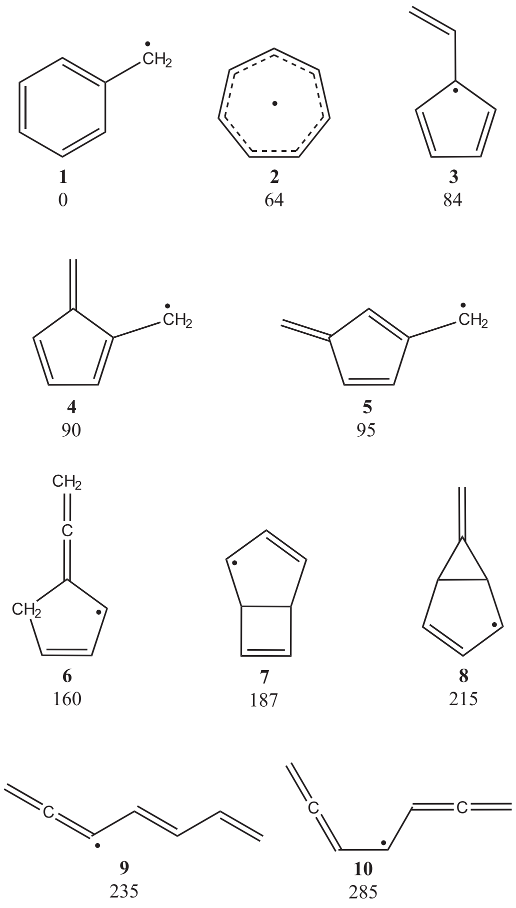

Figure 1. Resonance-stabilized radicals that are known or thought to be important minima on the C_7H_7 surface. Energies (reported in kJ/mol relative to benzyl, the global minimum) have been compiled from references 17, 25, 26, and 28. Only the top three isomers, benzyl, tropyl, and vinylcyclopentadienyl, have been detected.

A similarly important process in flames is the synthesis of C_7H_7 by sequential addition of acetylene to propargyl (nC_2H_2 + C_3H_3), being one of the simplest examples of a reaction between an unsaturated, closed-shell hydrocarbon and an RSR. In a recent VUV-PIMS study, Savee et al. detected only tropyl and no benzyl or vcpr from the c-C_5H_5 + C_2H_2 reaction at 1000 K.[29] This result is consistent with predictions by da Silva[25] but difficult to reconcile with ref 15 in which the very same reactants, acetylene and c-C_5H_5, apparently produced *only* vcpr and no detectable tropyl or benzyl, perhaps implying a special role for five-membered ring species on particle surfaces. Remarkably, the m/z = 91 PI spectrum at 800 K showed evidence of another C_7H_7 isomer, apparently produced by addition of acetylene to 1-vinpropargyl, the second most stable C_5H_5 isomer.[30,31] PI signal from the unknown isomer could not be readily assigned to any of the usual suspects on the C_7H_7 surface, and the carrier remains unidentified.

Figure 1 hints at a major reason for the complexity of the above problems: there are myriad similarly stable C_7H_7 RSRs that should be accessible under combustion conditions. Of these species, only benzyl, tropyl, and vinylcyclopentadienyl have been detected. Benzyl, of course, has a celebrated spectroscopic history, beginning in 1952 with the observation of its $\tilde{A} \leftarrow \tilde{X}$ transition in a glow discharge[32] and followed in the laser and molecular beam era by a slew of investigations of vibronic coupling within its low-lying excited states.[33−37] Tropyl is an exceedingly complex radical owing to Jahn−Teller activity in its $\tilde{X}^2E_2''$ and $\tilde{A}^2E_3''$ states, the interpretation of which is a challenge existing at the frontiers of theoretical spectroscopy.[38−42] For vcpr, ref 15 provides the only report of its detection. For every other C_7H_7 RSR of postulated significance to combustion and astrochemistry, there exist no experimental data of any utility for gas-phase diagnosis.

It is in this context that we set out to interrogate discharges of various C_7H_8 precursors, in search of C_7H_7 RSRs that report on hydrocarbon growth and decomposition. We use a combination of resonant two-color two-photon ionization and laser-induced fluorescence spectroscopies, an approach that has proved particularly fruitful for the discovery of radicals formed in jet-cooled hydrocarbon discharges, which are fertile RSR sources.[43−45] In this paper, we describe the identification of a new isomer of C_7H_7 by spectroscopic analysis, chemical tests, and quantum chemical calculations. It has a π-system highly similar to that of 1-vinylpropargyl—a C_5H_5 RSR that is emerging as ubiquitous in combustion environments[46−49]—recommending its inclusion in mechanisms of C_7H_7 chemistry. Implications for the formation of C_7H_7 from known or postulated intermediates in combustion and stellar atmospheres are discussed.

2. EXPERIMENTAL SECTION

Experiments were carried out in two vacuum chambers: one for resonance-enhanced two-color two-photon ionization (R2C2PI) and the other for laser-induced fluorescence/dispersed fluorescence (LIF/DF). The account here is brief; further details are provided in the Supporting Information. A pulsed discharge nozzle[50] was used to generate C_7H_7 radicals from a range of C_7H_8 precursors (toluene, 1,6-heptadiyne, norbornadiene, cyclic and linear heptatrienes), each used separately and diluted in Ar to give a seed ratio in the range 0.5−1%. A negative high voltage pulse (typically 600−1000 V, 30 μs duration) was applied to the electrode nearest the valve orifice through a ballast resistance (typically 20 kΩ).

The R2C2PI chamber is similar to that used in recent work on interconversion of xylyl radicals.[51] Cold C_7H_7 radicals in a skimmed molecular beam were probed in the extraction region of a 1 m time-of-flight tube by tunable output (440−470 nm) from a pulsed dye laser, followed by UV radiation from a frequency-quadrupled Nd:YAG laser (266 nm) or a KrF excimer (248 nm). Ion signal at m/z = 91 was integrated as a function of dye laser wavelength. For AIE measurements, the frequency-doubled UV output of a second dye laser was tuned through the ionization threshold, with the temporally preceding optical photon fixed to the C_7H_7 origin transition. Optical-optical hole-burning (OOHB) measurements were performed with two tunable lasers: a

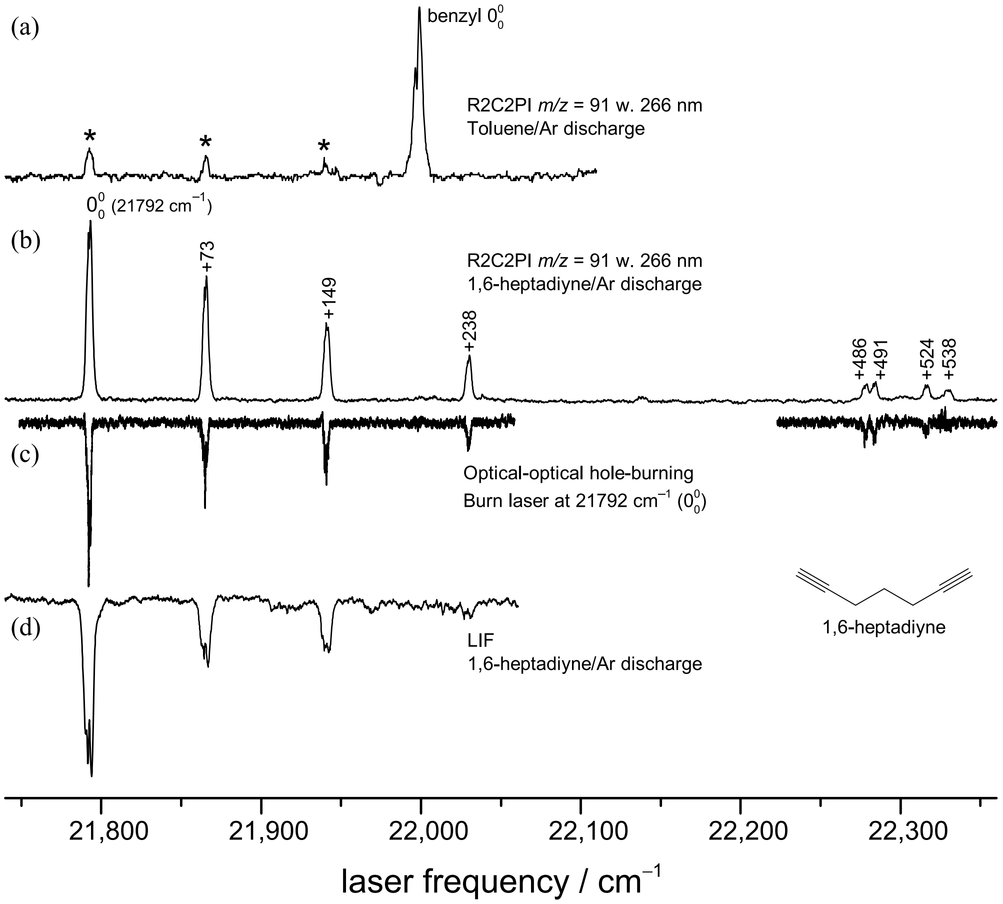

Figure 2. (a) The R2P2CI spectrum at $m/z = 91$ obtained from a toluene discharge after optimizing on the benzyl $\tilde{A} \leftarrow \tilde{X}$ transition. Bands designated with asterisks are due to a different C_7H_7 isomer, which is most conspicuous in the R2C2PI spectrum of a discharge of 1,6-heptadiyne (b). The reflected optical−optical holeburning scan (c) measured with the burn laser at 21792 cm^{-1} implicates a single isomer. Trace (d) shows the LIF spectrum of the 1,6-heptadiyne/Ar discharge, measured with a 1 m monochromator as wavelength-scanned narrow bandpass. The broader rotational contours in the LIF spectrum are due to the higher temperature of the free-jet expansion in comparison to the skimmed beam employed in R2C2PI.

wavelength-scanned probe beam and a 266 nm ionizing pulse were preceded by 1 μs on every other shot by a burn laser fixed to the origin band. Active baseline subtraction was employed to account for fluctuations in probe signal.

The chamber used for LIF/DF is adapted from one described previously.[52] Jet-cooled radicals were interrogated by tunable dye laser radiation and fluorescence was imaged separately through small (0.14 m) and large (1 m) monochromators equipped with photomultiplier tubes. The small monochromator was used as a broad bandpass filter to mitigate spectral contamination in LIF scans, and the 1 m monochromator was used as a tunable narrow bandpass filter and for measuring DF spectra. The wavelength of the 1 m monochromator was calibrated with lines from a mercury arc lamp. Laser frequencies were calibrated with a wavemeter. All pulsed instruments were triggered at 5/10 Hz with digital delay generators.

3. COMPUTATIONAL DETAILS

AIEs were predicted from B3LYP/6-311G++(d,p) and CBS-QB3 calculations. The former method has been shown, for a modestly sized test set, to consistently underestimate known AIEs of RSRs by ∼0.1 eV.[53] The latter method is widely used to diagnose reactive intermediates in combustion, though we are not aware of a systematic study of its accuracy for predicting AIEs of large RSRs. However, for the 17 isomers considered herein, the CBS-QB3 AIE consistently exceeds the B3LYP/6-311G++(d,p) AIE, with a mean deviation of +0.18 eV. Because the B3LYP calculation appears to undershoot experiment by ∼0.1 eV on average, the two methods should, in general, bracket the true AIE. Where excited state geometries could be optimized and frequency calculations carried out, adiabatic electronic transition energies were computed using TD-DFT (B3LYP/6-311G++(d,p)). These calculations were performed with the *Gaussian 09* suite of electronic structure programs.[54]

For RSRs with optical chromophores and having predicted B3LYP and CBS-QB3 AIEs within 0.2 eV of observation, AIEs were then computed using the high-level CCSD(T)[55] methodology with atomic natural orbital (ANO0, ANO1, and ANO2)[56] and Dunning correlation-consistent basis set sequences (cc-pVXZ; X = D, T, Q).[57] Restricted open-shell Hartree−Fock reference functions were used for the doublet ground states of neutral radicals. To estimate ZPE contributions to computed AIEs, equilibrium geometries and harmonic vibrational frequencies were also obtained at the CCSD(T) level of theory, using the smallest of the ANO and Dunning basis sets. Application of this methodology to well-studied systems[58,59] has shown that calculated AIEs should be accurate to better than 0.02 eV. All coupled cluster calculations were done in the frozen-core approximation with the CFOUR quantum chemical program package.[60]

4. RESULTS

4.1. Resonant Two-Color Two-Photon Ionization. The $m/z = 91$ R2C2PI spectrum of a toluene discharge, measured after optimizing production of benzyl, is shown in the top trace of Figure 2. The weak bands designated with asterisks are not hot bands of the benzyl transition, they are unshifted in Ar and Ne expansions, and as the mass spectrum shows (Figure S1), they do not arise from dissociative ionization of a heavier species. Consequently, they must belong to one or more unknown isomers of C_7H_7. After trying several C_7H_8 precursors (norbornadiene, and linear and cyclic heptatrienes), it was found that 1,6-heptadiyne most efficiently produces the carrier. Though benzyl was generally a conspicuous product from every precursor, use of a lower discharge voltage and higher resistance (600 V; 50 kΩ) suppressed its production, with a relatively modest diminution in signal from the unknown isomer. The middle trace of Figure 2 shows the R2C2PI spectrum of the 1,6-heptadiyne discharge measured under these conditions, and trace c is the OOHB spectrum measured with the burn laser at 21792 cm^{-1}, clearly implicating a single isomer.[61] No bands were observed (within 1000 cm^{-1}) to the red of the feature at 21792 cm^{-1}, which is therefore assigned as the origin. The transition is highly origin-dominated (Figure S3) and shows little vibronic structure beyond ca. 0° + 500 cm^{-1}, perhaps because of nonradiative processes.[62] The LIF spectrum d is discussed further in the section Laser-Induced Fluorescence and Dispersed Fluorescence, and vibrational assignments are outlined in the section Spectroscopic Assignments for 3-Ethynylcyclopentenyl Radical.

The ion-yield curve recorded with the resonant photon at 21792 cm^{-1} is shown in Figure 3. It was established that signal was linear with the fluence of the UV beam, indicating a true 1 + 1′ process. Strictly, one should emphasize that a 2-color ion-yield curve gives an upper limit to the AIE, being dependent on FC access from the intermediate vibronic level of the neutral to the vibrationless level of the cation. Here, we observe a distinct onset near 6.925 eV; we have examined the influence of the electric field in the extraction region[63] and are confident that the field-free AIE is at most 0.01 eV higher than the observed threshold.

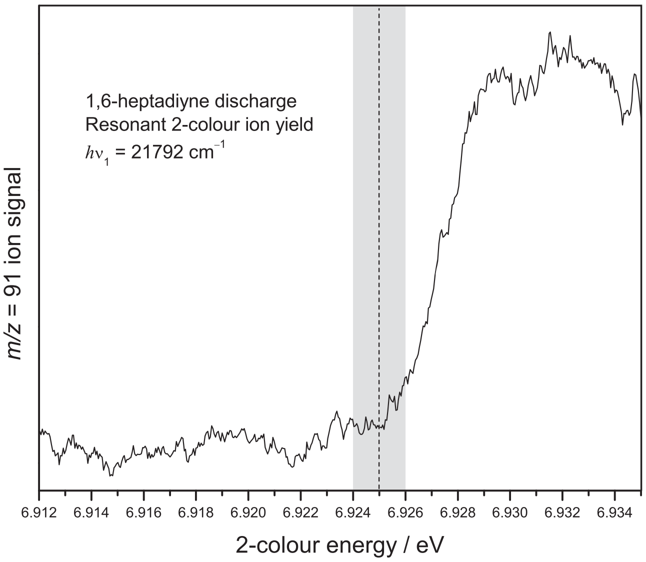

Figure 3. Mass-selected two-color ion-yield scan of the newly detected isomer of C_7H_7, with the resonant photon fixed at 21792 cm^{-1} and the frequency of the UV photon tuned through threshold. The field-free adiabatic ionization energy is at most 0.01 eV higher than the observed threshold of 6.925 eV.

4.2. Laser-Induced Fluorescence and Dispersed Fluorescence. The LIF survey spectrum of the 1,6-heptadiyne discharge (Figure S4) is congested with features of other RSRs, including benzyl, 1-vinylpropargyl, and 1-phenylpropargyl. To extract a somewhat pristine spectrum of the carrier, the large monochromator was scanned in synchronization with the laser wavelength, serving as a tunable narrow bandpass filter. The resulting spectrum (trace d in Figure 2) exhibits several clear correspondences with the mass-selected one, affording us security that ground state levels observed in DF spectra belong to a species of known molecular mass and AIE.

DF spectra for the four lowest bands in the LIF spectrum are shown in Figure 4. Because the discharge nozzle constricts the jet expansion, we adopted a large nozzle-laser distance (5 cm, or $x/D = 100$) to guarantee collision-free measurements.[64,6566] Our signal-to-noise ratio and spectral resolution (~25 cm^{-1}) under these conditions are modest owing to the diminished radical number density in the laser interaction region, although it was possible to measure portions (bottom of figure) of the origin DF spectrum at higher resolution (15 cm^{-1}).

We focus on ground state levels below 600 cm^{-1}, because low frequencies are quite diagnostic of molecular structure, and the DF spectra are from similarly low-lying excited state levels. A DF spectrum from a single vibronic level illustrates the projection of the excited state vibrational wave function onto ground-state vibrational levels and in the Franck−Condon approximation is governed by the FC factors for the transition. For origin-dominated transitions, as applies here, the most intense emission is generally to modes that have similar character to the emitting state and with the same number of quanta. The DF spectra from the levels at +73 and +149 cm^{-1} show that they are not members of a single vibrational progression but in fact correspond to different vibrational modes. Assignment of these transitions is important to the molecular identification and is discussed further in the section Spectroscopic Assignments for 3-Ethynylcyclopentenyl Radical.

5. DISCUSSION

5.1. Identifying the C_7H_7 Spectral Carrier. The jet-cooled hydrocarbon discharge is a fertile source of reactive molecules, but it is not a rational one. Nevertheless, it is overwhelmingly the case that the large radicals that persist are resonance-stabilized;[45] we thus ignored any isomer with a localized radical site. To further constrain the candidates, we insisted that (1) the radical should have a (cheaply) predicted AIE in the (generously broad) range 6.75−7.1 eV; (2) it must harbor an optical chromophore; and (3) the frequencies and symmetries of its vibrational modes should be consistent with DF spectra. Many of the candidates are intermediates predicted by computational studies of benzyl formation and decomposition or have been implicated in the reaction of propargyl and acetylene.[17,25,26,28,29] Table S1 (see also Figures S4 and S5) shows all 17 isomers considered, along with predicted AIEs, CBS-QB3 0 K energies relative to benzyl, vertical $\tilde{A} \leftarrow \tilde{X}$ transition energies and oscillator strengths, and ground state frequencies below 600 cm^{-1}.

An important step was to recognize that substituted cyclopentenyl radicals with allylic or propargylic stabilization could have the desired spectroscopic properties and be plausible products of the 1,6-heptadiyne discharge. As Figure 5 shows, 1,6-heptadiyne[67,68] (a) has three types of C−H bonds, with the

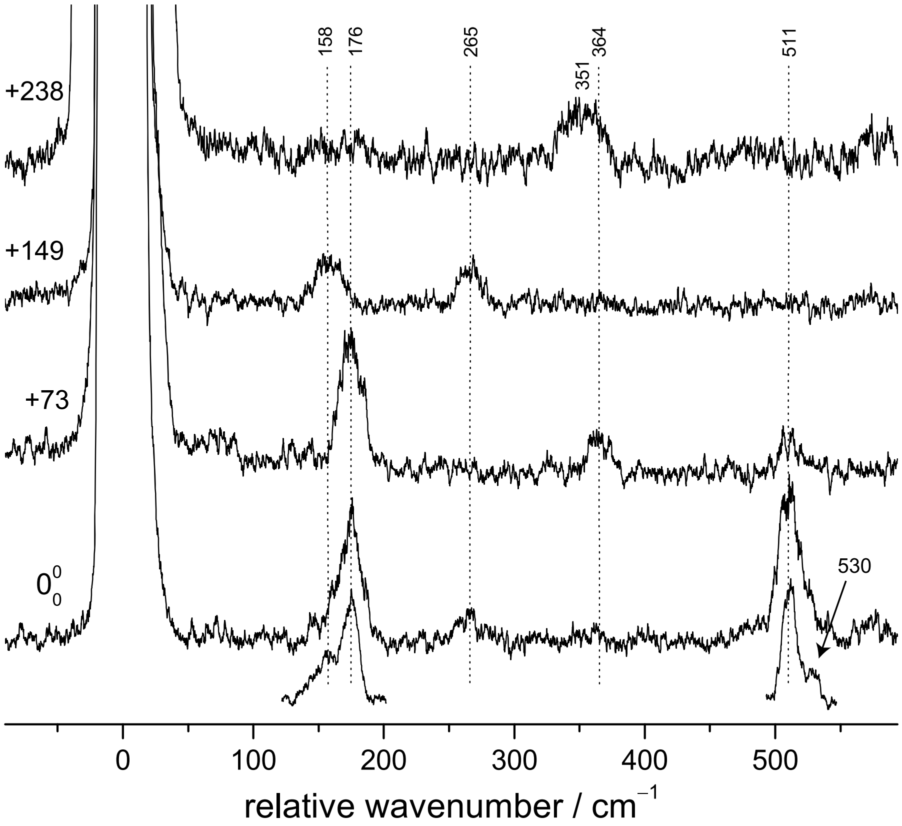

Figure 4. Dispersed fluorescence (DF) spectra from four excited vibronic levels of a previously unreported isomer of C_7H_7. Vibrational assignments are discussed in Section 5.2 and in further detail in the SI.

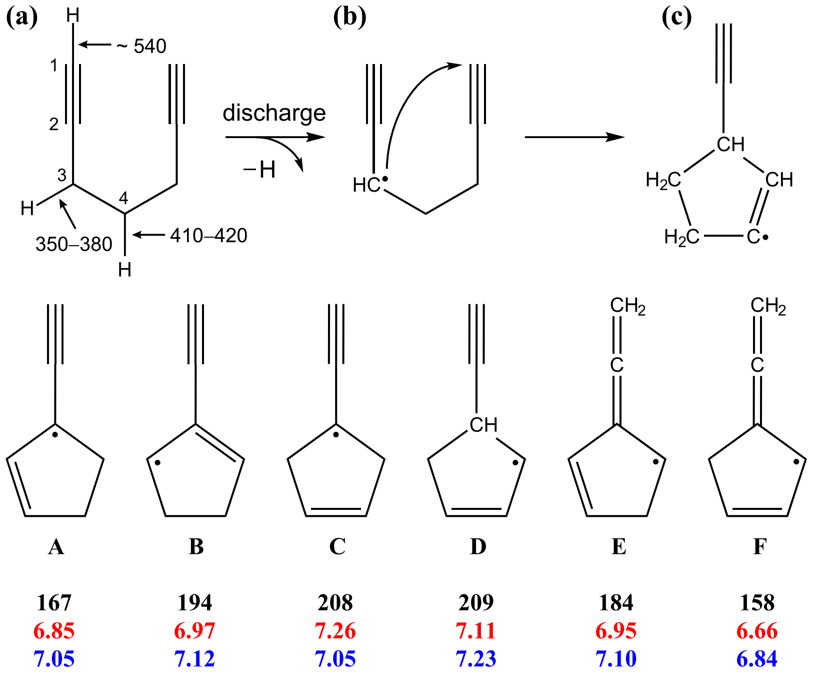

Figure 5. Likely initial steps in the decomposition of 1,6-heptadiyne. Indicated bond energies (kJ/mol) are recommended from measurements for similar alkynes (see, e.g., ref 69). Beneath are the cyclopentenyl RSRs that can conceivably result from H atom migration or recombination with isomers of C_7H_6. Numbers beneath indicate: (black) the CBS-QB3 0 K energy relative to benzyl, in kJ/mol; (red) the B3LYP/6-311G++(d,p) AIE; and (blue) the CBS-QB3 computed AIE. The latter two values (in eV) are expected to bracket the true AIE of each species.

indicated bond energies recommended from measurements for similar alkynes.[69−72] While H-loss from the central or a terminal carbon produces localized radicals, C−H cleavage at C3 yields the substituted propargyl radical (b), and should thus be relatively facile. Intramolecular reaction of (b) will produce the ethynylcyclopentenyl radical (c), which is predicted to be the

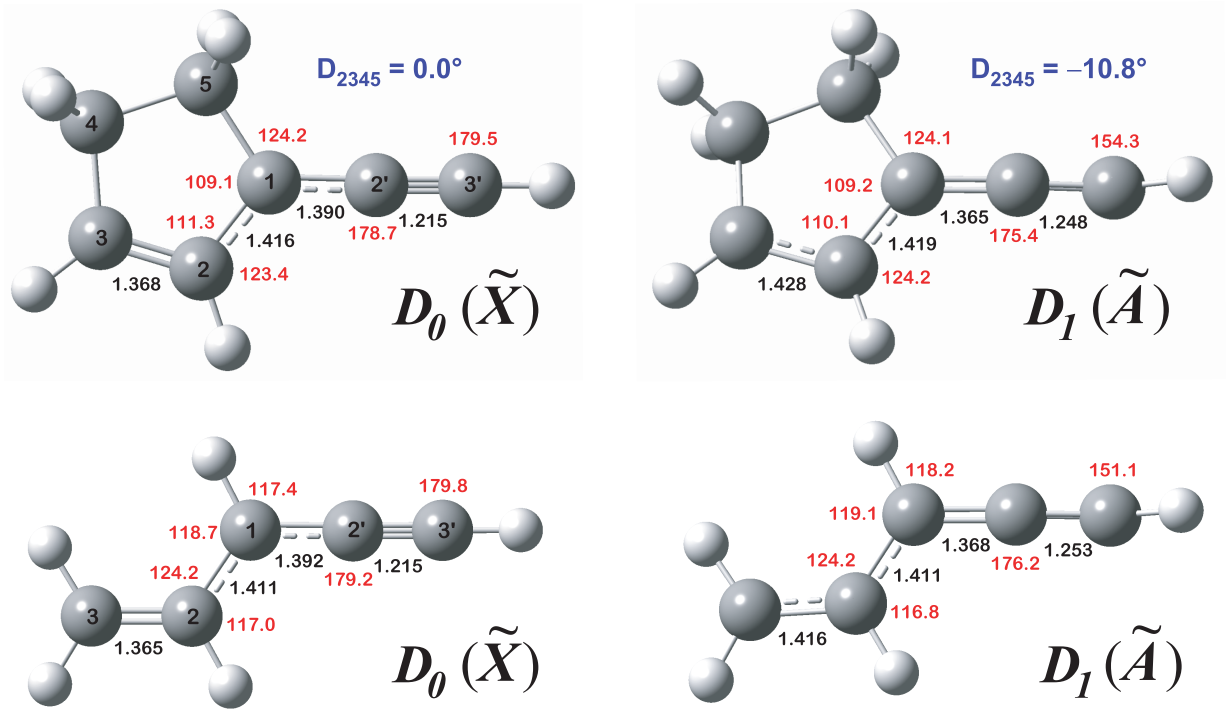

Figure 6. Optimized geometries (B3LYP and TD-B3LYP with 6-311G++(d,p) basis) of the ground (D_0, or $\tilde{X}$) and first excited (D_1, or $\tilde{A}$) states of 3-ethynylcyclopentenyl radical and the related *trans*-1-vinylpropargyl radical, which has a topologically similar π-chromophore.

most stable initial cyclic adduct, and has the smallest barrier to cyclization (only ~8 kJ/mol).[73] The vinylic radical (c) may undergo H atom migration to produce a range of RSRs but more likely will decompose to ethynylcyclopentadiene (C_7H_6) by β-scission.[74] The cyclopentenyl RSRs **A−F** in Figure 5 can conceivably result from a combination of pericyclic rearrangements and H addition to various C_7H_6 isomers, as shall be further discussed in Chemical Implications.

Shown beneath each isomer in Figure 5 are its predicted AIE (red = B3LYP/6-311G++(d,p); blue = CBS-QB3) and CBS-QB3 0 K energy (black; kJ/mol relative to benzyl). Because the most and least stable isomers are separated by only ~ 50 kJ/mol, a perhaps more important property to consider is the radical stabilization energy (RSE). A common metric of the RSE of a radical $R^\bullet$ is the difference in bond dissociation enthalpies BDE(CH_3-H)−BDE(R-H),[75] a positive RSE indicating that $R^\bullet$ is more stabilized than methyl. The R-H BDEs required to evaluate RSEs of isomers **A−F** have not been measured nor is the calculation of accurate RSEs trivial.[76,77] However, because isomers **B** and **D−F** are allylic radicals and **C** is a propargylic radical, their RSEs should be similar to those of propargyl and allyl (55 and 70 kJ/mol, respectively[72,78]).

In contrast, isomer **A**, 3-ethynylcyclopentenyl (3ecpr), has a π-chromophore kindred to that of *trans*-1-vinylpropargyl (see Figure 6). The 1-vinylpropargyl radical (1vpr) is the most stable isomer of C_5H_5 after cyclopentadienyl and is a persistent intermediate observed in flames,[46−49] crossed-beam studies,[79,80] and discharges.[43,81] Both 1vpr and 3ecpr can be depicted by three canonical forms, implying extensive radical delocalization. Indeed, the RSE of 1vpr is approximately 110 kJ/mol[53,82,83] on which basis it is expected that the RSE of 3ecpr is the largest of isomers **A−F** by a factor of 1.5−2. The similar π-systems of 3ecpr and 1vpr should also engender electronic transitions at similar wavelengths; the observed C_7H_7 electronic origin (near 459 nm) is indeed close to that of *trans*-1-vpr (near 462 nm).[43] Further, the B3LYP and CBS-QB3 AIEs of isomer **A** almost symmetrically bracket the experimental AIE of 6.93 eV, and most importantly, the computed CCSD(T)/pVQZ AIE of 3ecpr is 6.93 eV, in quantitative agreement with experiment, strongly favoring 3ecpr as the carrier. It should be shown, however, that the optical data are consistent with this diagnosis.

5.2. Spectroscopic Assignments for 3-Ethynylcyclopentenyl Radical.

In its ground electronic state, 3ecpr belongs to the C_s point group, with A'' symmetry. The electronic transition is assigned as $\tilde{A}^2A'' \leftarrow \tilde{X}^2A''$. The predicted (TD-B3LYP) adiabatic transition energy, including ZPE, is 3.00 eV; that of *trans*-1vpr is 2.99 eV (cf. 2.68 eV expt.[43]). For both species, the transition can be described as an admixture of SHOMO−HOMO (bonding to nonbonding) and HOMO−LUMO (nonbonding to antibonding) excitations within the π-system, lengthening the C2′C3′ (acetylenic) and C1C2 (vinylic) bonds and reducing the C1C2′ distance (calculated D_0 (or $\tilde{X}$) and D_1 (or $\tilde{A}$)) structures for 3ecpr and *trans*-1vpr are shown in Figure 6). The ring is slightly distorted away from C_s symmetry (the C2C3C4C5 dihedral angle is ~11°), and the ethynyl hydrogen is bent significantly out-of-plane, with a CCH angle of 154.3°. Symmetry-breaking displacement of the ethynyl H atom is a known pathology of excited states of propargyl.[84−87] A quasi-C_s $\tilde{A}$-state geometry is implied by TD-B3LYP calculations for distortions along the out-of-plane CCH angle and ring-torsion coordinates (SI Figure S6), in which case FC-allowed transitions from the vibrationless level of either electronic state are those that terminate on any level with even quanta excitation in a'' modes.

Partially resolved structure in the R2C2PI origin band rotational contour (Figure 7) is consistent with the above calculations.[88] The contour was simulated with PGOPHER[89] using a standard rigid rotor asymmetric top Hamiltonian.[90] Five of the six rotational constants (*A*, *B*, and *C* for each state) were taken from B3LYP calculations, and the calculated excited state

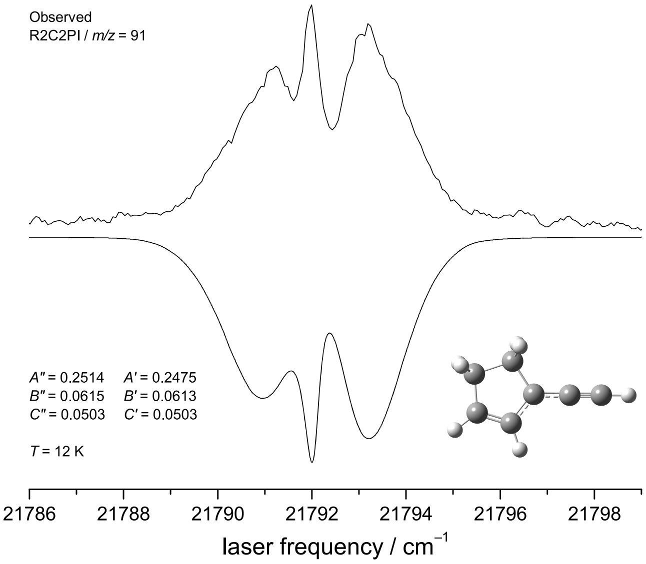

Figure 7. Observed origin band profile and simulation for 3ecpr. All constants other than A' are from B3LYP/TD-B3LYP calculations; the computed A'-constant is 0.250 cm^{-1}, which is 1% larger than the value used in the simulation.

A-constant was scaled by 0.99 to provide a good match with experiment. Orientation of the electronic transition moment along the molecular a-axis (μ_a: μ_b = 5:1) and a slight decrease in the A-constant upon excitation produce a prominent red-degraded stack of $\Delta K_a = 0$ transitions — the central feature that is well-reproduced in the simulation. Encouraging though this result is, such simulations are sensitive to small differences in several constants, and distinct isomers can exhibit similar contours at modest resolution. We therefore sought further confirmation from the DF data, an approach crucial to similar discoveries.[43,91]

To assign the DF spectra, a correspondence was sought between modes that engage the π-chromophore in 3ecpr and those that are FC-active in the *trans*-1vpr electronic spectrum. A number of $\tilde{X}$-state a' fundamentals of *trans*-1vpr were determined previously,[43] and several a'' modes have been identified recently (to be published elsewhere; but see ref 63). By inspection of displacement vectors for the FC-active a' modes ν_{17} (ethynyl wag), ν_{16} (C3C2C1/C1C2′C3′ bend), and ν_{15} (C2C1C2′/C1C2′C3′ bend) of *trans*-1vpr, the clear analogues ν_{23}, ν_{22}, and ν_{21} of 3ecpr were identified, with predicted $\tilde{X}$-state frequencies (scaled by 0.97[43,92]) of 158 cm^{-1}, 510 cm^{-1}, and 530 cm^{-1}, respectively. For a'' modes relevant to levels below 600 cm^{-1}, the out-of-plane ethynyl wag (ν_{24} in 1vpr) is analogous to ν_{35} of 3ecpr, with frequency 180 cm^{-1}. The ring torsion (ν_{36}, 91 cm^{-1}) of 3ecpr obviously has no counterpart in 1vpr, but it should be modestly FC-active owing to slight out-of-plane distortion of the ring upon electronic excitation.

Table 1. Comparison of Observed DF Band Positions (from Figure 4) with Harmonic Predictions, the Latter from a B3LYP/6-311G++(d,p) Calculation, Scaled by 0.97[a]

Assignment	Obs.	Calc.
23_1	158	158
36_2	176	177
$35_1 36_1$	265	269
36_4	364	352
22_1	511	510
21_1	530	530

[a] All frequencies are in cm^{-1}.

As shown in Table 1, every feature below 600 cm^{-1} can be assigned in terms of these modes, with compelling agreement between observed and predicted harmonic band positions, although some subtleties should be addressed. The a' modes are relatively simple to assign. The upper state level at 148 cm^{-1} clearly shares the character of the ground state level at 158 cm^{-1}, both in good agreement with predictions for ν_{23} in the $\tilde{A}$- and $\tilde{X}$-states, respectively ($\tilde{A}$-state frequencies are unscaled). The band at 511 cm^{-1} in the origin DF spectrum matches the prediction for ν_{22}; it also exhibits a shoulder to the blue, which at higher resolution (lowest trace in Figure 4) emerges as a weak band at 530 cm^{-1}, concordant with the computed ν_{21} frequency.

Assignment of levels involving a'' modes is straightforward on the basis of calculated frequencies but requires consideration of both FC-allowed and forbidden transitions. The most important assignment, which we therefore describe in detail, involves the ring torsion mode, ν_{36}. It has a predicted $\tilde{A}$-state frequency of 76 cm^{-1}, suggesting a FC-forbidden assignment of 36^1 for the excitation band at 73 cm^{-1}. The prominent band at 176 cm^{-1} in the DF spectrum from this level agrees closely with the prediction for 36_2, implying a selection rule ($\Delta\nu = \pm 1$) redolent of a first-order Herzberg—Teller-induced transition. One might therefore expect a linear dependence of the z-polarized (out-of-plane) electronic transition moment as the nuclear configuration is distorted along Q_{36}. Indeed, evaluation of μ_z from vertical TD-DFT calculations at a series of displacements along Q_{36} gives a function (Figure S7) with a dominant linear term, entirely consistent with our interpretation, as well as a modest cubic term, the latter potentially giving rise to weak $\Delta\nu = 3$ transitions, on which basis we tentatively assign the feature at 364 cm^{-1} as 36_4^1. The observed and simulated 73 cm^{-1} band contours (Figure S8) are furthermore consistent with the acquisition of z-polarized transition moment. Assignments involving combinations or overtones of ν_{36} with ν_{35} (a'' symmetry) and ν_{23} (a') have similarly detailed justifications, including Herzberg—Teller coupling and Duschinsky mixing,[93] the latter being a pervasive feature of the 1vpr electronic spectrum,[63] as well as significant positive anharmonicity associated with ring torsion, which is common in cyclopentene systems.[94,95] The reader is directed to the SI for the particulars of these assignments and for possible assignments for the weak excitation bands near 0° + 500 cm^{-1}.

A final chemical test was carried out to support our molecular assignment. The most readily available[96] precursor that contains the 3ecpr carbon framework is 1-ethynylcyclopentanol. Figure 8 shows the m/z = 91 R2C2PI spectra of discharges of 1,6-heptadiyne (top) and 1-ethynylcyclopentanol (reflected), which are in obvious agreement. Significantly, because of the likely low vapor pressure of the alcohol at 298 K,[97] the seed ratio is well below 0.1%, under which conditions bimolecular chemistry should be inoperative; i.e., the radical is produced by unimolecular decomposition of the precursor. On the basis of chemical and spectroscopic evidence, we thus assert that the identification of 3ecpr is secure.

5.3. Chemical Implications. *Decomposition of Benzyl Radical.* The Benson fragmentation pathway[98,99] is perhaps the most important channel in the thermal decomposition of benzyl.[23,24,27] The putative first steps are shown in Figure 9. While the C_7H_6 product is usually assumed to be fulvenallene ($C_5H_4{=}C{=}CH_2$), decomposition must also go by way of

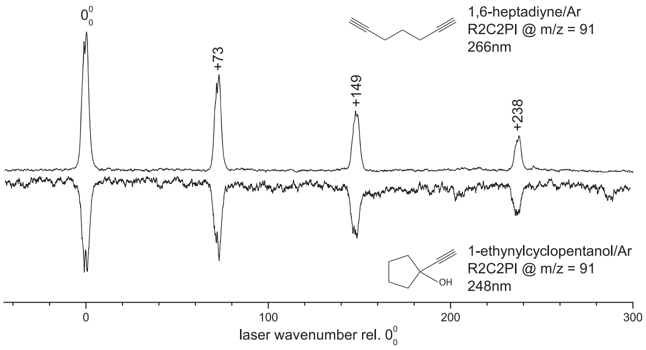

Figure 8. R2C2PI spectra recorded at m/z = 91 using 1,6-heptadiyne (upper) and 1-ethynylcyclopentanol (reflected) precursors diluted in Ar.

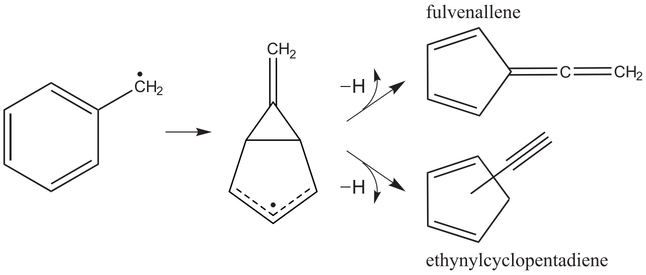

Figure 9. First steps in the Benson[98,99] fragmentation of benzyl, producing ethynylcyclopentadiene and fulvenallene. Adapted from ref 24.

ethynylcyclopentadiene ($C_5H_5-C\equiv CH$): both H and D atoms have been detected from shock-tube pyrolysis of $C_6H_5-CD_2$;[100] and VUV-PIMS analysis of flash pyrolysis of $C_6H_5CD_2CD_3$ indicated products at m/z = 92 ($C_5H_4{=}C{=}CD_2$) and m/z = 91 ($C_5H_5-C\equiv CD$).[23,24]

The C_7H_7 RSRs that may result from recombination of H atoms, which are abundant in our experiment (Figure S1), with the three interconvertible[101−104] isomers of ethynylcyclopentadiene are the radicals **A**−**F** (Figure 5). Of these possibilities, 3ecpr should be a favored product because it is highly resonance-stabilized, with an RSE likely in excess of 100 kJ/mol, as argued above. Further, as we speculate in a mechanism that builds on Benson's scheme (SI, Figure S9), formation of 3ecpr by H atom recombination should be statistically advantageous. It would thus be of interest to see how inclusion of 3ecpr in current mechanisms[17,25,28] of benzyl decomposition and C_7H_6 + H recombination affects the interplay between C_7H_7 and C_7H_6 surfaces.

Formation of C_7H_7 from Reactions of Acetylene and Propargyl. In a recent VUV-PIMS study of the sequential addition of acetylene to propargyl ($nC_2H_2 + C_3H_3$), Savee et al. inferred the presence of tropyl at 1000 K but found no evidence of benzyl or vinylcyclopentadienyl. Intriguingly, the m/z = 91 PI spectrum at 800 K exhibited a significant deviation from the tropyl curve beyond ∼ 9.1 eV. The deviation was posited to arise from an unknown C_7H_7 species (hereafter U−C_7H_7) formed by reaction of C_2H_2 with 1vpr and not with c-C_5H_5, the latter reaction yielding only tropyl. The optimal conditions for 3ecpr in our experiments also yield 1vpr (SI Figure S3), similar to the observation that U−C_7H_7 and 1vpr were present under the same conditions.

Threshold ionization of 3ecpr would not have been observable in ref 29 because its AIE (6.93 eV) is well below the lower energy limit of those experiments (7.2 eV). However, ionization to a triplet state could produce an onset at higher energy (as the authors indeed suggested). Significantly, we calculate (B3LYP/6-311G++(d,p)) that adiabatic ionization from the 3ecpr neutral ground state to the cation T_1 state requires 9.15 eV, close to the onset of unassigned m/z = 91 PI signal. The prospect that U−C_7H_7 is 3ecpr, produced by addition of acetylene to 1vpr, therefore warrants further investigation. Computed barriers for the first steps of this reaction lie in the range 16−18 kJ/mol,[105] and all subsequent steps have energy below the initial addition,[106] implying the process should be feasible under the conditions of ref 29. Because 1-ethynylcyclopenta-1,3-diene (C_7H_6) has recently been shown from RRKM simulations to be a significant product of the reaction of C_2H_2 with c-C_5H_5 (with a predicted yield of ca. 60% at 2500 K),[107] C_7H_6 + H reactions may provide an additional source of 3ecpr at high temperatures and pressures in environments where propargyl and acetylene are abundant.

Of similar interest to the observation of U−C_7H_7 in ref 29 is a recent PEPICO study of m-xylene decomposition under fuel-rich conditions in which aC_7H_7 product with an AIE below 7 eV was found to coexist with benzyl[108] and was assigned as 3ecpr from a calculated AIE and a Franck−Condon simulation. The measurement of PI or photoelectron spectra of 3ecpr, as well as an accurate calculation of its $D_0 - T_1$ AIE, should be undertaken to facilitate its detection in combustion environments.

Connection to Astrochemistry. In stellar atmospheres where temperatures and particle number densities can reach several 1000 K and $10^{15}/cm^3$, PAH formation has long been modeled as beginning with reactions involving small RSRs.[4,109] Because the hydrogen abstraction/acetylene addition[110] mechanism likely produces PAHs too slowly to compete with their destruction by shocks or harsh radiation,[111] rapid reactions of larger RSRs may drive further hydrocarbon growth.[112] The strong likelihood that 3ecpr can be formed from acetylene, propargyl, and 1vpr via reactions with modest barriers renders it a plausible intermediate in this context.[105,106] Acetylene is an abundant constituent of circumstellar gas;[113] propargyl has not yet been detected in the ISM, presumably because of its small dipole moment (0.15 D[114−118]), but it is commonly included in astrochemical models;[4,109,119] 1vpr has been observed under single-collision conditions in crossed-beam experiments as a major product of barrierless reactions involving known interstellar species, including atomic carbon, C_2, and propene.[31,79,80]

It is thus worth noting that the prospects for laboratory microwave characterization of 3ecpr are strong. RSRs are not, in general, amenable to study by rotational spectroscopy: their spectral lines are split by spin-rotation doubling, and they are often weakly polar because of radical delocalization.[114,115,120] However, the computed dipole moment of 3ecpr is 1.15 D, and rotational transitions of the closely related C_7H_6 isomers 1- and 2-ethynylcyclopentadiene were recently observed in a benzene discharge.[121] An even better candidate for detection in the laboratory, and perhaps also the ISM, would be the isoelectronic but presumably much more polar 3-cyanocyclopentenyl radical; a report of the tentative astronomical detection of the structurally similar cyanocyclopentadiene molecule[122] offers promise on that front.

6. CONCLUSION

A new isomer of C_7H_7 was observed in jet-cooled discharges of a variety of hydrocarbons including toluene and was conclusively identified as the 3-ethynylcyclopentenyl radical from a battery of spectroscopic assays employing laser-induced fluorescence and mass-selected resonant 2-color ionization. A high-quality calculation of the adiabatic ionization energy and the assignment of several low-frequency vibrational modes in dispersed fluorescence spectra were key elements of the diagnosis. Because this radical contains essentially the same π-system as 1-vinylpropargyl, a highly resonance-stabilized C_5H_5 isomer that is now routinely observed in flames and crossed molecular beams, it may have a similarly important role in molecular growth in terrestrial combustion and stellar outflows. Attention should be given by theorists and experimentalists to the strong possibility that 3-ethynylcyclopentenyl can be produced by reactions involving intermediates of known or postulated importance to combustion and astrochemistry, including acetylene, propargyl, 1-vinylpropargyl, and isomers of C_7H_6. Measurement of a VUV spectrum that covers ionization to the S_0 and T_1 states of the cation as well as microwave detection of the radical, which appears quite feasible, will be of significant interest and merit to the combustion and astrochemistry communities. There now exists a solid platform for such efforts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c01579.

> Further details of experiments; resonant photoionization mass spectrum of the 1,6-heptadiyne discharge; saturation behavior of the excitation spectrum; survey LIF spectrum evincing multiple radicals; calculated properties of C_7H_7 candidates (Table S1); Franck−Condon simulation for 1,2,5,6-heptatetraen-4-yl; PES scans for 3ecpr; computed ν_{36} transition moment function; low resolution +73 cm^{-1} band contour; justifications for other assignments in DF spectra; putative mechanism of 3ecpr formation via isomers of ethynylcyclopentadiene; optimized Cartesian coordinates and vibrational frequencies of ground and first excited states of 3ecpr (PDF)

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Notes

The authors declare no competing financial interest.

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