Pentadiynylidene and its Methyl-Substituted Derivates: Threshold Photoelectron Spectroscopy of $R_1-C_5-R_2$ Triplet Carbon Chains

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ABSTRACT

Mass-selective threshold photoelectron spectroscopy in the gas phase was employed to characterize the dialkynyl triplet carbenes pentadiynylidene (HC_5H), methylpentadiynylidene (MeC_5H) and dimethylpentadiynylidene (MeC_5Me). Diazo compounds were employed as precursors to generate the carbenes by flash pyrolysis. The $\text{R}_1\text{-C}_5\text{-R}_2$ carbon chains were photoionized by vacuum ultraviolet (VUV) synchrotron radiation in photoelectron photoion coincidence (PEPICO) experiments. High-level *ab initio* computations were carried out to support the interpretation of the experiments. For the unsubstituted pentadiynylidene ($\text{R}_1 = \text{R}_2 = \text{H}$) the recorded spectrum yields an adiabatic ionization energy (IE_{ad}) of 8.36 ± 0.03 eV. In addition, a second carbene isomer, 3-(didehydrovinylidene)cyclopropane, with a singlet electronic ground state, was identified in the spectrum based on the IE_{ad} of 8.60 ± 0.03 eV and Franck Condon simulations. We found that multireference computations are required to reliably calculate the IE_{ad} for this molecule. CASPT2 computations predicted an $\text{IE}_{\text{ad}} = 8.55$ eV, while coupled-cluster computations significantly overestimate the IE. The cyclic isomer is most likely formed from another isomer of the precursor present in the sample. Stepwise methyl-substitution of the carbene leads to a reduction of the IE to 7.77 ± 0.04 eV for methylpentadiynylidene and 7.27 ± 0.06 eV for dimethylpentadiynylidene. The photoionization and dissociative photoionization of the precursors is investigated as well.

INTRODUCTION

In this paper we report threshold photoelectron spectra of the triplet carbene pentadiynylidene, HC_5H and its methyl-substituted derivatives, $\text{R}_1\text{-C}_5\text{-R}_2$, as depicted in Figure 1 (**1**, **2** and **3**). While chains with even n like acetylene, di- and triacetylene are stable closed-shell molecules, odd n carbon chains are highly reactive biradicals or triplet carbenes in the electronic ground state of the neutral. Nevertheless, they occur as intermediates under extreme conditions, for example in combustion processes, the interstellar medium or in planetary atmospheres. In space they are hard to detect by radioastronomy due to their small (HC_3H) or absent (HC_5H) permanent dipole moment,¹⁻⁴ however they have been suggested to be involved in the atmospheric chemistry of Titan, the largest moon of Saturn.⁵ In combustion, especially in acetylene containing fuels^{6,7} odd n carbon chains like propargylene ($n=3$) or pentadiynylidene ($n=5$) dimerize efficiently and are thus possible intermediates towards the formation of polycyclic aromatic hydrocarbons (PAHs), soot or fullerenes.⁸

Recently, we investigated propargylene ($n=3$) in the gas phase, reported a threshold photoelectron spectrum,⁹ and studied the photodissociation dynamics by velocity map imaging and by surface hopping computations.¹⁰ In contrast, $n=5$ carbon chains have so far been investigated predominately in low temperature matrices. Infrared, UV/Vis and EPR spectra in Ar or N_2 matrix are available for **1**, **2** and in part for **3**.¹¹⁻¹³ While propargylene favors a slightly bent geometry with C_2 symmetry,¹⁴ a linear geometry with $D_{\infty h}$ symmetry was found for **1**^{15,16} as confirmed by coupled cluster calculations.¹⁷ In a valence bond picture, pentadiynylidene can be described by two resonance structures (see Figure 1), one corresponding to a 1,5-biradical, a second, dominating one to a diethynylcarbene. Computations indicated that the corresponding triplet state is lower in

energy than the singlets. A third structure with the carbene center on a single terminal carbon atom does not contribute significantly.^{14,17} For the methyl-substituted compound **2** the dominant carbene character has also been confirmed.¹² Further interest in **2** and **3** is due to the increased stability compared to **1** and the additional photochemistry observed.¹²

Fig. 1. Pentadiynylidene **1**, methylpentadiynylidene **2** and dimethylpentadiynylidene **3** were generated by flash pyrolysis from 1-diazo-penta-2,4-diyne **4**, 1-diazo-hexa-2,4-diyne **5** and 2-diazo-hepta-3,5-diyne **6**.

Several C₅H₂ isomers exist and it has been computed that all but pentadiynylidene possess a singlet ground state.¹⁷⁻²⁰ A number of them have been investigated by Fourier transform microwave spectroscopy,²¹⁻²³ but electronic transitions have only been investigated computationally. For pentadiynylidene a weak band at around 400-500 nm was computed to correspond to the A ³Σ_u → X ³Σ_g⁻ transition.^{24,25} In contrast, for the cation HC₅H⁺, **1**⁺ and the cation of the isomer pentatetraenylidene electronic absorption spectra were recorded.²⁶ However, the ionization energy (IE) of **1** has not yet been determined.

Here, we employ photoelectron spectroscopy to explore the photoionization of **1**, **2** and **3**, using threshold photoelectron-photoion coincidence techniques (TPEPICO).²⁷ This method permits to record photoion mass-selected threshold photoelectron spectra (ms-TPES) for each molecule present in a reaction mixture by correlating ions and electrons, thus contributions from the

precursor or possible side products with different molecular mass can be excluded, in contrast to conventional photoelectron spectroscopy. Spectra of numerous reactive intermediates have been recorded by TPEPICO, including reactive species like allyl,²⁸ propargyl,²⁹ benzyl,³⁰ fulvenallenyl³¹, *c*-C₃H₂³² CH_x,³³⁻³⁵ CF₃,³⁶ C₃H³⁷ and HBBH.³⁸ The method also permits to distinguish different isomers as shown for example for picolyl,³⁹ xylyl^{40,41} and xylylenes.⁴² Since TPEPICO recently evolved into a versatile chemical analysis tool to probe elusive intermediates in reactive environments such as model flames,⁴³⁻⁴⁵ catalytic reactors^{46,47} or in kinetics experiments^{48,49} clean and isomer-specific spectroscopic data of radicals and carbenes are much-needed.

METHODS

The experiments were carried out at the x04db beamline of the Swiss Light Source (SLS) storage ring in Villigen, Switzerland. The CRF-PEPICO instrument has been described in detail elsewhere, thus only a brief overview on the setup⁵⁰ and the beamline⁵¹ is given here. The molecules were ionized by vacuum ultraviolet (VUV) synchrotron radiation provided by a bending magnet and collimated onto a 150 lines mm⁻¹ plane grating monochromator. The photon energy resolution of $E/\Delta E$ is about $1.5 \cdot 10^3$ and higher order radiation was absorbed by a MgF₂ window. The energy was calibrated using the 11s'-13s' argon autoionization resonances in first and second order. All spectra are corrected for photon flux.

The PEPICO endstation contains velocity map imaging (VMI) spectrometers for both photoelectrons and photoions.⁵¹⁻⁵³ Cations and electrons were extracted vertically in opposite directions, accelerated by electric fields, which are designed to allow for simultaneous Wiley-McLaren space focusing as well as velocity map imaging conditions. The charged particles are detected by position sensitive delay-line anode (Roentdek DLD40) detectors. Cations and

electrons were correlated employing a multiple start/multiple stop data acquisition scheme and thus analyzed in coincidence.⁵⁴ Threshold photoelectrons were selected with a resolution of 5-10 meV and the contribution of hot electrons was subtracted as described in the literature.⁵⁵ Averaging times were between 60 and 150 s per data point.

As indicated in Fig. 1, pentadiynylidene **1**, methylpentadiynylidene **2** and dimethylpentadiynylidene **3** were generated by flash pyrolysis of diazo precursors (1-diazo-penta-2,4-diyne **4**, 1-diazo-hexa-2,4-diyne **5** and 2-diazo-hepta-3,5-diyne **6**).⁵⁶ These precursors were synthesized following a procedure similar to the one described in the literature.^{11,57} Since **4**, **5** and **6** are unstable under ambient conditions, we employed the sodium salts of the corresponding tosylhydrazones and synthesized the diazo compounds *in situ*. The sodium salts were heated to 60-70 °C in an in-vacuum sample container to produce the diazo compounds directly in the gas phase. For part of the discussion below it is important to point out that due to this approach we could not determine the purity of the diazo compound. Subsequently the vapors were picked up by Ar carrier gas and expanded through a 100 μ m nozzle directly into the pyrolysis reactor, an electrically heated silicon carbide (SiC) tube of 1 mm inner diameter.⁵⁶ Here the diazo compounds were pyrolyzed to the carbenes **1**, **2** and **3**. The resulting jet was skimmed and directed towards the ionization volume of the CRF-PEPICO endstation.

DFT (ω B97xD,⁵⁸ M05-2X(D3),^{59,60} M06-2X⁶¹), CBS-QB3⁶² and Coupled Cluster (CCSD) calculations were performed using the Gaussian 16 program package.⁶³ The single-reference methods were used in their unrestricted variant in all cases. CASPT2 evaluations^{64,65} used MOLCAS 7.8⁶⁶ with the active space being iteratively built from pseudo-natural orbitals of smaller spaces, starting at (2,2). All reported stationary geometries were evaluated to be true minima of

the potential energy surface by computation of the molecular Hessian using the respective method, except for the numerical CASPT2(10,10) optimization of compound **9**⁺ (see below for definition). Values of the T_1 diagnostic are obtained from converged CCSD amplitudes.⁶⁷

The TPE spectra of the precursors were modeled by Franck-Condon simulations at 0 K with the program FCfit version 2.8.20, while ms-TPE spectra of the carbenes **1**, **2** and **3** were simulated at 600 K using the program ezSpectrum, which takes hot and sequence band transitions into account.^{68,69}

RESULTS AND DISCUSSION

Fig. 2. From top to bottom: Mass spectra of 1-diazo-penta-2,4-diyne **4**, 1-diazo-hexa-2,4-diyne **5** and 2-diazo-hepta-3,5-diyne **6** without pyrolysis (left-hand column) and with pyrolysis (right-hand

column). Efficient conversion to the carbenes is visible upon pyrolysis. Note that for each compound a photon energy only slightly above the IE of the precursor was employed.

a. Mass spectra. Figure 2 shows selected mass spectra with and without pyrolysis. Without pyrolysis (left-hand column) the precursor signals of **4**, **5** and **6** dominate the spectrum. In addition, a small peak originating from dissociative photoionization (N_2 loss) is observed in all three spectra. The mass spectra recorded with pyrolysis turned on (right-hand column) show a complete conversion of the precursor even at low pyrolysis power and generation of the carbenes **1** ($m/z=62$, top right), **2** ($m/z=76$, center right) and **3** ($m/z=90$, bottom right). For 1-diazo-penta-2,4-diyne **4** (top row) further peaks appear at $m/z = 57$ and $m/z = 104$, identified as styrene by ms-TPES. Both originate from previous experiments, are independent of the pyrolysis temperature and will thus not be discussed further. Signals at $m/z = 63$ and $m/z=124$ are due to C_5H_3 (H-addition to the carbene) and the dimerization product of **1**, $C_{10}H_4$. A ms-TPE spectrum of the dimer, identified as tetraethynylethene ($C_{10}H_4$) is presented in the SI. While efficient dimerization of **1** has been observed before,^{11,70} signals for the dimers of **2** and **3** are small. Stabilization of the carbene by the CH_3 group and/or steric effects might be responsible. In the pyrolysis of **6** a small peak appears at $m/z = 91$. It originates from the ^{13}C isotope of $m/z = 90$ as evident from the relative peak intensities in the mass spectrum and not from a H-atom addition product.

b. Photoionization of precursors 4, 5 and 6. In the next step photoionization and dissociative photoionization of the precursors **4**, **5** and **6** were investigated without pyrolysis. As the loss of N_2 in the cation was computed to be associated with a reverse barrier, no binding energies could be derived. Therefore, the breakdown diagrams are only discussed in the SI.

Fig. 3. TPE spectrum of 1-diazo-penta-2,4-diyne **4** and corresponding Franck-Condon simulation for the precursor (blue line: stick spectrum convoluted with a Gaussian of 20 meV fwhm) shows a reasonable agreement. The ionization energy of **4** is determined to be 8.15 ± 0.01 eV.

The threshold photoelectron spectrum of **4** (black line with open circles) is depicted in Figure 3. Based on *ab initio* calculations of the neutral **4** and the cation **4**⁺, a Franck-Condon simulation (blue line) was carried out. Hot and sequence band transitions were ignored, nevertheless the simulation shows a good agreement with the experiment. While the band positions are well represented, there are some deviations in the band intensities. The first major band at $8.15 \text{ eV} \pm 0.01 \text{ eV}$ is assigned to the adiabatic ionization energy IE_{ad} and is in excellent agreement with the computed value at 8.14 eV. The error is derived from the full width at half maximum (fwhm) of the band. Further peaks are found at 8.27 eV (+970 cm^{-1}) and 8.41 eV (+2100 cm^{-1}). The first one corresponds to the fundamental of the C-N stretching mode with a computed value of 1001 cm^{-1} . The second band (computed value 2172 cm^{-1}) is a combination of the C-C and the N-N stretching motions. At 8.35 eV the H-C-N bending vibration (1437 cm^{-1}) also contributes to the TPE

spectrum. This is in line with the most pronounced change in geometry upon ionization affecting the length of the C-N bond, R_{C-N} and the C-C bond, R_{C-C} next to the diazo (N_2) group. While R_{C-C} decreases from 1.40 Å to 1.35 Å, R_{C-N} increases from 1.32 Å to 1.36 Å. All other geometry parameters change only slightly and in particular R_{N-N} and $R_{C\equiv C}$ remain almost constant. All geometry parameters are summarized in the Supporting Information. Note that the intensity of the band at + 970 cm^{-1} (around 8.25 eV) is significantly underestimated by the simulation. Contributions of another isomer may be a plausible explanation for this observation. Indeed, an isomer of **4** with the N_2 at the central carbon atom possesses a computed IE_{ad} of 8.20 eV (CBS-QB3). Interestingly, when the pyrolysis was turned on, the spectrum shown in Figure 3 disappeared and a second band appeared around 8.7 eV, see Figure S2. Obviously an isomer of $C_5H_2N_2$ is formed at elevated temperature, most likely from the tosyl hydrazone salt employed as the sample. This will be further discussed below.

Fig. 4. TPE spectrum of 1-diazo-hexa-2,4-diyne **5**. An IE_{ad} of 7.86 ± 0.02 eV can be extracted from the first major peak. For comparison, the Franck-Condon simulation (blue line: stick spectrum convoluted with a Gaussian of 25 meV fwhm) is given.

The threshold photoelectron spectrum of **5** is shown in Fig. 4. The Franck-Condon simulation (blue line) agrees again well with the experimental data and the simulated intensities match the experimental ones. However, the spectrum is broadened due to the torsion of the methyl group, which is not properly represented in the simulation that is based on the harmonic approximation. It is included in the simulations by simply using a Gaussian with a larger fwhm of 25 meV. Again, the first major band at 7.86 ± 0.02 eV represents the IE_{ad} in agreement with the computed value of 7.81 eV. Two features are visible in the experimental TPES at 7.95 eV and 8.10 eV, which correspond to a excitation of the C-N stretching mode (897 cm^{-1}) and a combination of CC and NN stretching vibrations (2153 cm^{-1}), similar to what was found for **4**. Further combination bands with the methyl torsional mode occur (106 cm^{-1}), which lead to an additional broadening of the

experimental features. Similar to **4** we also find changes in R_{C-C} and R_{C-N} upon ionization. The latter increases from 1.32 Å to 1.37 Å, while the former decreases from 1.40 Å to 1.36 Å. In addition, the C-C bond to the methyl group decreases from 1.52 Å to 1.50 Å, while the remaining bond lengths differs only slightly, see SI for details. Note that the simulations performed for **5** do not differ from the experiment as found for **4** for the band at + 970 cm^{-1}

Fig. 5. TPE spectrum of 2-diazo-hepta-3,5-diyne **6**. An IE_{ad} of 7.53 ± 0.03 eV can be extracted from the first peak. For comparison, the Franck-Condon simulation (blue line: stick spectrum convoluted with a Gaussian of 35 meV fwhm) is given.

Figure 5 depicts the TPE spectrum of **6** (black line) and the corresponding Franck-Condon simulation (blue line). From the Franck-Condon (FC) fit a reasonable agreement with the experimental data is visible. An IE_{ad} at 7.53 ± 0.03 eV is derived from the first major peak in the experiment, agreeing again well with the value of 7.48 eV, calculated on the CBS-QB3 level of theory. Beside the first major band, two broad features around 7.65 eV and 7.79 eV are visible in

the experimental spectrum and are accounted for by the simulation. Those bands can again be assigned to a C-N stretching (1135 cm^{-1}) mode and to a combination of CC and NN stretching vibrations at 2123 cm^{-1} . A low frequency methyl torsion (39 cm^{-1}) is responsible for the peak broadening. In **6** we find again that $R_{\text{C-N}}$ increases from $1.31\text{ \AA}$ to $1.37\text{ \AA}$ and $R_{\text{C=C}}$ decreases from $1.40\text{ \AA}$ to $1.36\text{ \AA}$ upon ionization, almost identical to compounds **4** and **5**, confirming the small influence of the methyl group on the structure of the carbon chain. As visible in the mass spectra in Fig. 2 dissociative photoionization sets already in at around 7.5 eV , therefore all electrons were collected.

c. Photoionization of the carbenes 1, 2 and 3. After the photoionization and the dissociative photoionization of the precursors **4**, **5** and **6** have been investigated, the pyrolysis was turned on to study the three carbenes pentadiynylidene **1**, methylpentadiynylidene **2** and dimethylpentadiynylidene **3**.

Fig. 6. Ms-TPE spectrum of $m/z = 62$ (black line with open circles). A Franck-Condon simulation including pentadiynylidene **1** (blue line) and 3-(didehydrovinylidene)cyclopropane **9** (red line)

agrees well with the experimental spectrum. From the two major peaks IE_{ad} of 8.36 ± 0.03 eV for **1** and 8.60 ± 0.03 eV for **9** can be extracted.

Figure 6 depicts the ms-TPE spectrum of $m/z = 62$ recorded upon pyrolysis of **4**. Due to the low signal/noise ratio, 5-point smoothing was employed. Two intense bands are observed at 8.36 eV and 8.60 eV, in addition, several smaller bands are identified at 8.53 eV, 8.75 eV, 8.87 eV and 9.10 eV.

CBS-QB3 computations predict an ionization energy of 8.41 eV for **1**, in excellent agreement with the band at 8.36 eV. However, the FC-simulation (blue line) shows little vibrational activity in the ion, as expected for ionization from a non-bonding *p*-type orbital. Only the CC stretching vibration at 783 cm^{-1} along with some hot- and sequence band transitions contribute to the band, which is well reproduced by a vibrational temperature of 600 K. Thus, the second band at 8.60 eV cannot be reasonably assigned to ionization from the triplet ground state (T_0) of pentadiynylidene **1**. For the S_1 state of **1** on the other hand an IE of 7.70 eV was computed, in strong disagreement with any of the major bands in the spectrum. A possible source for this band is dissociative photoionization of the precursor. We rule this explanation out for two reasons: First, the precursor was completely converted in the pyrolysis and second, the kinetic energy distribution of the ions in the images with pyrolysis on shows that the band originates from a species in the molecular beam and not from a fragment ions. The ion images with pyrolysis on and off are depicted in Figure S7. Interestingly the band at 8.60 eV becomes smaller, when the temperature of the sample container is lowered at a constant pyrolysis temperature. Since the band cannot be due to dissociative ionization, we computationally investigated the other C_5H_2 isomers depicted in Figure 7 as potential carriers of the band at 8.60 eV. Initial CBS-QB3 computations did not yield satisfactory agreement for any of the isomers. To validate the IE's predicted by these

computations, we systematically investigated them on a using a variety of computational methods, ranging from density functional theory (DFT) up to CASPT2(14,14). The results are summarized in Tables 1 and 2. While Table 1 shows the relative energies of the neutral isomers, Table 2 compares the adiabatic IE's. For most isomers the deviation from the CBS-QB3 results is small, as expected due to the accuracy of the approach.

Fig. 7. The five C_5H_2 isomers: Penatadiynylidene **1**, ethynylcyclopropenylidene **7**, pentatetraenylidene **8**, 3-(didehydrovinylidene)cyclopropane **9**, and ethynylpropadienylidene **10**.

Tab. 1. Relative energies E_{rel} of the C_5H_2 isomers in their lowest singlet and triplet states using a variety of quantum-chemical approaches. The energy of the thermodynamically most stable isomer **1** in its T_0 ground state is set to zero. Relative energies are given in eV.

Molecule	u ω B97xD /6- 311++G(d ,p)	uM05- 2X(D3)/6- 311++G(d,p)	uM06-2X/6- 311++G(d,p)	uCCSD/c c-pVTZ	uCCSD(T)/cc- pVTZ//uCCSD/cc -pVTZ	CASPT2(14,14)/cc- pVTZ//u ω B97xD/6 -311++G(d,p)
1 E_{rel} (S_1)	0.41	0.50	0.55	1.07	0.87	0.70

1 E_{rel} (T₀)	0.0	0.0	0.0	0.0	0.0	0.0
7 E_{rel} (S₀)	0.04	0.01	-0.16	-0.08	-0.15	0.01
7 E_{rel} (T₁)	2.02	2.05	1.93	2.16	2.06	2.03
8 E_{rel} (S₀)	0.72	0.73	0.67	0.65	0.40	0.72
8 E_{rel} (T₁)	1.50	1.56	1.57	1.57	1.51	1.84
9 E_{rel} (S₀)	0.78	0.74	0.63	0.80	0.67	0.78
9 E_{rel} (T₁)	3.09	3.13	3.04	--- ^[a]	--- ^[a]	3.15
10 E_{rel} (S₀)	0.81	0.82	0.75	0.62	0.47	0.67
10 E_{rel} (T₁)	1.93	2.49	1.25	1.68	1.72	1.76

[a]: Geometry optimization does not converge.

Tab. 2. Ionization energies (IEs) of the C₅H₂ isomers in their singlet (S) and triplet (T) ground state using a variety of quantum-chemical approaches. Zero-Point Vibrational energy corrections are included. Energy differences are given in eV.

Molecule	u ω B97x D/6- 311++G(d,p)	uM05- 2X(D3)/6- 311++G(d,p)	uM06-2X/6- 311++G(d,p)	uCCSD/cc- pVTZ	uCCSD(T)/cc- pVTZ//uCCSD/cc- pVTZ	CASPT2(14,14)/cc- pVTZ//u ω B97xD/6- 311++G(d,p)	CBS/QB3
1 IE(S₁)	8.07	8.16	8.04	7.36	7.36 ^[b]	7.55	7.70
1 IE(T₀)	8.43	8.68	8.60	8.30	8.26 ^[b]	8.20	8.41

7 IE(S₀)	8.82	8.93	8.92	8.78	8.77 ^[b]	8.70	8.90
7 IE(T₁)	6.96	7.01	6.94	6.65 ^[a]	6.68 ^[b]	6.82	6.95
8 IE(S₀)	9.57	9.32	9.32	9.25	9.40 ^[b]	9.10	9.44
8 IE(T₁)	8.49	8.56	8.49	8.40	8.36 ^[b]	8.06	8.47
9 IE(S₀)	8.85	9.02	8.80	9.82	9.96 ^[b]	8.55	8.80
9 IE(T₁)	6.64	6.73	6.49	--- ^[a]	--- ^[a]	6.28	7.08
10 IE(S₀)	9.74	9.94	9.68	9.71	8.92 ^[b]	9.62	9.84
10 IE(T₁)	8.64	8.30	9.20	8.67	8.61 ^[b]	8.55	8.71

[a]: Geometry optimization does not converge.

[b]: ZPE contribution from u ω B97xD/6-311++G(d,p).

The only isomers with a predicted ionization energy in the range of the second band at 8.60 eV are **7** and **9**. As the S₀ ground-state of **7** is almost isoenergetic with the T₀ of **1**, it might be formed in the pyrolysis and was therefore investigated first. Although the predicted IE's do not vary much with the computational method and are not too far off the experimental peak, all methods consistently predict an IE that is at least hundred meV higher than the measured IE of 8.60 eV. Franck-Condon (FC) simulations of the TPE-spectrum of **7** are given in the SI. They qualitatively agree for all methods, but show a pronounced vibrational progression and are thus in disagreement with the experimental data. In fact they strongly resemble the spectrum obtained for c-C₃H₂,³² because in both cases ionization occurs at the carbene center. We therefore conclude that the second band of m/z=62 in Figure 6 does not originate from the ionization of isomer **7**.

We now focus on isomer **9**: Interestingly, for the singlet ground-state of **9** the various computational approaches predict vastly different ionization energies (see Tab. 2). They result from small variations in the predicted equilibrium geometry of **9**⁺ and problems in the convergence of the geometry optimization due to a very flat potential energy surface (see SI Table S9). For a CCSD(T) calculation of the cation with the geometry being obtained at the ω B97xD level of theory, the $\mathcal{T}_1$ diagnostic, which is a measure for the multi-reference character of a wavefunction,⁶⁷ has a value of 0.16. This indicates that a single-reference method is unable to predict the equilibrium geometry correctly.⁷¹⁻⁷³ Further informations are given in the SI. Therefore, we optimized the geometry of **9**⁺ by CASPT2(10,10)/cc-pVDZ. Tab. S7 in the SI compares the single-reference approaches to the CASPT2 geometry and shows that density functional methods are able to reproduce the CASPT2 geometry, while CCSD fails to predict a correct geometry for **9**⁺. Using the ω B97xD optimized geometry for the cation, the ionization energy of **9** from the singlet ground state is predicted to be 8.55 eV at the CASPT2(14,14)/cc-pVTZ level of theory (including ZPE-corrections taken from ω B97xD Hessians). Using the CASPT2(10,10) optimized geometry an IE of 8.58 eV is obtained. This is in excellent agreement with the second band in the spectrum at 8.60 eV. Furthermore, FC-simulations including transitions from the T_0 of **1** and the S_0 of **9** (red line in Figure 6) show very good agreement with the experimental spectrum. Vibrational transitions are assigned to a progression of the CC stretch between the three-membered ring and the adjacent carbon chain (2260 cm⁻¹) located at 8.88 and 9.14 eV. In addition, the small feature at 8.77 eV can be described by a C-C-C ring bending vibration at 1400 cm⁻¹.

This leads to the question how **9** is formed, although it is 0.78 eV (75 kJ·mol⁻¹) less stable compared to **1**. A previous theoretical investigation predicted all isomerization barriers between C₅H₂ isomers to be larger than 2.3 eV,⁷⁴ as confirmed by our own DFT calculations. These barriers are

significant, and therefore rearrangements to higher lying isomers are unlikely under mild pyrolysis conditions. The best explanation relies on the *in situ* preparation of the diazo precursor **4** from the sodium salt of the tosyl hydrazone. This is supported by our investigations of C₅H₂N₂: Here a second C₅H₂N₂ isomer appears in the ms-TPES when the pyrolysis is turned on, see Figure S2. Hence, we suggest that the *in situ* generation of the diazo-precursor is responsible for the appearance of other C₅H₂N₂ isomers, which upon pyrolysis may yield the singlet carbene **9**.

Note that for the sake of completeness, we also computed IE's for the isomers of C₄N, which also have $m/z = 62$, are known to be stable^{75,76} and might be formed during pyrolysis. However, the computations ruled out any contributions to the spectrum. Details are therefore only given in the SI (Figure S4).

For comparison and to study the influence of a methyl group on the carbene, we recorded ms-TPE spectra of the methyl-substituted carbene **2** and the dimethyl-substituted one **3**, which are presented in Fig. 8. Again 5-point smoothing was employed to account for the small signal intensity and the subsequently low signal/noise ratio. The spectrum of H₃C-C₅-H (Figure 8, left-hand column, average over five spectra) is dominated by a broad band at 7.77 eV, which was assigned to the ionization energy of methylpentadiynylidene **2**. From the fwhm of the major peak, error bars of ± 0.04 eV are assumed. CBS-QB3 calculations yield a value of 7.80 eV for the IE_{ad}, again in excellent agreement with the experimental value. The geometry change upon ionization is small and the bond length of R_{C-CH₃} decreases only from 1.45 Å to 1.42 Å.

The FC-simulation at an estimated temperature of 600 K shows a very good agreement with the experiment. The peak at 7.77 eV is broadened due to hot and sequence band transitions and contributions of the CC stretching vibration (609 cm⁻¹). The fact that the spectrum of **2** shows only

one dominant peak, confirms that the second peak in the ms-TPE spectrum of **1** is due to a second isomer and not due to an unaccounted vibrational or electronic transition.

Fig. 8. ms-TPE spectrum of $m/z = 76$ and Franck-Condon simulation of methylpentadiynylidene **2** (blue line) is shown in the left-hand column. The ionization energy is determined to be 7.77 ± 0.04 eV. In the right-hand column the ms-TPE spectrum of $m/z = 90$ (black line with open circles) and Franck-Condon simulation of dimethylpentadiynylidene **3** (blue line) is pictured. An ionization energy of 7.27 ± 0.06 eV can be extracted.

The right-hand side of Figure 8 depicts the corresponding TPE spectrum of dimethylpentadiynylidene **3** $m/z = 90$, which constitutes an average of ten spectra. The FC-simulation represents the experimental data quite well. Two methyl rotors contribute to the ms-TPE spectrum of **3**, leading to an even more pronounced band broadening, which does not allow to resolve individual transitions in the experiment. The value of $IE_{ad} = 7.27 \pm 0.06$ eV extracted from the band maximum is in excellent agreement with the computed value of 7.25 eV. The

shoulder on the high energy side is due to excitation of a C-C stretch (computed value 512 cm⁻¹), which is associated with torsional excitations at 33 cm⁻¹.

The IE_{ad} of the three carbenes are summarized in Tab. 3. As all three molecules can reasonably well be described as triplet carbenes, ionization occurs from a *p*-type orbital. A comparison shows that the methyl groups lower the ionization energy of **1** by 590 meV and 1090 meV upon substitution of H by CH₃. Since the radical cations are electron-deficient, a methyl group increases the electron density of the cation **2**⁺ and **3**⁺ and thus stabilizes the cation. A comparison of the IE's shows that the effect is slightly larger for the first methyl group, but still substantial for the second one. The stabilization is slightly lower compared to even C_n chains with e.g. *n* = 4. Butadiyne has an IE = 10.17 eV, which is lowered by 670 meV and 1270 meV, respectively upon replacing the H-atoms subsequently by methyl groups.⁷⁷ The IE decrease is also observed for the diazo compounds, but is only around 300 meV per methyl group. In the diazo compounds the lone pair of the nitrogen atoms already stabilizes the cations, so the additional contribution of the methyl groups is smaller. The increased stability of the neutral chain upon methyl addition is reflected in two further observations: First, a dimer is only observed for **1**, but not for **2** and **3**. Second, the mass spectra in Figure 2 show a more intense peak for C₅H₃ than for **1**, while for **2** the H-addition is less important and for **3** it is absent. Most likely the steric influence of the methyl groups slows down secondary reactions.

Tab. 3. Ionization energies (IEs) of the un-, mono- and di-substituted pentadiynylidenes **1**, **2**, **3** and of 3-(didehydrovinylidene)cyclopropane **9**. Computed IEs are given for comparison.

Molecule	IE _{exp} [eV]	IE _{theo} [eV]
1	8.36 ± 0.03	8.41 ^[a]
9	8.60 ± 0.03	8.55 ^[b]
2	7.77 ± 0.04	7.80 ^[a]
3	7.27 ± 0.06	7.25 ^[a]

[a] CBS-QB3 computations

[b] CASPT2 computations

CONCLUSIONS

The three triplet carbenes pentadiynylidene **1**, C₅H₂ methylpentadiynylidene **2**, H₃C-C₅H and dimethylpentadiynylidene **3**, H₃C-C₅-CH₃ were characterized by mass-selected threshold photoelectron spectroscopy. The carbenes were generated by pyrolysis of the diazo precursors **4**, **5** and **6**. An ionization energy of 8.36 ± 0.03 eV was determined for the C₅H₂ isomer pentadiynylidene. A second peak appears in the spectrum at 8.60 eV that cannot be assigned to **1**. Since the precursor was completely converted in the pyrolysis and the kinetic energy distribution of the ions shows that the signal originates from a species present in the molecular beam, dissociative ionization can be ruled out. With the aid of computations the peak at 8.60 eV was assigned to isomer **9**, 3-(didehydrovinylidene)cyclopropane. Interestingly the calculated IE

depends strongly on the computational level and varies over almost 1.5 eV. We found that a proper description of the ionic ground state **9**⁺ requires a multi-reference approach. We consequently computed an IE of 8.55 eV by CASPT2, in agreement with the peak at 8.60 eV. It is noticeable that the CBS-QB3 approach, which usually performs well for ionization energies, overestimated the IE by 0.20 eV, while the CCSD(T) value was even more than 1 eV off. As the barriers between the isomers are substantial, isomer **9** is most likely not formed from **1** in the pyrolysis, but rather from an isomer of the precursor, HC₅H(N₂).

Substitution of H by CH₃ leads to a stepwise reduction of the IE to 7.77 ± 0.04 eV for methylpentadiynylidene and 7.27 ± 0.06 eV for dimethylpentadiynylidene, due to the stabilizing effect of the electron-deficient cation by a methyl group. No indication of a second isomer is present in the ms-TPE spectra of **2** and **3**. While carbene **1** tends to dimerize to tetraethynylethene, **2** and **3** are more stable due to the additional methyl group and show no dimerization product.

In addition, the photoionization of the precursors 1-diazo-penta-2,4-diyne **4**, 1-diazo-hexa-2,4-diyne **5** and 2-diazo-hexa-3,5-diyne **6** has been explored. Ionization energies and vibrational frequencies have been determined. The dissociative photoionization was also investigated and breakdown diagrams have been recorded. However, computations indicate the presence of a reverse barrier for dissociation in the ion, so no bond dissociation energies could be experimentally determined.

ASSOCIATED CONTENT

Supporting Information. Further computational information on geometries of all molecules as well as additional spectra are presented as supporting information. This material is available free of charge via the internet at <http://pubs.acs.org>

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