

Reactive Carbon-Chain Molecules: Synthesis of 1-Diazo-2,4-pentadiyne and Spectroscopic Characterization of Triplet Pentadiynylidene ($\text{H}-\text{C}\equiv\text{C}-\ddot{\text{C}}-\text{C}\equiv\text{C}-\text{H}$)

Nathan P. Bowling,[†] Robert J. Halter,[†] Jonathan A. Hodges,[†] Randal A. Seburg,[†] Phillip S. Thomas,[†] Christopher S. Simmons,[‡] John F. Stanton,^{*,‡} and Robert J. McMahon^{*,†}

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706-1396, and Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712

Received December 7, 2005; E-mail: stanton@jfs1.cm.utexas.edu; mcmahon@chem.wisc.edu

Abstract: 1-Diazo-2,4-pentadiyne (**6a**), along with both monodeuterio isotopomers **6b** and **6c**, has been synthesized via a route that proceeds through diacetylene, 2,4-pentadiynal, and 2,4-pentadiynal tosylhydrazone. Photolysis of diazo compounds **6a–c** ($\lambda > 444$ nm; Ar or N₂, 10 K) generates triplet carbenes HC₅H (**1**) and HC₅D (**1-d**), which have been characterized by IR, EPR, and UV/vis spectroscopy. Although many resonance structures contribute to the resonance hybrid for this highly unsaturated carbon-chain molecule, experiment and theory reveal that the structure is best depicted in terms of the dominant resonance contributor of penta-1,4-diyne-3-ylidene (diethynylcarbene, $\text{H}-\text{C}\equiv\text{C}-\ddot{\text{C}}-\text{C}\equiv\text{C}-\text{H}$). Theory predicts an axially symmetric ($D_{\infty h}$) structure and a triplet electronic ground state for **1** (CCSD(T)/ANO). Experimental IR frequencies and isotope shifts are in good agreement with computed values. The triplet EPR spectrum of **1** ($|D/hc| = 0.6157$ cm⁻¹, $|E/hc| = 0.0006$ cm⁻¹) is consistent with an axially symmetric structure, and the Curie law behavior confirms that the triplet state is the ground state. The electronic absorption spectrum of **1** exhibits a weak transition near 400 nm with extensive vibronic coupling. Chemical trapping of triplet HC₅H (**1**) in an O₂-doped matrix affords the carbonyl oxide **16** derived exclusively from attack at the central carbon.

Introduction

Studies involving carbon clusters,¹ carbon chain radical anions,^{2–4} neutral carbon chains,^{5–7} carbon ring chains,^{8,9} and other related species have emerged in chemistry and astronomy in recent years. Much of the impetus of this research stems from the fact that many of these species are abundant in the interstellar medium.^{10–12} The linear carbon chains HC₂H (acetylene), HC₄H (diacetylene), and HC₆H (triacetylene) have been detected in

space by infrared spectroscopy.¹³ Although the existence of the symmetrical carbon chains HC_{*n*}H cannot be confirmed by radio astronomy because of the absence of permanent dipole moments, the corresponding radicals (HC_{*n*}, *n* = 1–8) have been detected in space.¹³ The polar, cyano-substituted carbon chains have been detected in space, not only in the case of the closed-shell cyanopolynes HC_{*n*}N (*n* = 1, 3, 5, 7, 9, 11) but also in the case of the triplet carbenes HC₂N and HC₄N.¹³

The alternation in structure within the series of carbon chain molecules HC_{*n*}H (*n* = even or odd) is widely recognized: HC_{*n*}H (*n* = even) are closed-shell polyacetylenic molecules with alternating triple and single bonds, while HC_{*n*}H (*n* = odd) are open-shell species with delocalized carbene or diradical structures. Less widely appreciated is the alternation in structure that is predicted to exist *within* the HC_{*n*}H (*n* = odd) series (vide infra).^{3,14} From a desire to investigate this problem, experimentally, and with the perspective of our previous studies of triplet HC₃H,^{15–17} we turned our attention to triplet HC₅H.

[†] University of Wisconsin.

[‡] University of Texas.

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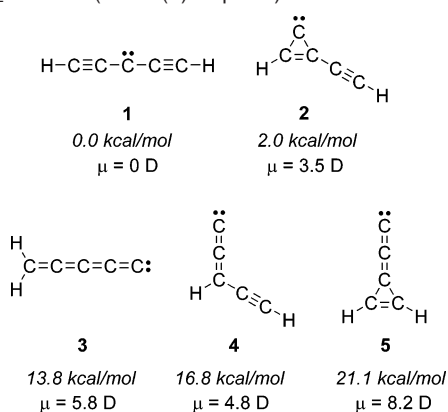
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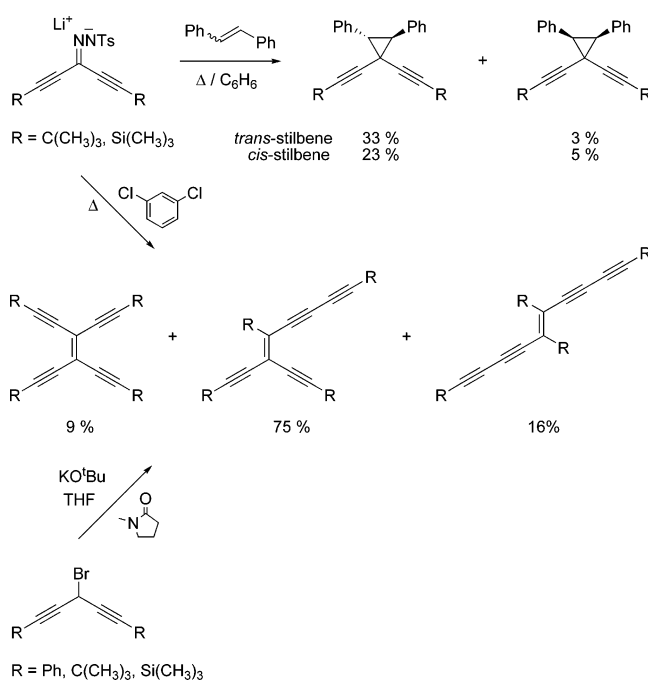
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Scheme 1. Computed Relative Energies and Dipole Moments of Five C₅H₂ Isomers (CCSD(T)/cc-pVTZ)¹⁸

In the current study, we describe a general synthetic strategy for preparing diazo compound precursors to diacetylenic carbenes. 1-Diazo-2,4-pentadiyne (**6a**) serves as a photochemical precursor of linear triplet HC₅H, which is characterized by IR, UV/vis, and EPR spectroscopy under matrix isolation conditions. The electronic spectrum of HC₅H clarifies some ambiguities concerning earlier attempts to detect this species^{6,7} and provides a foundation for further gas-phase spectroscopic studies. These studies expand the current understanding of the structural and electronic differences within the HC_nH ($n = \text{odd}$) series of carbon chains.

Background

In a previous computational survey of the C₅H₂ potential energy surface, we identified five isomers that lie within ca. 20 kcal/mol of one another in energy (Scheme 1).¹⁸ The carbon chain molecule HC₅H (**1**), predicted to be a linear triplet ($D_{\infty h}$), is the apparent global energy minimum. Each of the four polar singlet isomers, ethynylcyclopropenyliene (**2**), pentatetraenylidene (**3**), ethynylpropadienyliene (**4**), and 3-(didehydrovinylidene)cyclopropene (**5**) was subsequently generated in a pulsed discharge and characterized by Fourier transform microwave spectroscopy.^{8,19,20} Although each of the singlet isomers bears a close structural relationship to an interstellar molecule, none of the C₅H₂ isomers has yet been detected in space. The electronic absorption spectrum of triplet HC₅H (**1**) was obtained in a neon matrix using mass selection techniques.⁶ Although beautiful spectra were obtained for higher members of the homologous series (HC₇H, HC₉H, HC₁₁H, and HC₁₃H), the signal-to-noise ratio for the spectrum of HC₅H was notably smaller, leaving some uncertainty in the assignment. In studying the same series of compounds in the gas phase by cavity ringdown spectroscopy, Ball et al. obtained electronic spectra of the longer chains (HC₇H, HC₉H, HC₁₁H, and HC₁₃H) but were unable to detect HC₅H.⁷ The signals of HC₅H (**1**) may be weak in the gas-phase experiments if the linear isomer is not actually the lowest-energy isomer or if conditions in the discharge favor the formation of cyclic isomers.⁷ The small oscillator strength also hampers detection. Theoretical studies

Scheme 2. Solution Chemistry of Substituted HC₅H Derivatives^{31,32}

of the electronic excited states of C₅H₂ isomers predict a weak $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transition ($f = 0.007$) at ca. 400–450 nm for triplet HC₅H.^{21,22} Barriers to interconversion of C₅H₂ isomers on the lowest singlet and triplet surfaces are, for the most part, substantial.²³

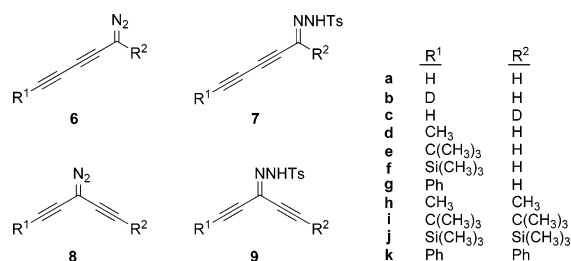
Triplet EPR spectra of three monosubstituted derivatives of carbene **1** (RC₅H, R = Me, *t*-Bu, Ph),^{24,25} as well as that of the diphenyl derivative, PhC₅Ph,²⁶ have been reported and will be discussed in the context of the current findings (vide infra). Triplet HC₅H (**1**) also bears a close structural relationship to triplet dicyanocarbene (N≡C–C̈–C≡N).^{27–30} Solution studies of symmetrically disubstituted RC₅R derivatives exhibit reactivity at both C1 and C3. Trapping of RC₅R with *cis*- and *trans*-stilbene resulted in non-stereospecific cyclopropane formation at C3, suggesting the intermediacy of a triplet carbene.³¹ As generated from independent precursors (thermolysis of substituted 3-diazo-1,4-pentadiyne³¹ or base-induced α -elimination of substituted 3-bromo-1,4-pentadiyne³²), RC₅R affords a regioisomeric mixture of formal carbene dimers, reflecting coupling at C1–C1, C1–C3, and C3–C3 (Scheme 2).

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Results and Discussion

Carbene Precursors. We envisioned 1-diazo-2,4-pentadiyne (**6a**), 3-diazo-1,4-pentadiyne (**8a**), or their corresponding dia-

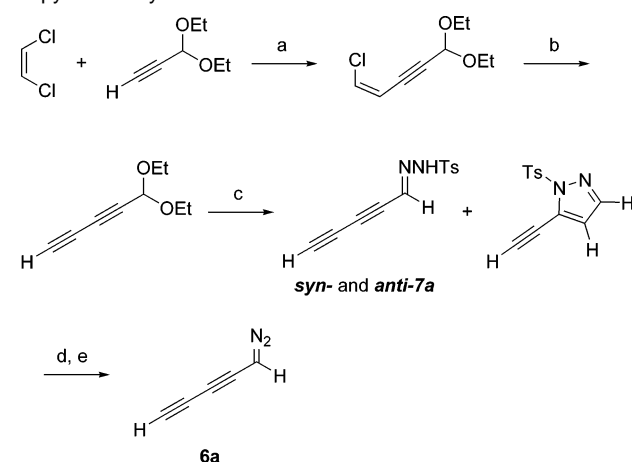


zirines as suitable photochemical precursors for triplet HC₅H. Mono- and disubstituted derivatives of 1-diazo-2,4-pentadiyne (**6**) have been generated from the corresponding *N*-nitrosourea²⁴ or *N*-nitrosoacetamide²⁶ precursors, while disubstituted derivatives of 3-diazo-1,4-pentadiyne (**8**) have been generated from the corresponding tosylhydrazone salts.^{31,33,34} Syntheses of the unsubstituted diazo compounds or diazirines have not been reported. We prepared the known tosylhydrazone of 1,5-bis-(trimethylsilyl)penta-1,4-diyn-3-one (**9j**),^{31,33} but all attempts to remove the trimethylsilyl protecting groups failed, leading to pyrazole formation and/or decomposition.^{35–37} Attempts to deprotect 1,5-bis(trimethylsilyl)-3-diazopenta-1,4-diyne (**8j**) also failed. We therefore focused our attention on the preparation of 1-diazo-2,4-pentadiyne (**6a**).

Synthesis of 1-Diazo-2,4-Pentadiyne (6a). Our initial synthesis, proceeding via propynal diethyl acetal, afforded tosylhydrazone **7a** and 1-diazo-2,4-pentadiyne (**6a**) (Scheme 3).^{38,39} The successful preparation of the fragile diazo compound, albeit in low yield, spurred the development of an improved procedure (Scheme 4). Dehydrohalogenation of commercially available 1,4-dichloro-2-butyne (**10**) affords diacetylene. Mono-deprotonation, followed by reaction with paraformaldehyde,⁴⁰ gives 2,4-pentadiynol (**11**) in 70% yield. Oxidation of alcohol **11** with Dess–Martin periodinane⁴¹ gives 2,4-pentadiynal (**12**), which was not isolated because of its anticipated instability. Transfer of a diethyl ether solution of aldehyde **12** into a flask containing *p*-toluenesulfonylhydrazide affords a 3:2 (anti/syn) mixture of 2,4-pentadiynal tosylhydrazone (**7a**) in excellent yield. The syn and anti isomers produced are separable by flash chromatography.⁴² Deprotonation of either isomer with sodium hydride provides the sodium salt of the tosylhydrazone. With gentle heating, the sodium salt is converted to 1-diazo-2,4-pentadiyne (**6a**).

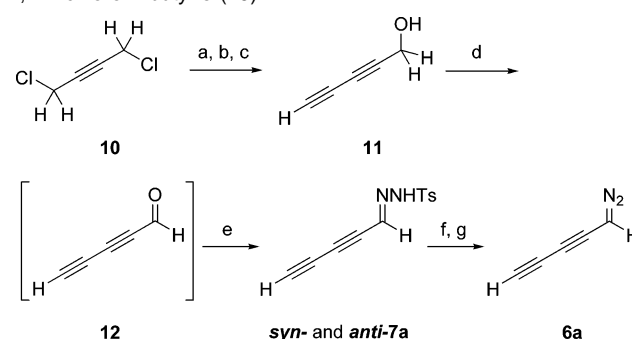
Computational Results. We utilized coupled-cluster methods (CCSD(T)/cc-pVTZ and CCSD(T)/ANO) to compute the struc-

Scheme 3. Synthesis of 1-Diazo-2,4-pentadiyne (**6a**) from Propynal Diethyl Acetal^a



^a Reagents and conditions: (a) Pd(PPh₃)₄, CuI, *n*-BuNH₂, benzene, 25 °C, 16 h, 77%; (b) 1.0 M TBAF, THF, 25 °C, 20 h, 58%; (c) NH₂NHTs, EtOH, 45 °C, 6%; (d) NaH, CH₂Cl₂; (e) 70 °C, 0.02 mmHg.

Scheme 4. Synthesis of 1-Diazo-2,4-pentadiyne (**6a**) from 1,4-Dichloro-2-butyne (**10**)^a



^a Reagents and conditions: (a) NaNH₂ (3 equiv), NH₃, cat. Fe(NO₃)₃·9H₂O, THF, −40 °C; (b) (CH₂O)_{*n*} (1.0 equiv) suspension in THF, −40 °C, 1.75 h; (c) NH₄Cl, 15 min, 70% from **10**; (d) Dess–Martin periodinane (1.3 equiv), CH₂Cl₂, 1.5 h, 25 °C; (e) NH₂NHTs (1.0 equiv), ether, 25 °C, 93% over two steps (3:2 mixture of anti and syn isomers); (f) NaH, CH₂Cl₂; (g) 70 °C, 0.02 mmHg.

Table 1. Computed Structural Parameters of Triplet HC₅H (**1**)^a

parameter	HC ₅ H ^b	HC ₅ H ^c	parameter	HC ₅ H ^b	HC ₅ H ^c
<i>r</i> (HC ₁)	1.0594	1.0634	<i>A_e</i>	2270	2252
<i>r</i> (C ₁ C ₂)	1.2365	1.2408	<i>μ</i>	0	0
<i>r</i> (C ₂ C ₃)	1.3079	1.3137			

^a Bond length (Å), bond angle (deg), rotational constant *A_e* (MHz), dipole moment *μ* (D). ^b CCSD(T)/cc-pVTZ. ^c CCSD(T)/ANO.

ture, rotational constant, dipole moment, and harmonic vibrational frequencies for triplet HC₅H (**1**) and HC₅D (**1-d**) (Tables 1 and 2). The two basis sets provided similar predictions for the harmonic vibrational frequencies of the stretching modes but provided surprisingly different predictions for the frequencies of the bending modes and for the isotopic shifts (H/D) on these modes. Bending frequencies and isotope shifts obtained with the ANO basis exhibit much better agreement with experimental values. The current calculations, therefore, represent a notable improvement over our earlier results concerning the structure

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(35) Considerable experience in our group suggests that propargyl tosylhydrazones bearing a syn relationship between the *N*-imino substituent and the alkyne are prone to undergo conjugate addition of the sulfonamide nitrogen to the β-position of the unsaturated system, resulting in pyrazole formation. This syn relationship is intrinsic to derivatives of penta-1,4-diyn-3-one. In these systems, the ability to prepare tosylhydrazones or diazo compounds depends critically on the substituents. Our efforts to obtain the unsubstituted compounds **8a** or **9a** (R¹ = R² = H) were unsuccessful.

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(41) In our hands, Dess–Martin periodinane consistently outperforms other oxidation protocols (e.g., PCC and MnO₂) in the oxidation of primary acetylenic alcohols to aldehydes. Our attempts to synthesize Dess–Martin periodinane using the combined procedures of Santagostino (Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537–4538) and

Table 2. Experimental and Computed Infrared Frequencies and Intensities^{a,b}

mode	sym	HC ₅ H		HC ₅ H		sym	HC ₅ D		HC ₅ D		$\Delta\nu_{\text{H-D}}$	
		freq	int	expt	int ^b		freq	int	expt	int ^b	expt	calcd
ω_1	σ_g^+	3459	—			σ	3455	93				4
ω_2	σ_g^+	1954	—			σ	3455	93	3294	100	-2 ^c	-4 ^c
ω_3	σ_g^+	748	—			σ	1917	0.6				37
ω_4	σ_u^-	3451	189	3292	100	σ	737	0.006				11
ω_5	σ_u^-	1618	5			σ	2611	51	2512	21	780	840
ω_6	σ_u^-	1532	11			σ	1592	12				26
ω_7	π_g	456	—			σ	1520	6				12
ω_8	π_g	379	—			π	378	0.06				78
ω_9	π_u	463	170	478, 470	11, 15	π	369	0.4				10
ω_{10}	π_u	367	8			π	460	90	478, 470	15, 18	0	3
ω_{11}	π_u	98	9			π	345	43				22
	combination band (?)			873	2	π	95	9				3

^a CCSD(T)/ANO computed harmonic vibrational frequencies (cm⁻¹) and infrared intensities (km/mol). Frequencies have not been scaled. ^b Experimental intensities reported relative to strongest absorption = 100. ^c Comparison of the experimentally observable C–H stretching vibrations of HC₅H and HC₅D. For HC₅H, the observable vibration is the asymmetric stretch (ω_4), while for HC₅D, it is the symmetric stretch (ω_1). In comparing these vibrations, the isotope shift is negative (-2 cm⁻¹ expt, -4 cm⁻¹ calcd).

(CCSD(T)/cc-pVTZ) and harmonic vibrational frequencies (CCSD/DZP) of triplet HC₅H (**1**).¹⁸ Calculation of the fundamental vibrational frequencies of HC₅H (**1**) via second-order vibrational perturbation theory proved to be problematic because of the low-frequency vibrational modes. Computed structures and harmonic vibrational frequencies for diazo compound **6a**, as well as various isomeric products associated with the trapping of carbene **1** with dioxygen, were obtained using density functional theory (B3LYP/6-31G*).³⁹

Generation and Spectroscopic Characterization of Linear Triplet HC₅H. Long-wavelength photolysis ($\lambda > 497$ nm, 13.5 h; $\lambda > 472$ nm, 2.25 h; $\lambda > 444$ nm, 0.5 h) of matrix-isolated 1-diazo-2,4-pentadiyne (**6a**) (N₂, 10 K) affords the IR spectrum depicted in the top panel of Figure 1. The same photoproduct is formed at each of the three different wavelengths. Since the disappearance of diazo compound **6a** occurs significantly faster at $\lambda > 444$ nm than at longer wavelengths, these irradiation conditions were utilized in most subsequent experiments. The experimental infrared spectrum of the photoproduct displays reasonable agreement with the computed spectrum of triplet HC₅H (**1**) (vide infra). The experimental IR spectrum is inconsistent with spectra predicted for alternative C₅H₂ structures **2–5**.¹⁸ Isomers **3**, **4**, and **5** are computed to have intense absorptions near 1900 cm⁻¹, which are not observed in the experimental spectrum (Figure 2). The cyclopropenylidene derivative **2** is computed to have multiple absorptions throughout the IR spectrum, which are not observed in the experimental spectrum (Figure 2).

Triplet HC₅H (**1**) is computed to exhibit four IR-active vibrational modes that fall within the range of our spectrometer (>400 cm⁻¹). The two most intense bands are readily observed in the experimental spectrum. The assignment of a third, weak band at 1518 cm⁻¹ in the experimental spectrum remains tenuous. The fourth vibration, computed at 1618 cm⁻¹ with extremely low intensity, is likely to be obscured by the omnipresent water bending vibration at ca. 1600 cm⁻¹. The

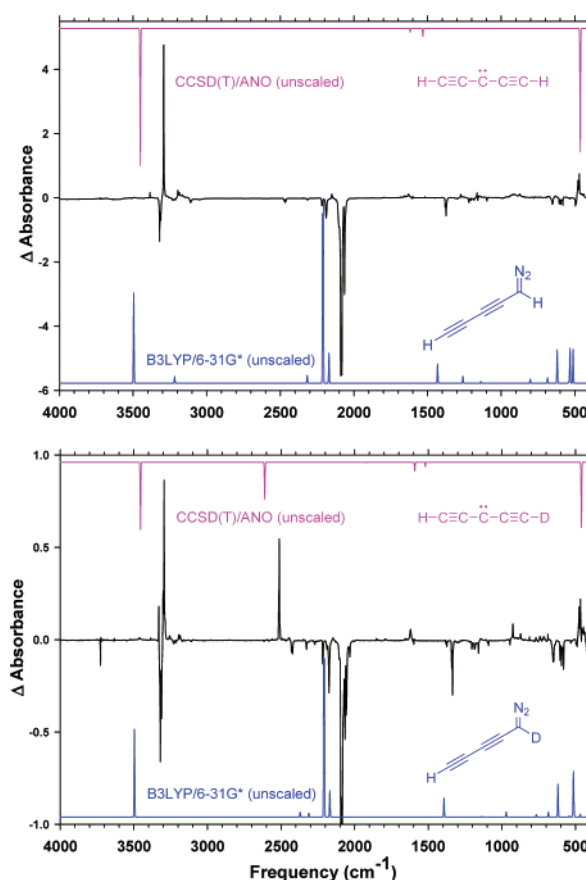


Figure 1. Top: infrared subtraction spectrum showing the disappearance of 1-diazo-2,4-pentadiyne (**6a**) and the appearance of triplet HC₅H (**1**) upon irradiation ($\lambda > 497$ nm, >472 nm, >444 nm; N₂, 10 K), along with computed spectra for **1** and **6a**. Bottom: infrared subtraction spectrum showing the disappearance of 1-diazo-2,4-pentadiyne-1-*d* (**6c**) and the appearance of triplet HC₅D (**1-d**) upon irradiation ($\lambda > 444$ nm; N₂, 10 K), along with computed spectra for **1-d** and **6c**. (Intensities of $\nu_{\text{C=N=N}}$ stretch for **6a** and **6c** have been truncated to keep the bands on scale.)

experimental spectrum exhibits two bands near 470 cm⁻¹, while the computed spectrum predicts a single band of greater intensity.⁴³ Although the computed low-frequency bending mode is doubly degenerate (ω_9 , π_u ; Table 2), a variety of subtle effects in the matrix could break the degeneracy, giving rise to two bands of roughly equal intensity, as observed in the experimental

Ireland (Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899) often resulted in a mixture of the desired reagent and the acetoxyiodinane oxide (Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549–7552), both of which effectively oxidize propargylic alcohols.

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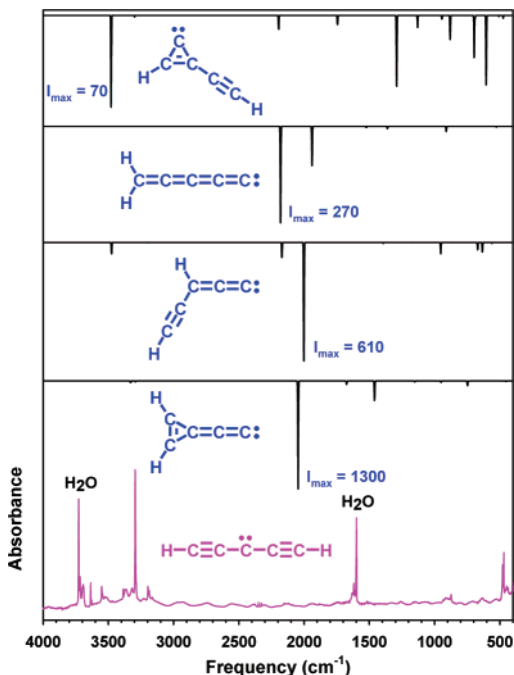


Figure 2. Experimental infrared spectrum of triplet HC_5H (**1**) (N_2 , 10 K; bottom trace) obtained after long-wavelength photolysis ($\lambda > 497$ nm, 13.5 h; $\lambda > 472$ nm, 2.25 h; $\lambda > 444$ nm, 0.5 h) of 1-diazo-2,4-pentadiyne (**6a**) compared to unscaled, computed harmonic vibrational frequencies (CCSD/DZP) for C_5H_2 isomers **2–5**.¹⁸ (I_{max} is the computed intensity (km/mol) of the most intense IR vibration for each species.)

spectrum. The local matrix site in which the carbene is generated is inherently unsymmetrical by virtue of the structure of the diazo precursor. The unsymmetrical nature of the local matrix environment—whatever the origin—appears to be manifest in the EPR and UV/vis spectra, as well (vide infra). The splitting of the low-frequency IR vibration depends on the matrix medium; in argon, the band appears as a single, broadened absorption.³⁹ Finally, we note that a weak band at 873 cm^{-1} appears consistently in all the experiments but does not correspond to a computed harmonic vibration. We tentatively assign this feature as a combination band of triplet HC_5H (**1**), possibly $\nu_8 + \nu_{10}$.

To confirm the infrared assignment of **1**, the monodeuterio isomer HC_5D was generated upon photolysis of either of the isomeric precursors, 1-diazo-2,4-pentadiyne-5-*d* (**6b**) or 1-diazo-2,4-pentadiyne-1-*d* (**6c**) (Figure 1).⁴⁴ The observed isotope shifts in the experimental infrared spectrum are in excellent agreement with computed isotope shifts for the monodeuterio carbene HC_5D (**1-d**) (Table 2).

Long-wavelength photolysis ($\lambda > 444$ nm) of diazo compound **6a** affords the EPR spectrum of triplet HC_5H (**1**) (Figure 3). The spectrum is similar to those observed for other triplet acetylenic carbenes,^{15,24–26,45,46} although it is important to note that our interpretation of these spectra in terms of the structures

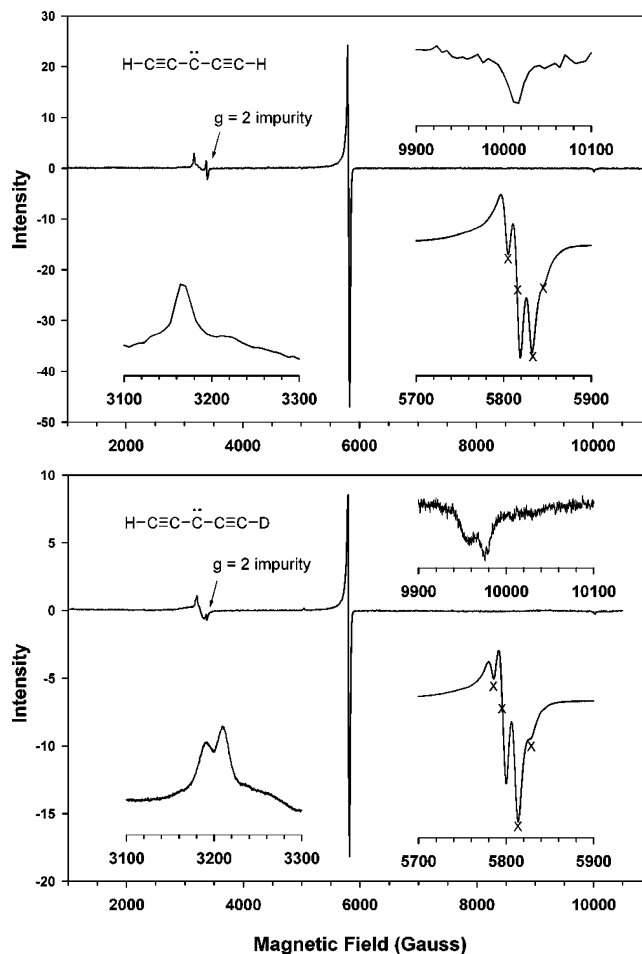


Figure 3. Top: EPR spectrum of triplet HC_5H (**1**), obtained upon irradiation ($\lambda > 444$ nm) of diazo compound **6a** (Ar, 15 K). Bottom: EPR spectrum of a mixture of triplet HC_5H (**1**) and HC_5D (**1-d**), obtained upon irradiation ($\lambda > 444$ nm) of diazo compound **6b** (Ar, 15 K). Magnetic field positions of the X_2 and Y_2 transitions, used in calculating the ZFS parameters, marked with \times .

of the triplet carbene differs from those of other workers (vide infra). When displayed at full sweep width, the EPR spectrum appears to be a classic example of an axially symmetric triplet species (Figure 3). Upon expansion of the region near 5800 G, however, it becomes apparent that the EPR signal is not the single XY_2 transition of an axial triplet. We interpret the spectrum in terms of a triplet species with slight deviation from axial symmetry (i.e., distinct X_2 and Y_2 transitions instead of a single XY_2 transition) that exists in two different matrix sites in the argon matrix. Splitting is not seen in the Z_1 or Z_2 transitions. The D and E values determined for the different matrix sites are very similar (Table 3). The zero-field splitting parameter, D , of triplet HC_5H (**1**) (ca. 0.61 cm^{-1}) is similar to that of the alkyl-substituted analogues (MeC_5H , 0.609 cm^{-1} ; *t*- BuC_5H , 0.606 cm^{-1}),^{24,25} and as expected, is larger than those of the mono- and diphenyl-substituted analogues (ca. 0.53 cm^{-1}).^{24–26,46} Interestingly, the D value of HC_5H is also similar to that of the smaller homologue, HC_3H (ca. 0.63 cm^{-1}).^{15,17,24,25} The small E value of triplet HC_5H (0.0007 cm^{-1}) implies that the deviation from axial symmetry is quite small. The deviation from axial

(43) The absence of any other IR bands in the experimental spectrum precludes the assignment of either one of the pair of absorptions to a different isomer of C_5H_2 or to impurities within the matrix. The bands do not change upon annealing.

(44) The synthetic route to 1-diazo-2,4-pentadiyne-1-*d* (**6c**), which utilizes perdeuterio-paraformaldehyde, affords a higher degree of isotopic incorporation (ca. 98%) than the synthetic route to 1-diazo-2,4-pentadiyne-5-*d* (**6b**), which involves base-catalyzed isotopic exchange in the tosylhydrazone precursor (ca. 65%). Both precursors afford triplet HC_5D ; spectra obtained using 1-diazo-2,4-pentadiyne-1-*d* (**6c**) are easier to interpret because of the absence of unlabeled diazo compound **6a** and carbene HC_5H (**1**).

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Table 3. EPR Data for Triplet HC₅H (**1**) and HC₅D (**1-d**)

parameter ^a	HC ₅ H in Ar		HC ₅ H in MCH			HC ₅ H MCH- <i>d</i> ₁₄	HC ₅ D in Ar	
	site 1	site 2	site 1	site 2	site 3		site 1	site 2
Z ₁	3164	3164	3203	3203	3203	3281	3190	3210
X ₂	5805	5815	5733	5746	5760	XY ₂ 5753	5785	5796
Y ₂	5832	5848	5764	5778	5791		5814	5828
Z ₂	10 017	10 017				10 006	9956	9976
frequency	9.535	9.535	9.366	9.366	9.366	9.358	9.490	9.490
D/hc	0.6157	0.6159	0.6123	0.6125	0.6130	0.6147	0.6147	0.6166
E/hc	0.0006	0.0007	0.0007	0.0008	0.0007	0.0	0.0006	0.0007

^a Magnetic field position (G), microwave frequency (GHz), zero-field splitting parameter (cm⁻¹).

symmetry likely arises by virtue of matrix effects and does not necessarily imply a disagreement with the axial equilibrium structure computed for triplet HC₅H in the gas phase. Whether a carbene of axial symmetry resides in a matrix cavity of lower symmetry or whether the carbene actually suffers a subtle distortion from axial symmetry under the influence of the matrix, we cannot distinguish. The EPR spectrum obtained in a methylcyclohexane (MCH) glass at 4.2 K is qualitatively similar to that observed in Ar.³⁹ In MCH, the *D* and *E* values for three different sites are similar (Table 3) and are in good accord with those found in argon. Annealing the glass to 30 K followed by recoiling to 4.2 K did not remove the site effects.

The temperature dependence of the EPR spectrum of triplet HC₅H was investigated in order to obtain experimental information concerning the ground electronic state of the carbene.^{37,39} For a molecule with a triplet ground state, the intensity of the EPR signal varies inversely with temperature (Curie law).^{47,48} Conversely, if the triplet state is not the ground state, but rather a thermally populated state, then the EPR signal varies directly with temperature. The doubly integrated area of the X₂ and Y₂ peaks between 4.2 and 30 K varied linearly with inverse temperature, indicating that the triplet state of HC₅H (**1**) is the ground state, as predicted by computations. Care was taken to obtain spectra using a power level that did not result in saturation of the signal. Hydrogen abstraction did not occur upon warming to 30 K, as the original signal shape and intensity was recovered upon recoiling to 4.2 K. Warming above 30 K in MCH, however, leads to irreversible loss of the triplet EPR signal of HC₅H (**1**), presumably by hydrogen atom abstraction from the host. In MCH-*d*₁₄, the triplet EPR signal is recoverable at temperatures below 80 K but is lost, irreversibly, upon warming to 100 K. The Curie law behavior of triplet HC₅H (**1**) in MCH-*d*₁₄ was not determined due to the probable saturation of the signal.

Long-wavelength photolysis ($\lambda > 444$ nm) of 1-diazo-2,4-pentadiyne-5-*d* (**6b**) affords the EPR spectrum of triplet HC₅D (**1-d**) (Figure 3). As with HC₅H (**1**), HC₅D (**1-d**) apparently resides in two slightly different matrix sites ($|D/hc| = 0.6147$ cm⁻¹, $|E/hc| = 0.0006$ cm⁻¹ and $|D/hc| = 0.6166$ cm⁻¹, $|E/hc| = 0.0007$ cm⁻¹). The zero-field splitting parameters of triplet HC₅H (**1**) and HC₅D (**1-d**) are quite similar (Table 3). In favorable cases, isotopic data may be used to infer motional effects that may occur in the frozen matrix.^{38,49,50} In light of

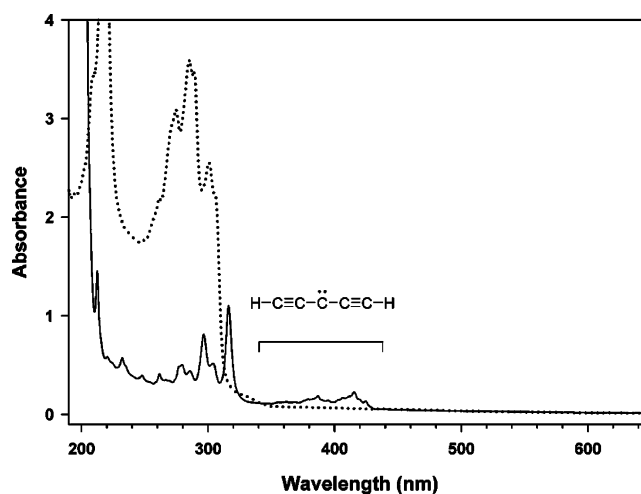


Figure 4. Dotted line: UV/visible spectrum of 1-diazo-2,4-pentadiyne (**6a**) (N₂, 10 K) prior to irradiation. Solid line: spectrum obtained upon irradiation of **6a** ($\lambda > 444$ nm; 1.7 h).

the small differences in the zero-field splitting parameters that are observed in this system, as well as the existence of multiple matrix sites, we are not comfortable interpreting these data in terms of motional effects.

The measurement and assignment of the electronic absorption spectrum of triplet HC₅H has been problematic in this investigation and in others.^{6,7} Interpretation of our matrix spectra has been hampered by an unfortunate combination of factors, including (i) weak absorption by triplet HC₅H, (ii) strong absorption by minor impurities, and (iii) the lack of photochemical reactivity of triplet HC₅H, which eliminates the possibility of confirming the spectroscopic assignment by bleaching the transitions. Nevertheless, we believe that we ultimately arrived at an appropriate interpretation of our absorption spectra. Irradiation (typically $\lambda > 444$ nm) of 1-diazo-2,4-pentadiyne (**6a**), matrix isolated in Ar or N₂, affords an electronic absorption spectrum of the type depicted in Figure 4. Through repeated experimentation, it became apparent that the relative intensities of three different components of the spectrum varied from experiment to experiment. As will be justified more fully in the subsequent discussion, the vibronic progression centered at 300 nm arises from the formal dimers of HC₅H (**1**), the vibronic progression centered at 400 nm arises from triplet HC₅H (**1**), and two broad, featureless absorptions that overlap the vibronic progression of HC₅H (**1**) arise from an unassigned carrier. The broad absorptions can be bleached from the spectrum upon short-wavelength irradiation ($\lambda > 237$ nm). The carrier of this absorption is apparently a minor component in the matrix, as no changes are observed when an IR experiment is performed under the same irradiation condi-

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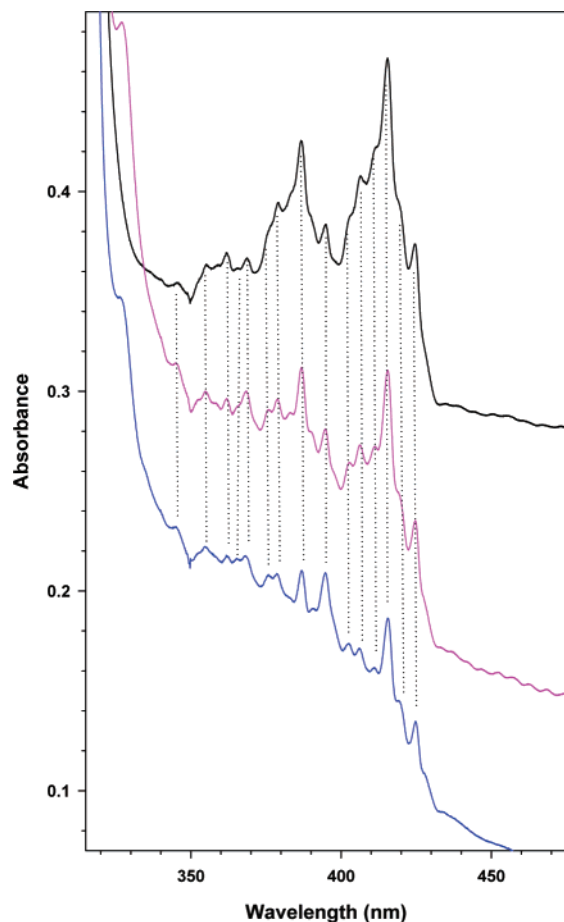


Figure 5. UV/visible spectra obtained upon irradiation of 1-diazo-2,4-pentadiyne (**6a**) (N_2 , 10 K). Top, $\lambda > 444$ nm, 1.7 h; middle, $\lambda > 237$ nm, 2 h; bottom, $\lambda > 237$ nm, 22 h. The bottom spectrum provides clearest depiction of the vibronic progression of triplet HC_5H (**1**).

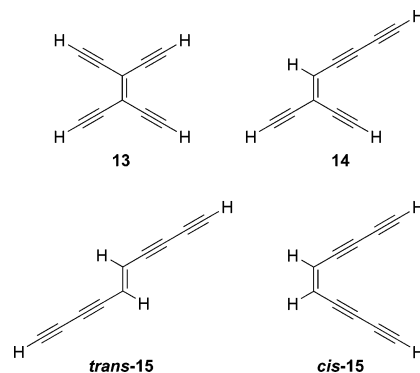
tions. The spectrum obtained after bleaching the broad absorptions ($\lambda > 237$ nm) provides the best spectrum of the vibronic progression at 400 nm.

We assign the weak vibronic progression (ca. 360–420 nm) to triplet HC_5H (Figure 5). The position and intensity of this transition are consistent with theoretical predictions for the $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ electronic transition in triplet HC_5H (449 nm, $f = 0.007$;²¹ 411 nm, $f = 0.02$).²² The observation of similar vibronic progressions for the methyl- and *tert*-butyl-substituted derivatives (CH_3-C_5H and $(CH_3)_3C-C_5H$)⁵¹ supports the spectroscopic assignment. The vibronic features assigned to triplet HC_5H remain unchanged under a variety of irradiation conditions, but they are readily consumed upon annealing a matrix doped with molecular oxygen—thereby providing chemical evidence in support of the spectroscopic assignment (vide infra). A subsequent publication will be devoted to a detailed analysis of the electronic absorption spectrum, excited states, and vibronic interactions in triplet HC_5H . The individual absorption features assigned to triplet HC_5H are 345.0, 348.0, 352.3, 355.0, 358.1, 361.9, 365.5, 368.4, 375.8, 378.8, 383.0, 386.8, 390.0, 394.7, 397.6, 402.7, 406.3, 411.2, 415.5, 419.1, 424.7, and 427.5 nm. The vibronic features that we observe for triplet HC_5H bear little resemblance to the spectroscopic features previously ascribed to the carbene, as generated by photoinduced charge neutralization of the corresponding cation in neon.⁶ We

(51) Thomas, P. S.; Bowling, N. P.; McMahon, R. J. Unpublished results.

speculate that the inability of Ball et. al to detect triplet HC_5H in the gas phase,⁷ by cavity ring-down spectroscopy, arises from their reliance on the spectroscopic features described by Fulara et al.⁶

The position of the vibronic progression observed near 300 nm is not consistent with the theoretical prediction for a transition-dipole-allowed excited state of triplet HC_5H (**1**),²¹ nor are these features associated with oxygen-trapping products of HC_5H (vide infra). A scan of the literature revealed that tetraethynylethene (**13**), a formal dimer of HC_5H , displays electronic absorptions that are in qualitative agreement with the unassigned absorptions.⁵² Independent synthesis of four isomeric dimers (**13**–**15**) enabled us to obtain authentic spectra of each



of these compounds under matrix isolation conditions.⁵³ Although the spectrum of tetraethynylethene (**13**) ultimately did not exhibit quantitative agreement with the unassigned absorptions, the combined spectra of dimers **14** and *trans*-**15** exhibit remarkably good agreement (Figure 6). Thus, we conclude that dimers of carbene HC_5H are present in the matrix and are responsible for the vibronic transitions in the region 200–320 nm. With authentic samples of the dimers in hand, we obtained their IR spectra under matrix isolation conditions and compared these spectra against the experimental IR spectrum of triplet HC_5H . We were unable to detect any of the dimers in the spectrum of HC_5H , leading us to conclude that the dimers **14** and *trans*-**15** exist only as minor impurities in our matrix experiments; that the dimers appear to dominate the electronic absorption spectrum is simply a consequence of the relative difference in oscillator strengths between the dimers and triplet HC_5H .⁵⁴

Trapping Studies. Oxygen-trapping experiments provide chemical evidence in support of the spectroscopic assignments and provide insight into the electronic structure and reactivity of triplet HC_5H . The chemistry associated with O_2 trapping of triplet carbenes is well established, involving carbonyl oxide, dioxirane, ester, and ketone intermediates.^{55–57} In principle, the current system is further complicated by the possibility that

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(54) The mechanism of dimer formation in our experiments is not understood. Careful inspection of the UV/vis spectrum of matrix isolated diazo compound **6a** establishes that dimer is not present prior to irradiation. The dimer could arise in sites of poor matrix isolation, which may result from either an insufficient flow of matrix gas and/or the deposition of a small fraction of volatile, dimeric diazo compound **6a**. Dimer formation may also be enhanced if the mobility of linear HC_5H (**1**) in the matrix were to be unusually high.

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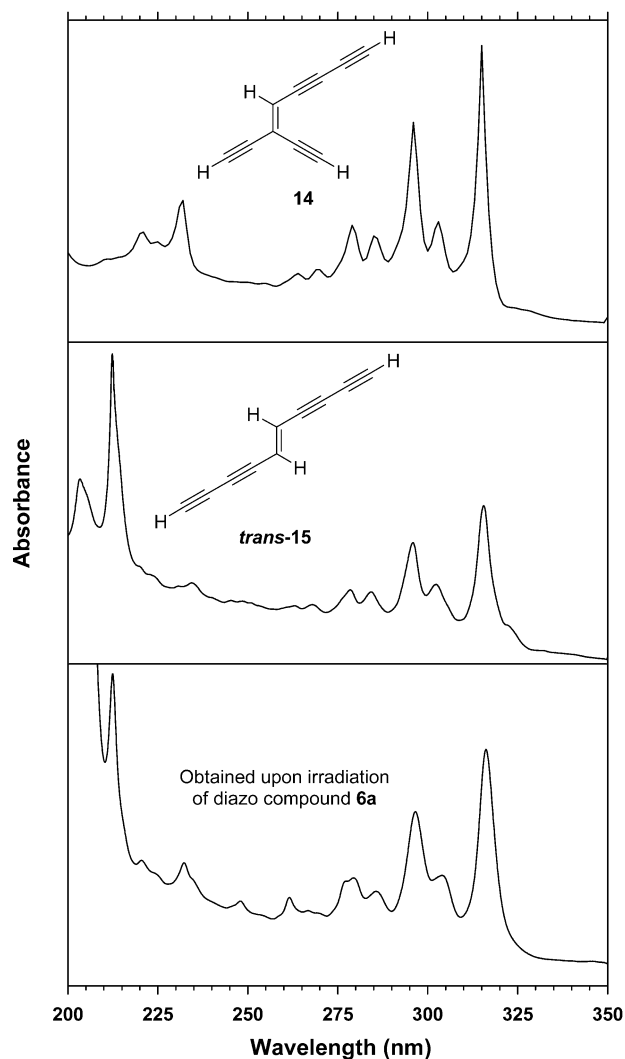
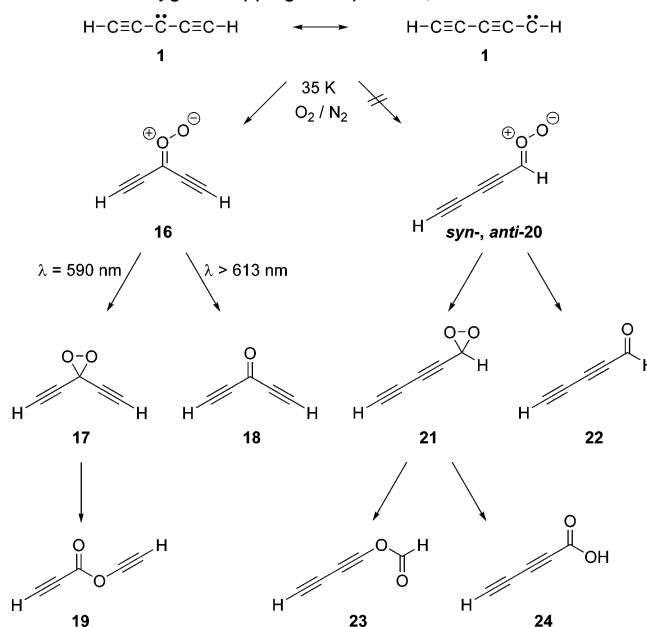


Figure 6. UV/visible spectra (N_2 , 10 K). Top: authentic spectrum of dimer **14**. Middle: authentic spectrum of dimer *trans*-**15**. Bottom: spectrum generated upon irradiation of 1-diazo-2,4-pentadiyne (**6a**) ($\lambda > 444$ nm, 1.7 h; $\lambda > 237$ nm, 22 h). This comparison implicates a mixture of **14** and *trans*-**15** as the species responsible for the absorptions in the 200–350 nm region of the spectrum.

regioisomeric products may arise from reaction of O_2 with HC_5H at either C1 or C3 (Scheme 5). Irradiation ($\lambda > 444$ nm) of diazo compound **6a** in an N_2 matrix doped with 0.4% O_2 afforded carbene **1**. Annealing the matrix at 35 K, followed by recooling to 10 K, led to the disappearance of the IR and UV/vis signals of triplet HC_5H (**1**) and the appearance of new spectroscopic features, with the matrix turning bright yellow. The IR spectrum of the trapping product (Figure 7) exhibits good agreement with the IR spectrum computed for carbonyl-*O*-oxide **16** and poor agreement with the IR spectra computed for the isomeric carbonyl-*O*-oxides *syn*-**20** and *anti*-**20**.³⁹ Thus, reaction of triplet HC_5H (**1**) with triplet O_2 occurs regioselectively at C3 to produce **16**. (This conclusion is further supported by the identity of the subsequent rearrangement products.) The UV/vis spectrum of the trapping product (Figure 8) exhibits an intense, broad absorption at 404 nm, characteristic of a carbonyl-*O*-oxide,^{55–57} which is responsible for the yellow color of the

Scheme 5. Oxygen Trapping of Triplet HC_5H



matrix. The annealing process also resulted in the slight growth of the UV absorptions of dimers **14** and *trans*-**15** (Figure 8). Long-wavelength irradiation of carbonyl-*O*-oxide **16** leads to the rapid bleaching of the IR and UV/vis absorptions of **16** and the appearance of two sets of IR absorptions, which are assigned to dioxirane **17** and ketone **18** on the basis of comparison with computed IR spectra (B3LYP/6-31G*³⁹). Both species are formed under all irradiation conditions employed, although the product ratio is wavelength dependent. At $\lambda > 613$ nm, ketone **18** is the major photolysis product; at $\lambda = 590$ nm, dioxirane **17** is the major photoproduct. Continued irradiation ($\lambda > 399$ nm) results in the disappearance of dioxirane **17** and the appearance of several new IR absorptions. Ester **19** is likely one of the photoproducts, but definitive assignment is precluded by the complexity of the resulting spectrum.

Electronic Structure of HC_5H . Coupled-cluster calculations (CCSD(T)/ANO) predict a triplet ground state ($^3\Sigma_g^-$) for HC_5H and a linear structure ($D_{\infty h}$) that exhibits bond alternation along the carbon chain. The computed C1–C2 bond length (1.237 Å) in HC_5H is slightly shorter, while the C2–C3 bond length

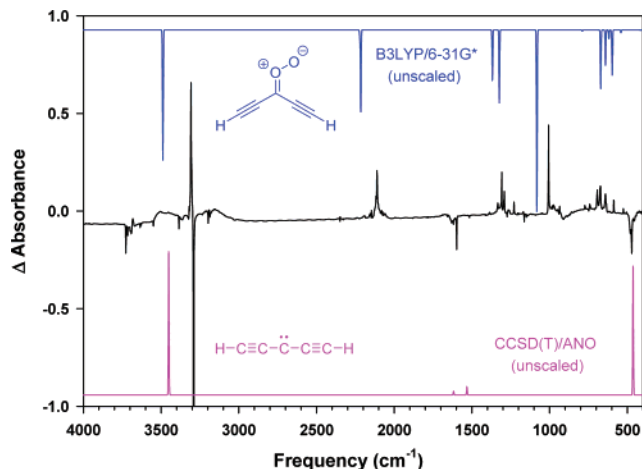


Figure 7. Infrared subtraction spectrum, along with computed spectra, showing the disappearance of triplet HC_5H (**1**) and the appearance of carbonyl-*O*-oxide **16** upon warming to 35 K in an O_2 -doped N_2 matrix.

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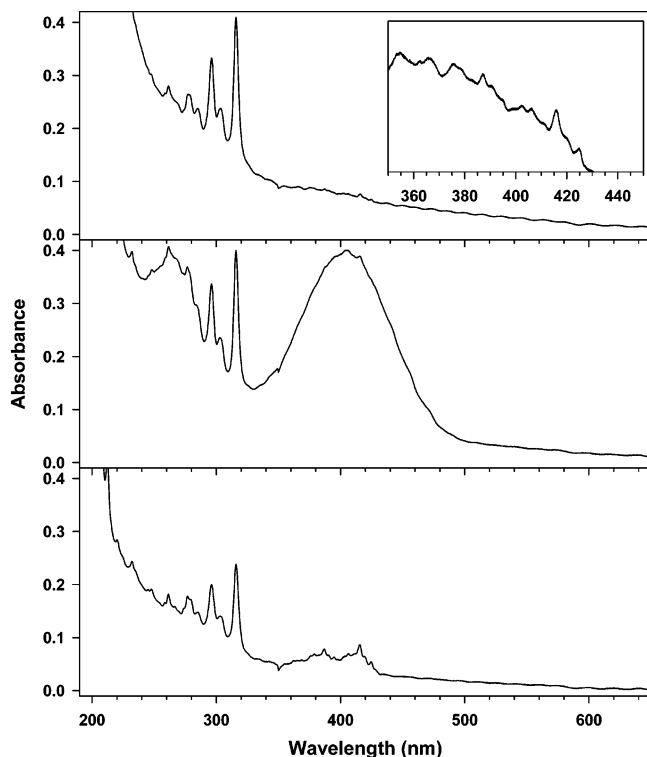


Figure 8. UV/visible spectra obtained upon irradiation of diazo compound **6a** in an O₂-doped matrix (N₂, 10 K). Bottom: irradiation ($\lambda > 444$ nm) to generate triplet HC₅H (**1**). Middle: formation of broad absorption of carbonyl-*O*-oxide **16**, along with growth of carbene dimers (280–320 nm), upon warming to 35 K and recooling to 10 K. Top: subsequent bleaching of carbonyl-*O*-oxide **16** absorption ($\lambda > 444$ nm).

Table 4. Computed Spin Densities for Triplet HC₅H (**1**)^a

atom	Fermi contact	Mulliken population
H	−0.015	−0.025
C1	0.027	0.781
C2	−0.097	−0.307
C3	0.042	1.102

^a CCSD(T)/cc-pVTZ.

(1.308 Å) is slightly longer, than the corresponding C–C bond length in triplet HC₃H (1.273 Å)—a structure with dominant cumulene character.¹⁷ Computed Fermi contact densities and Mulliken population analysis of spin densities reveal the greatest spin density at C3, although the combined spin densities at C1 and C5 exceed the spin density at C3 (Table 4). Experimental IR, UV/vis, and EPR spectra are consistent with this picture of triplet HC₅H, as is the regioselectivity observed in the chemical trapping reaction of HC₅H with O₂. In assessing the contribution of various resonance structures to the overall structure, the penta-1,4-diyne-3-ylidene structure (**A**) is the major resonance contributor (Figure 9). The degenerate penta-2,4-diyne-1-ylidene structures (**C** and **D**) are important in describing spin density at the terminal carbons, but they must contribute equally to the overall resonance hybrid and therefore cannot explain the bond alternation computed for the structure. (It is important to note that **C/D** is not computed to be a discrete minimum on the potential energy surface.¹⁸) Similarly, the penta-1,2,3,4-tetraene-1,5-diyl structure (**B**) describes spin density at the terminal carbons but does not satisfactorily describe bond alternation. Thus, in depicting triplet HC₅H with a single structural formula, we use the penta-1,4-diyne-3-ylidene structure (**A**). In the pioneering studies of Bernheim and Skell, monosubstituted

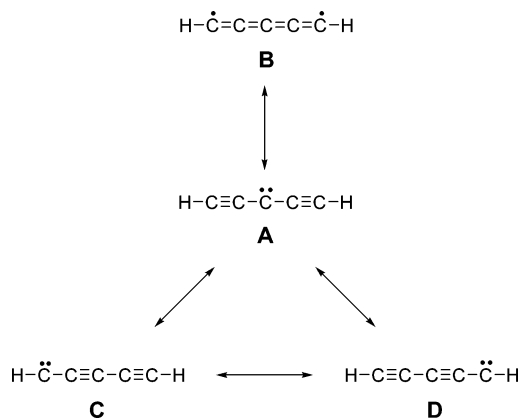
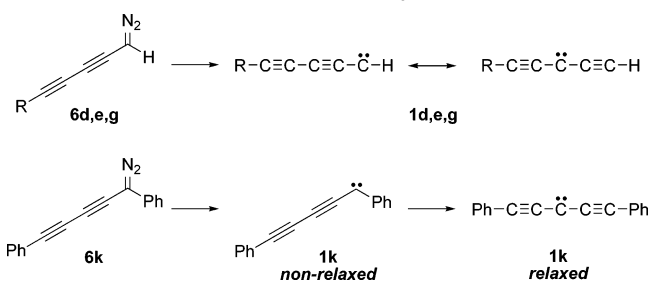


Figure 9. Experimental and computational results suggest that structure **A** is the major resonance contributor.

Scheme 6. Structures of Substituted HC₅H Carbenes



derivatives of HC₅H were depicted as penta-2,4-diyne-1-ylidene structures (Scheme 6)—a plausible interpretation, given the chemical structure of the 1-diazopenta-2,4-diyne precursors (**6**).^{24,25} Our findings for triplet HC₅H, however, suggest that these species are better depicted as substituted penta-1,4-diyne-3-ylidene structures (Scheme 6). In the diphenyl-substituted system, PhC₅Ph (**1k**), Iwamura and co-workers observed triplet EPR signals for two species: a nonrelaxed triplet, assigned as 1,5-diphenylpenta-2,4-diyne-1-ylidene and a relaxed triplet, assigned as the bond-shift isomer, 1,5-diphenylpenta-1,4-diyne-3-ylidene (Scheme 6).^{26,46} Our observations for triplet HC₅H do not provide evidence for a nonrelaxed penta-2,4-diyne-1-ylidene structure in the parent system, nor do our calculations support the idea that a bent structure with the same atomic connectivity is a minimum on the potential energy surface. The influence of the phenyl substituents is known to complicate the interpretation of triplet EPR spectra, even in cases where bond-shift isomerism is not possible.⁴⁵

Theory predicts alternating structural characteristics within the odd-membered series of carbon chains (HC_{4n+1}H vs HC_{4n+3}H).^{3,14} Carbon chains with the formula HC_{4n+1}H (HCH, HC₅H, HC₉H, ...) are best described as carbenes and exhibit the largest unpaired spin density at the center carbon. Carbon chains with the formula HC_{4n+3}H (HC₃H, HC₇H, HC₁₁H, ...) are best described as diradicals and exhibit the largest unpaired spin density at the carbons adjacent to the center carbon. The distinction between these two chain types, although implicit in Fan and Pfeiffer's depiction of the HOMOs of HC₂H through HC₁₀H (Figure 10)¹⁴ and later commented on by Schaefer,³ has not been subject to systematic experimental investigation. The results described herein provide experimental support for the prediction that HC_{4n+1}H systems are best represented as acetylenic carbenes with significant unpaired electron density

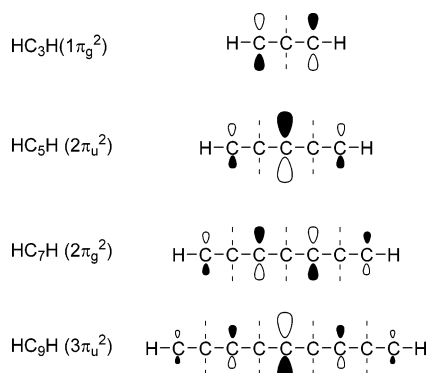


Figure 10. HOMOs for HC_3H , HC_5H , HC_7H , and HC_9H adapted from RHF predictions of Fan and Pfeiffer¹⁴ demonstrate the difference in electronic ground-state structures between HC_{4n+1}H and HC_{4n+3}H carbon chains.

at the central carbon. Our earlier studies of HC_3H support the prediction that HC_{4n+3}H systems are best represented as allenic diradicals.^{15,17}

Attempted Photorearrangement of Linear Triplet HC_5H . We hoped to access other C_5H_2 isomers via photochemical rearrangement of triplet HC_5H —a strategy that we employed successfully in our study of C_3H_2 isomers and many other systems. In particular, we considered the photoisomerization of triplet HC_5H (**1**) to singlet ethynylcyclopropenylidene (**2**) to be a likely possibility. This photo-rearrangement has precedent in the chemistry of C_3H_2 isomers. Moreover, ethynylcyclopropenylidene (**2**) is predicted to be only 2 kcal/mol higher in energy than HC_5H . Unfortunately, triplet HC_5H (**1**) is resistant to photoisomerization under all of the conditions employed. Neither disappearance of **1** nor appearance of new bands was observed upon irradiation, as monitored by IR spectroscopy.⁵⁸

Summary

Chemical synthesis of 1-diazo-2,4-pentadiyne (**6a**) enabled the generation and characterization of triplet HC_5H (**1**) under matrix isolation conditions. Experimental IR, UV/vis, and EPR spectra of the carbene are consistent with predictions of ab initio calculations. IR and EPR spectra reveal subtle deviations from axial symmetry, which almost certainly arise by virtue of matrix effects in the solid host. Coupled-cluster calculations and chemical trapping studies reflect a carbene structure with greatest spin density at the central carbon. The experimental investigation

of triplet HC_5H is significant in the context of (i) earlier experimental uncertainty concerning its electronic absorption spectrum and (ii) computational predictions of an alternating series of structures within the carbon chains HC_nH ($n = \text{odd}$). The current investigation provides experimental support for the prediction for the case $n = 5$. Developments in synthetic chemistry will enable the detailed study of other RC_5R and RC_7R carbon chain molecules.

Experimental Section

General. ^1H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.4 MHz) were obtained in CDCl_3 ; chemical shifts (δ) are reported as ppm downfield from internal SiMe_4 . The matrix isolation apparatus and technique have been described previously.^{39,59,60} Zero-field splitting parameters were determined by a best fit of the observed spectrum to the spin Hamiltonian (assuming $g_x = g_y = g_z$).⁶¹

Computational Methods. Density functional theory was used for geometry optimizations and vibrational frequency calculations of diazo, diazirine, and O_2 -trapped species. These calculations were performed using the three-parameter hybrid functional of Becke^{62,63} together with the correlation functional of Lee, Yang, and Parr⁶⁴ (B3LYP) using the 6-31G* basis set as implemented in the Gaussian 98 package.⁶⁵ Equilibrium geometries and harmonic vibrational frequencies for the open-shell carbenes (HC_5H and HC_5D) were obtained using coupled-cluster theory in the singles and doubles approximation,^{66–68} with a perturbative correction for the effects of triply excited determinants (CCSD(T)).^{69,70} The correlation-consistent cc-pVTZ basis set of Dunning⁷¹ or the atomic natural orbital (ANO) basis set of Almlöf and Taylor⁷² were used. (The latter basis was truncated to 4s3p2d1f on carbon and 4s2p1d on hydrogen.) Coupled-cluster calculations were performed with the Mainz–Austin version of the ACESII program system.⁷³

2,4-Pentadiynol (11**).** A literature procedure was followed.⁴⁰ Anhydrous ammonia (100 mL) was condensed into a dry round-bottom flask at -78°C . $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 g, 0.25 mmol) was added, forming a black suspension. Sodium metal (2.07 g, 90.0 mmol) was added in small pieces at -40°C . Once there were no unreacted sodium pieces remaining in the mixture, 1,4-dichloro-2-butyne (**10**) (3.0 mL, 30.7 mmol) was added dropwise via syringe. After the sides of the flask were rinsed with 20 mL of dry THF, a suspension of paraformaldehyde (0.902 g, 30.0 mmol) in 30 mL of dry THF was added via syringe. This mixture was stirred for 1.75 h at -40°C . NH_4Cl (4.5 g) was added to quench the basic mixture. After 15 min, the mixture was rinsed into a separate flask with diethyl ether. The mixture was allowed to warm to room temperature so that remaining NH_3 would evaporate. The mixture was then suction filtered. The precipitate was rinsed several

(58) The formation of a small amount of another C_5H_2 isomer during the photolysis of diazo compound **6a** remains a possibility. Upon initial generation of carbene **1** from diazo compound **6a** at $\lambda > 444$ nm, two broad signals appear in the 350–450 nm range overlapping the vibronic features of triplet HC_5H in this region (Figure 5). Close inspection of a similar IR experiment shows the presence of a trace amount of dioxirane under these conditions (presumably arising from a trace impurity of O_2 in the matrix) but little else. Thus, the species must have very strong electronic absorptions but weak infrared absorptions. Logical candidates for the unidentified species include (1) trapping products that may arise by reaction of triplet HC_5H with O_2 impurity in the matrix, (2) diazirine, which may arise by photoisomerization of diazo compound **6a**, or (3) a different C_5H_2 isomer, which may be formed during irradiation of diazo compound **6a** at $\lambda > 444$ nm. Oxygen trapping products, however, can be ruled out: carbonyl-*O*-oxide **16** is known to be photosensitive under the conditions used in the photolysis of diazo compound ($\lambda > 444$ nm), and other trapping/rearrangement products (dioxirane **17**, ketone **18**) do not absorb at 350–450 nm. The unassigned broad absorptions at 350–450 nm disappear on annealing an O_2 -doped matrix to 35 K, which would not be expected for the diazirine. The fact that the unknown species reacts with oxygen is consistent with the structure of a carbene or other reactive intermediate. Unfortunately, conditions could not be optimized to increase the production or reveal the identity of the carrier of the broad absorption at 350–450 nm.

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times with diethyl ether. The filtrate was concentrated under reduced pressure to remove remaining NH_3 . The remaining mixture was dried with anhydrous MgSO_4 , filtered, and concentrated to reveal a reddish-brown oil. This oil was purified via flash chromatography (5% EtOAc/ CH_2Cl_2) to afford 2,4-pentadiynol (**11**) (1.69 g, 21.1 mmol; 70% yield) as an amber oil. ^1H NMR δ 4.34 (dd, $J = 6.5, 0.9$ Hz, 2 H), 2.21 (t, $J = 0.9$ Hz, 1 H), 1.79 (t, $J = 6.3$ Hz, 1 H). MS (ESI, m/z) 81 (M + H), 63 (M - OH).

2,4-Pentadiynal Tosylhydrazone (7a). Dry CH_2Cl_2 (40 mL) was added to a flask containing 2,4-pentadiynol (**11**) (0.532 g, 6.64 mmol). To this stirring mixture was added Dess–Martin periodinane (3.72 g, 8.76 mmol). This mixture was stirred at room temperature for 1.5 h (until complete by TLC), at which point 50 mL of diethyl ether was added. This mixture was rinsed through a short silica gel column with diethyl ether into a flask containing *p*-toluenesulfonylhydrazide (1.24 g, 6.64 mmol). After being stirred at room temperature for 24 h, the contents were suction filtered to remove remaining insoluble Dess–Martin byproducts. The filtrate was washed with saturated aqueous NaHCO_3 to quench AcOH remaining from the oxidation. The aqueous layer was neutralized with NH_4Cl and extracted once with 30 mL of diethyl ether to recover any tosylhydrazone that may have been lost as the salt in the NaHCO_3 wash. The organic layers were combined, dried with MgSO_4 , filtered, and concentrated under reduced pressure to reveal an oily white solid. The product was purified via flash chromatography (5% EtOAc/ CH_2Cl_2) to reveal two separate white solids (1.52 g, 6.18 mmol, 93% yield over two steps). The assignment of *syn* vs *anti* is based on the observation that treatment of the *syn* isomer with D_2O /NaOH results in immediate cyclization to pyrazole, while treatment of the *anti* isomer affords H/D exchange (see below).

***syn*-2,4-Pentadiynal Tosylhydrazone (*syn*-7a).** (0.57 g) ^1H NMR δ 8.77 (s, 1 H), 7.84 (d, $J = 8.7$ Hz, 2 H), 7.34 (d, $J = 8.4$ Hz, 2 H), 6.62 (s, 1 H), 2.84 (s, 1 H), 2.44 (s, 3 H). ^{13}C NMR ($\text{Me}_2\text{SO}-d_6$) δ 144.0, 135.7, 129.7, 127.5, 124.6, 84.2, 81.3, 66.9, 65.0, 21.1. HRMS (ESI, m/z) $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{SNa}^+$ calcd 269.0361, found 269.0367.

***anti*-2,4-Pentadiynal Tosylhydrazone (*anti*-7a).** (0.95 g) ^1H NMR δ 8.23 (s, 1 H), 7.82 (d, $J = 9.9$ Hz, 2 H), 7.35 (d, $J = 8.1$ Hz, 2 H), 6.94 (s, 1 H), 2.56 (s, 1 H), 2.45 (s, 3 H). ^{13}C NMR ($\text{Me}_2\text{SO}-d_6$) δ 144.2, 135.8, 130.1, 128.3, 127.4, 78.6, 76.5, 70.2, 66.9, 21.2. EIMS (70 eV) m/z : M^+ 246 (45), 182 (85), 155 (55), 91 (100), 65 (70). HRMS (ESI, m/z) $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{SNa}^+$ calcd 269.0361, found 269.0356.

***anti*-2,4-Pentadiynal-5-*d* Tosylhydrazone (*anti*-7b).** *anti*-Tosylhydrazone ***anti*-7a** (303 mg, 1.23 mmol) was dissolved in 5 mL of dry CH_2Cl_2 . Deuterium oxide (5 mL) was added, creating a biphasic system. NaOH (0.01 g, 0.25 mmol) was added, and the mixture was stirred at room temperature for 24 h under nitrogen. The layers were separated. The aqueous layer was neutralized with NH_4Cl and extracted with CH_2Cl_2 . The organic layers were combined and washed once with 25 mL saturated aqueous NH_4Cl . After separation, the organic layer was dried with MgSO_4 , filtered, and concentrated to reveal the recovered tosylhydrazone as a white solid. The initial base-catalyzed exchange presumably produces the dideuterio isotopomer (N–D, C–D). Subsequent aqueous workup affords the monodeuterio isotopomer (N–H, C–D). Isotopic incorporation of ca. 60–80% was typical, as established by ^1H NMR spectroscopy. ^1H NMR δ 8.43 (s, 1 H), 7.82 (d, $J = 8.4$ Hz, 2 H), 7.35 (d, $J = 7.8$ Hz, 2 H), 6.95 (s, 1 H), 2.56 (s, 0.37 H; residual protio material) 2.45 (s, 3 H). MS (ESI, m/z) 270 ($\text{C}_{12}\text{H}_9\text{DN}_2\text{O}_2\text{SNa}^+$), 517 ($(\text{C}_{12}\text{H}_9\text{DN}_2\text{O}_2\text{S})_2\text{Na}^+$). EIMS (70 eV) m/z : M^+ 247 (8), 183 (30), 155 (25), 91 (100), 65 (25). Note: under identical reaction conditions, *syn*-tosylhydrazone **7a** yields only pyrazole, the product of intramolecular conjugate addition.

2,4-Pentadiynol-1,1-*d*₂ (11-d**₂).** The procedure described for the synthesis of the protio compound **11** was followed (on 2/3 scale), substituting paraformaldehyde-*d*₂ (CD_2O)_{*n*} for paraformaldehyde (CH_2O)_{*n*}. Purification via flash chromatography (5% EtOAc/ CH_2Cl_2) affords 2,4-pentadiynol-1,1-*d*₂ (**11-d**₂) (0.36 g, 4.4 mmol; 22% yield) as an amber oil. ^1H NMR δ 2.20 (s, 1 H), 1.90 (br s, 1 H).

2,4-Pentadiynal-1-*d* Tosylhydrazone (7c). The procedure described for the synthesis of the protio compound **7a** was followed (on 2/3 scale). The product was purified via flash chromatography (5% EtOAc/ CH_2Cl_2) to reveal two separate white solids (0.813 g, 3.29 mmol, 75% yield over two steps).

***syn*-2,4-Pentadiynal-1-*d* Tosylhydrazone (*syn*-7c).** (0.369 g) ^1H NMR δ 8.79 (s, 1 H), 7.83 (d, $J = 7.4$ Hz, 2 H), 7.34 (d, $J = 7.4$ Hz, 2 H), 2.84 (s, 1 H), 2.44 (s, 3 H). HRMS (ESI, m/z) $\text{C}_{12}\text{H}_9\text{DN}_2\text{O}_2\text{SNa}^+$ calcd 270.0423, found 270.0423.

***anti*-2,4-Pentadiynal-1-*d* Tosylhydrazone (*anti*-7c).** (0.444 g) ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 12.32 (s, 1 H), 7.68 (d, $J = 7.4$ Hz, 2 H), 7.43 (d, $J = 7.1$ Hz, 2 H), 4.24 (s, 1 H), 2.39 (s, 3 H). MS (ESI, m/z) 270 ($\text{C}_{12}\text{H}_9\text{DN}_2\text{O}_2\text{SNa}^+$), 517 ($(\text{C}_{12}\text{H}_9\text{DN}_2\text{O}_2\text{S})_2\text{Na}^+$).

1-Diazo-2,4-pentadiyne (6a). *anti*-Tosylhydrazone ***anti*-7a** (0.075 g, 0.30 mmol) was dissolved in CH_2Cl_2 (5 mL). NaH (11.5 mg, 0.30 mmol), as a 60% dispersion in mineral oil, was added. The reaction stirred for 1 h at room temperature. The flask was cooled to -40 °C, and the solvent was removed under vacuum (0.2 mmHg). Once the solvent was removed, the flask was warmed to room temperature and left under vacuum for an additional 30 min. The remaining solid was briefly heated to 35 °C then placed in a preheated (70 °C) oil bath. A liquid N_2 cooled trap was used to collect the resulting yellow solid during sublimation. After 1 h of sublimation, the trap was closed and was transferred to the matrix isolation apparatus.

Extinction coefficients were determined by preparing a stock solution of diazo compound in a known volume of CD_3OD containing a known concentration of CH_3CN as an internal standard. The concentration of diazo compound was determined, relative to CH_3CN , by ^1H NMR integration. Subsequent dilution with CH_3OH afforded solutions with absorbance values of 1–2. The extinction coefficients represent lower limits, as the diazo compound decomposes slowly during the measurement procedure. ^1H NMR (CD_3OD) δ 3.40 (s, 1 H); the other resonance undergoes exchange in CD_3OD . UV/vis (CH_3OH): λ_{max} (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 442 (65), 302 (13,969), 288 (19,843), 277 (16,841), 221 (33,947) nm. IR (N_2 , 10 K; relative intensity): 3320 (17), 3312 (9), 2188 (8), 2085 (100), 2065 (37), 1374 (8), 581 (3), 496 (3), 489 (2) cm^{-1} . UV/vis (N_2 , 10 K): λ_{max} 305.4, 300.7, 288.9, 285.1, 274.6, 271.6, 261.6, 248.3 nm.

1-Diazo-2,4-pentadiyne-5-*d* (6b). IR (N_2 , 10 K; relative intensity): 3321 (17), 3312 (9), 2587 (12), 2583 (11), 2185 (11), 2087 (100), 2064 (26), 1373 (9), 496 (6), 489 (5) cm^{-1} .

1-Diazo-2,4-pentadiyne-1-*d* (6c). IR (N_2 , 10 K; relative intensity): 3320 (11), 3311 (7), 2218 (2), 2214 (2), 2174 (5), 2094 (22), 2088 (100), 2065 (9), 2058 (7), 2055 (7), 2034 (2), 1337 (5), 652 (3), 648 (2), 605 (2), 594 (2), 581(3) cm^{-1} .

Acknowledgment. The Wisconsin group gratefully acknowledges the National Science Foundation for financial support of this project (CHE-0412707 and CHE-0110769), the Departmental parallel computing center (CHE-0091916), and the electron paramagnetic resonance spectrometer (CHE-9013030). The Texas group was supported by the National Science and Welch Foundations.

Supporting Information Available: Details concerning experimental techniques; experimental procedure for the initial synthesis of 1-diazo-2,4-pentadiyne (**6a**) (Scheme 3); infrared

spectra of HC₅D (**1-d₁**) in N₂, oxygen trapping experiments, and HC₅H (**1**) in Ar; EPR spectra of HC₅H (**1**) in MCH glass establishing triplet ground state; UV/vis spectra of 1-diazo-2,4-pentadiyne (**6a**) in MeOH, HC₅H (**1**) in Ar; computed energies, harmonic vibrational frequencies, infrared intensities, and

Cartesian coordinates for all computed structures; complete citation for ref 65. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA058252T