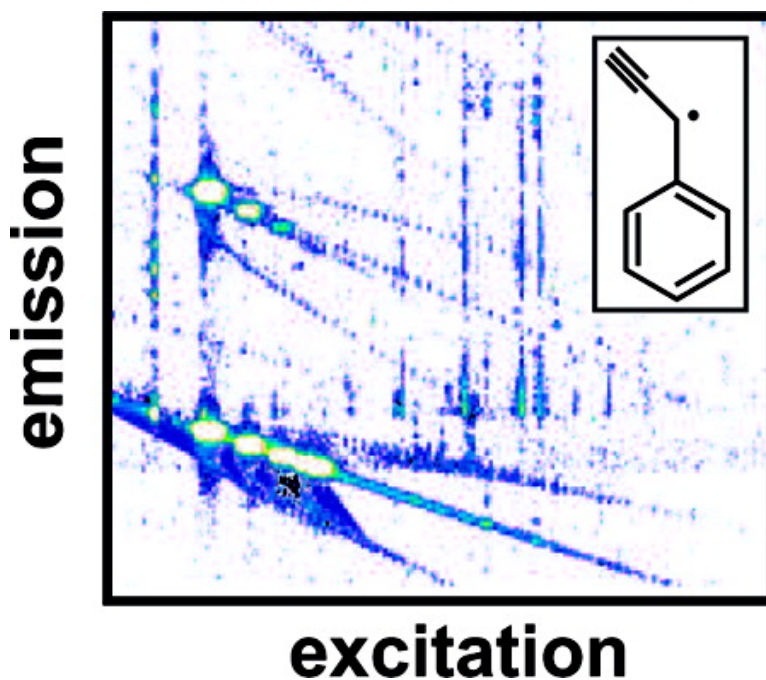


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Spectroscopic Observation of the Resonance-Stabilized 1-Phenylpropargyl Radical

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Abstract: The gas-phase laser-induced fluorescence (LIF) spectrum of a 1-phenylpropargyl radical has been identified in the region 20800–22000 cm^{-1} in a free jet. The radical was produced from discharges of hydrocarbons including benzene. Disregarding C_2 , C_3 , and CH , this radical appears as the most strongly fluorescing product in a visible wavelength two-dimensional fluorescence excitation–emission spectrum of a jet-cooled benzene discharge. The structure of the carrier was elucidated by measurement of a matching resonant two-color two-photon ionization spectrum at $m/z = 115$ and density functional theory. The assignment was proven conclusively by observation of the same excitation spectrum from a low-current discharge of 3-phenyl-1-propyne. The apparent great abundance of the 1-phenylpropargyl radical in discharges of benzene and, more importantly, 1-hexyne may further underpin the proposed importance of the propargyl radical in the formation of complex hydrocarbons in combustion and circumstellar environments.

1. Introduction

It is widely accepted that the formation of benzene in combustion processes occurs predominantly via propargyl (H_2CCCH) self-reaction.^{1–7} Although it is thought that polycyclic aromatic hydrocarbon (PAH) formation depends crucially on the formation of the first aromatic ring, the path from benzene to PAHs remains unclear. Consequently, the experimental identification of post-benzene reactive intermediates will greatly inform our attempts to elucidate PAH formation in combustion and in the chemistry of planetary atmospheres, such as that of Titan, where the recent discovery of benzene by Cassini has aroused speculation about its role in organic aerosol production (via PAHs) in Titan's upper atmosphere.^{8,9} In combustion, the favored paradigm of PAH formation is the hydrogen abstraction–acetylene addition (HACA) mechanism, suggested independently by Bockhorn¹⁰ and Frenklach,^{11–13} proceeding via abstraction of a hydrogen atom from the reacting hydrocarbon by a hydrogen atom, followed by addition of an acetylene

molecule to the subsequently formed radical site. For example, a posited route to pyrene in the pyrolysis of benzene involves two HACA steps, producing phenanthrene from biphenyl and then pyrene from phenanthrene.¹²

Alternatively, the role of resonantly stabilized radicals (RSRs) in PAH formation has attracted much attention in recent years.^{14–19} RSRs possess multiple resonance structures with different radical sites. Delocalization of the unpaired electron stabilizes RSRs relative to their reaction products with stable molecules.^{17,20,21} In addition, they are formed preferentially from the decomposition of stable hydrocarbons. Consequently, their fast formation rates and slow oxidation and pyrolysis rates allow them to reach high concentrations in hydrocarbon flames. Moreover, the relative rapidity of RSR recombination reactions heightens their potential importance to aromatic formation. Two reactions involving RSRs that are thought to play a role in naphthalene formation are a cyclopentadienyl self-reaction¹⁴ and propargyl addition to benzyl.^{15,16} More generally, given that propargyl self-reaction produces benzene, it has been noted that the contribution to PAH formation by recombination reactions between substituted propargyl radicals, RCCCH_2 or RCHCCH , should not be neglected.¹⁷ Stein et al. have suggested a role for phenyl-substituted propargyl molecules in the formation of larger PAHs.¹⁸ One scheme involves the recombination of propargyl with 3-phenylpropargyl to produce biphenyl; another involves

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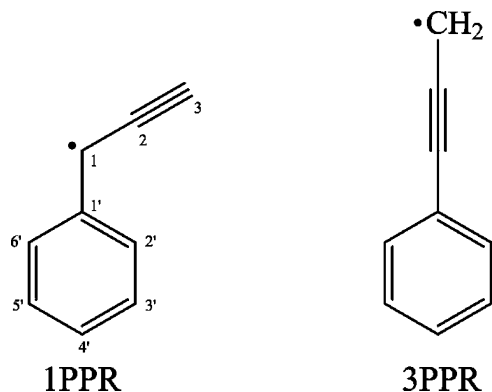


Figure 1. Structures of radicals relevant to this work. (Left) 1-Phenylpropargyl radical (1PPR) and (right) 3-phenylpropargyl radical (3PPR). A low current discharge of 3-phenyl-1-propyne (the molecular parent of 1PPR, with two hydrogens on C(1)) abundantly produces the carrier of an excitation at 476 nm; no significant signal at 476 nm is observed from a discharge of 1-phenyl-1-propyne.

combination of two 3-phenylpropargyl radicals to produce *o*-terphenyl. In the latter scheme, it is proposed that a doubly phenyl-substituted 1,5-hexadiyne intermediate is formed from the head-to-head recombination of two 3-phenylpropargyl fragments. By analogy with the formation of benzene from 1,5-hexadiyne via 1,2-dimethylcyclobutene^{22,23} and fulvene,^{24–27} a third phenyl ring is produced from the rearrangement of the hexadiyne moiety. The 3-phenylpropargyl (3PPR) and 1-phenylpropargyl (1PPR) radicals (see Figure 1) are RSRs that one might reasonably expect to result from the combination of benzene/phenyl with propargyl at either terminus. Both possess resonance structures containing the same chromophore as benzyl, the electronic spectrum of which is well-known, having an origin at 454.5 nm.²⁸ Simple molecular orbital theory considerations suggest that the electronic transitions of 1PPR and 3PPR should occur in the neighborhood of the benzyl absorption. Indeed, a weak absorption band has been observed at 478 nm following 220–1000 nm irradiation of 1-phenylpropyne (1PP) in an Ar matrix.²⁹ The authors attribute the band to the 3-phenylpropargyl radical (3PPR), produced by detachment of H from the methyl substituent.

In this article, we report the 2D excitation/emission spectrum³⁰ of a supersonically cooled benzene/Ar discharge in the region $427 \text{ nm} \leq \lambda_{\text{exc}} \leq 534$ and $355 \text{ nm} \leq \lambda_{\text{em}} \leq 643$ nm. The most brightly fluorescent hydrocarbon species in this region (apart from the ubiquitous CH radical) is assigned unambiguously as the RSR, 1-phenylpropargyl (1PPR).

2. Experimental Section

The vacuum chamber apparatus used for laser-induced fluorescence (LIF) in this experiment has been described elsewhere.³¹ A pulsed discharge nozzle (PDN) is used to produce 1PPR from benzene, toluene, 1-phenyl-1-propyne (1PP), 3-phenyl-1-propyne (3PP), or 1-hexyne, each

at room-temperature vapor pressure and seeded in 10 bar of argon. A voltage of -1.4 kV is applied to the outer electrode of the PDN, timed to strike during the gas pulse. The molecular beam is interrogated approximately downstream of the nozzle orifice with the output of a tunable laser. For 2D spectra, the fluorescence emission is dispersed in a wavelength across a CCD array exposed for 40 laser shots, producing a 1D emission spectrum. A 2D map of emission versus excitation is produced as the laser is scanned.³⁰ Once an appropriate region in emission wavelength space (one free of CH, C₂, and C₃, in this case) has been identified in the 2D spectrum for the unfettered detection of the radical of interest (highlighted in Figure 2), moderate resolution 1D LIF excitation scans are conducted at this fixed detection wavelength by focusing the emission into a monochromator. The monochromator is centered at 503 nm, admitting a 10 nm bandpass, to minimize scattered laser light and discharge afterglow. The imaged light is detected by a photomultiplier tube.

Resonant two-color two-photon ionization (R2C2PI) spectra are measured in a two-stage differentially pumped vacuum chamber. In brief, a skimmed molecular beam containing products of a discharge of benzene in argon, as above, is probed between the extraction grids of a time-of-flight tube by the fundamental and second harmonic (produced using a BBO crystal) output of a tunable dye laser. Simultaneous use of the fundamental and second harmonic circumvents the problems of timing and alignment that arise when a second laser is used for the ionizing photon. Nevertheless, a resonant signal was also observed with 266 nm as the ionizing wavelength, proving the dependence of the ion signal on the wavelength of the visible rather than the UV radiation. The positive ions are extracted vertically and perpendicularly to the laser and molecular beam into the TOF tube. An ion signal at $m/z = 115$ is viewed on an oscilloscope and integrated as a function of laser wavelength.

3. Results and Assignment

3.1. Identification of Spectral Carrier. The 2D fluorescence survey spectrum of a benzene discharge in the region $427 \text{ nm} \leq \lambda_{\text{exc}} \leq 534$ nm and $355 \text{ nm} \leq \lambda_{\text{em}} \leq 643$ nm obtained with a broadband ($\sim 2 \text{ cm}^{-1}$ line width) OPO is shown in Figure 2. Except for those features within the rectangle explicitly identified as belonging to 1PPR, every feature in this spectrum can be attributed to the C₂ “Swan”, C₃ “comet”, or CH “violet” bands. The strongest Swan bands observed belong to the $\Delta\nu = -2$ up to $+2$ sequences and exhibit vibrational and rotational bandheads and extensive rotational tails, with N approaching 50 for some bands. The C₃ bands are hot bands of the comet system, appearing predominantly in the lower right corner of the spectrum. The CH violet system is located at $\lambda_{\text{exc}} = \lambda_{\text{em}} = 430$ nm. Indeed, all features along the line, $\lambda_{\text{exc}} = \lambda_{\text{em}}$, are due to resonance fluorescence, not scattered light.

In the red box of Figure 2, the emission spectra derived from excitation at $\lambda_{\text{exc}} = 476, 459.5, 456.2,$ and 455.2 nm are clearly not due to CH, C₂, or C₃, having a pattern of emission immediately recognizable as different to that of the known species. The 2D map illustrates that a conventional scanning monochromator, fixed at a detection wavelength near 503 nm, will permit the collection of a 1D LIF excitation spectrum of the species of interest, largely free of spurious molecular features and scattered laser light. The LIF excitation spectrum of the unidentified species between 447 and 480 nm was collected in this manner and is shown in Figure 3. In LIF experiments the laser was scanned down to $19\,600 \text{ cm}^{-1}$ and no further peaks were observed to the red of $21\,007 \text{ cm}^{-1}$. In addition, as there are no peaks to the blue of the laser wavelength in the emission

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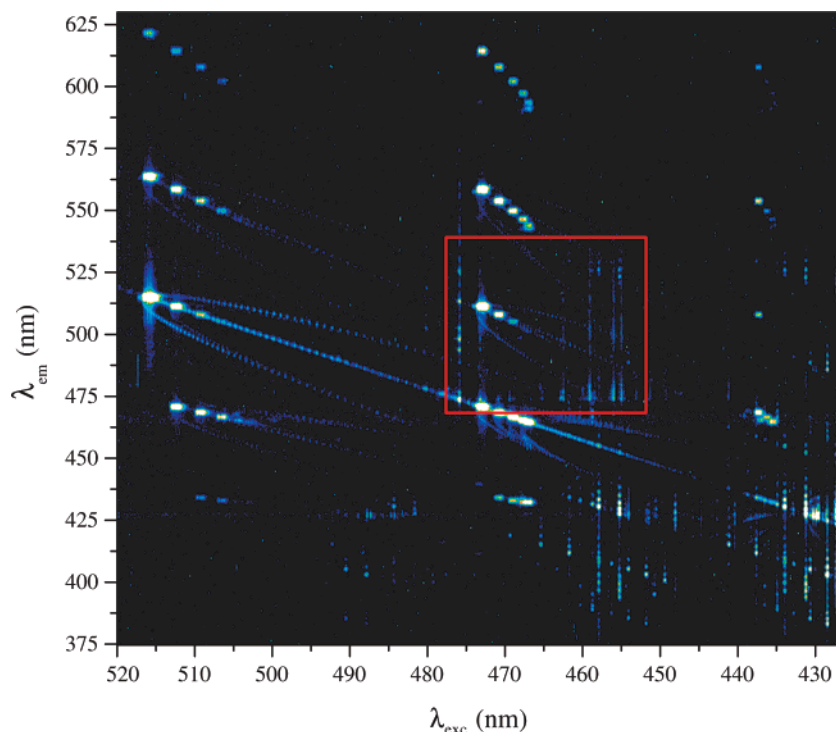


Figure 2. Two-dimensional laser-induced fluorescence spectrum of a benzene discharge. All of the spectral features outside the rectangle can be ascribed to either hot bands of the C_3 “comet” system (the “streaky” features predominating in the lower right corner) or the C_2 Swan bands (the curved features with extensive tails prevalent throughout). Features within the rectangle absorbing at 476, 459.4, 456.2, and 455.2 nm and emitting strongly to 476 and 503 nm are due to 1-phenylpropargyl. This radical is the most abundant/strongly emitting hydrocarbon observed in the benzene discharge under these conditions.

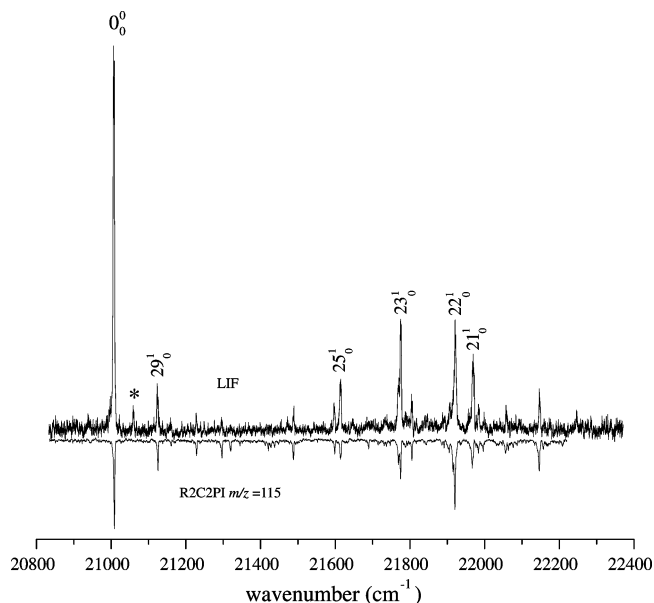


Figure 3. Assigned LIF spectrum of 1-phenylpropargyl produced in a benzene discharge. The spectrum was obtained with a detection wavelength of 503 nm, identified from the 2D scan as being relatively free of C_2 and C_3 emission. The peak marked by an asterisk is due to a different carrier. The assignment is discussed in the text. Reflected below: R2C2PI spectrum of 1-phenylpropargyl obtained from a discharge of 3PP ($\lambda_{\text{vis}} + \lambda_{266}$).

spectrum at $21\,007\text{ cm}^{-1}$ in Figure 2, we thus conclude that the $21\,007\text{ cm}^{-1}$ band is the origin.

One might reasonably expect that in a benzene discharge a multitude of species will be formed which absorb and emit in a narrow wavelength range. In the first instance, therefore, not every band in the LIF spectrum, viewed in one dimension, can

be assigned immediately to a single molecule. The 2D spectrum leads us to suspect that at least those intense bands at $\lambda_{\text{exc}} = 459.5$, 456.2 , and 455.2 nm have the same carrier as the 476 nm band, on the basis of their strong emissions to the same wavelengths. Closer analysis of the emission spectrum from each band reveals a common “fingerprint” pattern of peaks also exhibited in the emission spectrum of the 476 nm carrier. In fact, high resolution, high signal-to-noise dispersed fluorescence spectra measured with a 0.75 m scanning monochromator from 13 of the strongest bands in the LIF spectrum also exhibit this fingerprint, confirming their origin in a single species. (The LIF spectrum and DF spectra and their interpretation will be the focus of a separate paper.) Thus, 2D fluorescence is an ideal tool for the measurement of spectra of new species and an indispensable one for the expedient separation of unidentified bands by their common carriers.

Shown in Figure 3 is an R2C2PI spectrum at $m/z = 115$ inverted against the LIF spectrum in the wavelength range $469\text{--}477\text{ nm}$. These spectra unquestionably belong to the same species, which must have the molecular formula C_9H_7 . Only the peak marked with an asterisk does not appear in the R2C2PI spectrum. We therefore attribute this peak to another species.

There are many isomers of C_9H_7 that might be formed in a benzene discharge. The LIF spectrum exhibits several $\sim 900\text{ cm}^{-1}$ modes, suggestive of the “ring breathe” vibration in benzene. What is more, the observed excitation spectrum is highly reminiscent of those of the benzyl and substituted benzyl radicals, which have electronic absorptions in a similar wavelength range with similar intensities to the present C_9H_7 species.²⁸ To limit our range of C_9H_7 candidates we restricted

our consideration to resonance-stabilized radicals containing the benzene motif.

At 8.3 eV, the ionization potential of the indenyl radical³³ is too high to have been detected with the laser wavelengths in this experiment (indeed, its optical spectrum has been reported at ~ 415 nm in a matrix³⁴). However, as indene has been detected from a benzene discharge,³⁵ indenyl may well be present. We considered doubly substituted benzene structures less likely to be formed than singly substituted ones. Using this logical hierarchy, we hypothesized that either the 1PPR or 3PPR (see Figure 1) was the most likely carrier for the spectrum in Figures 2 and 3. 1PPR and 3PPR satisfy all the criteria above: they contain the benzene motif, they are resonance-stabilized, and they can likely result from the simple combination of the precursor benzene (or phenyl) with the abundant propargyl radical. To test the PPR hypothesis we conducted a number of theoretical calculations and further experiments.

Calculations were performed with the density functional theory (DFT) program of GAUSSIAN 03.³⁶ Using the 6-311+G-(d,p) basis, harmonic frequencies were obtained by normal-mode analysis following geometry optimization of the isomers illustrated in Figure 1. All harmonic frequencies were found to be real. Topologically, these species have the same π -system. Time-dependent density functional theory was used to predict the energies of excited states, yielding similar results for 1PPR and 3PPR. Vibrational frequencies calculated by DFT support 1PPR as the spectral carrier. In particular, the lowest frequencies of these species were considered important to reconcile with experiment. The lowest observed vibrational frequency in the excited state, 117 cm^{-1} , cannot be explained by the C_{2v} structure of 3PPR which requires two quanta to be populated in the low frequency b_1 and b_2 modes. Indeed, the lowest a_1 mode of 3PPR is calculated to be $\sim 400\text{ cm}^{-1}$. Contrastingly, this motion is satisfactorily explained by the a' mode ν_{29} of 1PPR (C_s , see Supporting Information).

To resolve any uncertainty in the structure of the carrier, stable precursors 1-phenyl-1-propyne (1PP) and 3-phenyl-1-propyne (3PP) were employed for a chemical test, the former being expected to preferentially produce 3PPR under soft discharge (low current and voltage) conditions, and the latter to produce 1PPR abundantly, each by removal of a single hydrogen atom from the parent (refer to Figure 1). 3PP (vapor pressure in 10 bar Ar) was discharged with half the current required in the benzene experiments, and an LIF signal at 476 nm was observed with nearly an order of magnitude greater strength than when benzene was used as the precursor. The dispersed emission spectrum was measured from 476 nm and found identical to that previously recorded. The sample was then removed, and the system was flushed with argon until only a very weak signal was observed. No increase in signal above this background level was observed in a discharge of 1PP in argon under any conditions; a signal returned immediately when 1PP was removed and replaced with 3PP. This is taken as conclusive evidence that the carrier of the spectrum is a 1-phenylpropargyl radical.

Under some experimental conditions it was possible to observe other $m/z = 115$ bands in the same spectral region as that in Figure 3. It is possible that these bands (the most prominent being at 485 and 464 nm) are due to the 3PPR isomer. The experimental conditions were difficult to reproduce. The absence of these bands from the fluorescence spectra may be due to fast internal conversion processes which would also make R2C2PI detection more difficult.

The radical position in propargyl is known to be situated primarily on the sp^2 carbon. As such, it would be expected that the radical lies mostly on the carbon α to the phenyl ring in 1PPR and on the terminal carbon in 3PPR. The relative stabilities of these radicals have been calculated in a high-level study of the thermochemistry of substituted propargyl radicals.³⁷ It is found that 1PPR is more stable than 3PPR by $\sim 10\text{ kJ mol}^{-1}$. Moreover, when the phenyl and ethynyl groups act in concert to stabilize the radical in 1PPR, the species is greatly stabilized ($\sim 100\text{ kJ mol}^{-1}$) with respect to H-exchange with methane to produce a methyl radical and 3PP. This is $\sim 40\text{ kJ mol}^{-1}$ greater than that obtained analogously for 3PPR.

The yield of 1PPR from a small range of readily available hydrocarbon precursors was investigated briefly. No 1PPR was observed from dilute acetylene/Ar premixes of various concentrations; a signal from a discharge of toluene was less than a third of that from benzene. Importantly, a discharge of 1-hexyne produced a 1PPR signal strength only a few times less than that from benzene. Indeed, benzene itself was observed using 1-hexyne as a precursor, with considerable signal strength. The potential significance of this result will be discussed below.

3.2. Assignment of the LIF Spectrum. Having established the carrier as 1PPR, we can now make some tentative assignments for the dominant structure in the spectrum (Figure 3). Due to the difficulty of calculating excited-state geometries and frequencies, to facilitate assignment of the spectrum the calculated ground state vibrational frequencies were scaled by 0.9 as a crude estimation of their reduction in magnitude upon excitation. From inspection of TDDFT results, the electronic transition is assigned as $A''-A'$ ($\pi^*-\pi$). The greatest Franck-Condon activity is expected in the ring breathe, ring deformation, and C-C stretching modes in the chain, while little activity is anticipated in the bending modes with the possible exception of the in-plane wagging of the chain fragment. The spectrum is dominated by the vibronic origin band and three bands at 21 775, 21 922, and 21 969 cm^{-1} . In light of the above argument these are assigned in the first instance to the a' ring-breathing modes ν_{23} , ν_{22} , and ν_{21} , respectively, by comparison with the scaled DFT frequencies as shown in Table 1. The full assignment of the spectrum is ongoing and will be published separately. A comparison of observed and calculated 1PPR excited-state frequencies that have been assigned is presented in Table 1.

The fluorescence lifetime of the excited state is 350 ns at the origin. Given that an ion $m/z=115$ signal was obtained with 266 nm and (resonant) 476 nm photons together, but not with a 238 nm photon alone, the IP can be bracketed between 5.1 and 7.3 eV. The calculated (vertical) IPs of 1PPR and 3PPR are similar, $\sim 6.8\text{ eV}$ (B3LYP/6-31G(d)).

4. Discussion

4.1. Connection with Combustion Chemistry. There are two likely routes to the formation of 1-phenylpropargyl in a

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Table 1. Comparison of Observed and Calculated B3LYP/6-311+G(d,p) Frequencies, the Latter Scaled by 0.9^a

mode	description	ω' (cm ⁻¹)	
		obsd	calcd
ν_{21}	ring breathe [C(3')C(4') + C(5')C(4')] symmetric stretch	962	935
ν_{22}	ring breathe [C(3')C(4')C(5') + C(2')C(1')C(6')] symmetric bend–stretch	915	901
ν_{23}	ring breathe [C(1')C(2') + C(1')C(6')] symmetric stretch	768	752
ν_{25}	ring deformation [C(2')C(1')C(6') + C(3')C(4')C(5')] symmetric bend	607	575
ν_{29}	C(2)C(1)C(1') bend	117	111

^a Labeling of atoms follows Figure 1.

benzene discharge: addition of the propargyl radical to benzene/phenyl and addition of acetylene to the benzyl radical. However, as the 2D map in Figure 2 demonstrates, benzyl is not observed with a significant intensity from the benzene discharge, although it has been known that the radical has an absorption and emits fluorescence in the present experimental wavelength region (we were able to produce benzyl radical in large amounts from a toluene discharge). On the other hand, the observation of IPPR from a discharge of 1-hexyne, with a signal strength that is not an order of magnitude less than that from benzene and comparable to that from toluene, is particularly suggestive of the role of propargyl in the formation of IPPR. The propargyl radical is a resonance-stabilized radical, having two resonance structures with the unpaired electron situated on either terminal carbon. 1-Hexyne contains the propargyl moiety and might be expected to produce the propargyl radical abundantly upon discharging. Based on the observation of benzene and IPPR as 1-hexyne discharge products, it is not unreasonable to suggest that formation of IPPR might proceed via the combination of a propargyl radical with benzene or phenyl radical (with the appropriate H-loss). The six-membered ring could be produced via 1,5-hexadiyne, derived directly from the precursor or the reaction of two propargyl radicals.

The importance of the propargyl self-reaction to benzene formation in hydrocarbon combustion has been well established by theory and experiments.^{1–7} As mentioned above, propargyl is a resonance-stabilized radical. Compared to nonresonantly stabilized radicals, propargyl reacts more slowly with closed-shell species, with consequently higher concentrations of propargyl in combustion systems. This is one of the reasons why propargyl is considered as a key intermediate for benzene formation in combustion. The phenylpropargyls have seven resonance forms, with the radical having three ring sites (2', 6', and 4' in Figure 1) in addition to those analogous to propargyl (these chain sites, 1 and 3, are double-counted due to the Kekulé structures of the phenyl moiety). As such, these species are expected to exhibit larger resonance stabilization energies than the propargyl radical, permitting us to consider that the substituted propargyl, IPPR itself, may be an important intermediate to form larger aromatic hydrocarbons, such as PAHs. Actually, a role for the nonsubstituted propargyl radical has been already suggested in small PAH generation. A kinetic model developed by D'Anna and Violi¹⁹ includes two reactions concerning propargyl, one of which forms biphenyl (phenyl + 2 × propargyl) and another naphthalene (benzyl + propargyl). They tested this model against experimental data of an atmospheric pressure ethylene–oxygen flame and showed that

the propargyl reactions play significant roles for formation of PAHs having up to three rings. Although comparably little is understood of larger PAH and soot formation in combustion, correlations of sooting with benzene concentration have been reported.^{6,38} The IPPR may therefore be considered a potentially important intermediate connecting benzene to larger PAHs, since the present study reveals that the radical exists in the benzene discharge with a high concentration. A chemical model including the phenylpropargyls might provide insight into PAH and soot formation in combustion. The present LIF observation of IPPR attracts our attention particularly in the point of view concerning laboratory chemical kinetics, because highly sensitive detection using an LIF technique is possible for experimental detection of the radical. Experimentally determined rate constants of reactions involving IPPR will be essential data for the chemical modeling of PAH and soot formation in many combustion systems.

4.2. Connection with Extraterrestrial Chemistry. Roles for the propargyl radical have been imputed in chemical evolution in circumstellar envelopes³⁹ and in the formation of benzene in the atmospheres of Jupiter, Saturn, and Titan.^{40,41} Due to the recent discovery of benzene in high concentrations in Titan's atmosphere by the *Cassini* spacecraft, it has been invoked in the production of the large quantities of organic aerosols observed in Titan's upper atmosphere,^{8,9} though a mechanism of PAH formation from benzene in this environment remains speculative. As for combustion, it might not be unreasonable to suggest a role for substituted propargyl radicals such as IPPR in this process. Both IPPR and 3PPR might be important reactive intermediates, so far not considered, in the reaction of phenyl and propyne, thought to be important to the formation of five-membered rings, and therefore nonplanar PAHs, in the interstellar medium.⁴² Comprising a chain attached to a ring, IPPR might be considered one of the smallest prototypes that marries the two in-vogue diffuse interstellar band (DIB) paradigms, those being carbon chains and PAHs.⁴³ It has not escaped our attention that the wavelength of the origin band exhibits a tantalizing coincidence with the 4760 Å DIB.⁴⁴ At 25 Å (fwhm), the line width of the DIB far exceeds the <1 Å line width (fwhm) of the IPPR origin band. If both bands were to possess a common carrier, this difference might be attributed to the differing rotational populations admitted by supersonic expansion (by collisional cooling) and the interstellar medium (by coupling to the interstellar radiation field). There is no perfect correlation in the strength of any pair of DIBs across different lines of sight. This can be interpreted as indicating that DIBs all arise from different carriers, and that the spectra of the carriers are dominated by the origin transition. The LIF spectrum shows that IPPR follows this behavior, with the origin band being several times stronger than any vibronic feature. Taken with the discovery of a molecular band at 4429 Å^{45,46} also from a benzene discharge, the present study indicates that

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benzene discharges present a fertile environment for the investigation of interstellar species in general and potential DIB carriers in particular.

5. Conclusion

The electronic spectrum of the 1-phenylpropargyl radical in the region 20 800–22 000 cm^{-1} has been measured by laser-induced fluorescence. The structure of the carrier was elucidated by a synergy of laser induced fluorescence (excitation), dispersed fluorescence (emission) and R2C2PI (mass-selective excitation) spectroscopies, and density functional theory. The DFT calculation of vibrational frequencies permitted a putative assignment of the strongest observed vibronic bands. The apparent great abundance of this molecule in a benzene discharge, based on the strength of the fluorescence observed here, suggests for it an important role in chemical processes in flames, planetary atmospheres, and the interstellar medium. In particular, recom-

bination reactions of 1-phenylpropargyl with other abundant RSRs, including itself and propargyl, may be important steps in the formation of PAHs in such environments. This study provides a valuable probe of post-benzene reactive intermediates for investigations of such processes.

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Supporting Information Available: Further experimental details in addition to geometries and harmonic frequencies calculated at the B3LYP/6-311+G(d,p) level of theory for the 1PPR and 3PPR radicals; complete ref 36. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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