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Facile pentagon formation in the dissociation of polyaromatics†

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Energetic processing of gaseous polycyclic aromatic hydrocarbons (PAHs) plays a pivotal role in the chemistries of inter- and circumstellar environments, certain planetary atmospheres, and also in the chemistry of combustion and soot formation. Although the precursor PAH species have been extensively characterized, the products from these gaseous breakdown reactions have received far less attention. It has been particularly challenging to accurately determine their molecular structure in gas-phase experiments, where comparisons against theoretical modeling are best made. Here we report on a combined experimental and theoretical study of the dissociative ionization of two nitrogen containing polycyclic aromatic hydrocarbons of $C_{13}H_9N$ composition, acridine and phenanthridine. The structures of HCN-loss fragments are resolved by infrared multiple-photon dissociation (IRMPD) spectroscopy of the mass-isolated products in an ion trap mass spectrometer. Quantum-chemical computations as well as reference IRMPD spectra are employed to unambiguously identify the molecular structures. Furthermore, computations at the density functional level of theory provide insight into chemical pathways leading to the observed products. Acenaphthylene^{•+} and benzopentalene^{•+} – two aromatic species containing pentagons – are identified as the main products, suggesting that such species are easily formed and may be abundant in regions where thermal or photoprocessing of polyaromatics occurs.

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their nitrogen containing analogs (PANHs) are known as very stable molecular entities explaining their pivotal role in the chemistries of diverse environments, ranging from the interstellar medium (ISM), planetary atmospheres, to combustion environments.^{1–7} Here we focus on these gas-phase environments, where energetic processing of PA(N)Hs induced by photo- and/or collisional excitation is common and may cause isomerization or dissociation to occur.^{8,9} The dissociation of large PAHs in the ISM has been suggested to lead to the formation of fullerenes,^{9–11} but spectroscopic evidence supporting this hypothesized conversion has not yet been reported.

The loss of C_2H_2 units from PAHs or the loss of an isoelectronic HCN unit from PANHs constitute the most common carbon loss channel for irregular PAHs. Recently, our group identified the structure of the product formed in the dissociative

ionization of the smallest PAH, naphthalene, by infrared multiple-photon dissociation (IRMPD) spectroscopy.¹² We confirmed theoretical predictions that suggest that isomerization to azulene^{•+} precedes the loss of a C_2H_2 -unit, yielding pentalene^{•+} as the main product.^{13–15} The products that form from the dissociation of larger PAHs remain elusive.^{16–20} Identification of these products and the characterization of the underlying potential energy surface (PES) is critical to fully understand the chemical networks involving polyaromatics.

The high degree of symmetry of homocyclic PAHs consisting of three or more aromatic rings hampers unique identification of the underlying chemical mechanism, as a number of indistinguishable C_2H_2 units can be removed. Here, we address this challenge by investigating the loss of an isoelectronic HCN-unit from N-heterocyclic PAHs (PANHs). The nitrogen atom is placed at a specific position in the molecule and traced back in the $[M-27]$ mass loss channel, allowing for an unambiguous determination of the underlying dissociation mechanism. Additionally, the loss of HCN from nitrogen heterocycles typically requires less energy than C_2H_2 removal from their carbon-only counterparts,^{20,21} having the added advantage of enhanced dissociation resulting in larger ion intensities in the experiment.

We chose to study HCN-loss products from two PANHs of $C_{13}H_9N$ composition, acridine and phenanthridine (Fig. 1), as they comprise the smallest representatives of two classes of polyaromatics: PAHs with zigzag and with armchair edges,

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Fig. 1 Structures of the two $C_{13}H_9N$ isomers investigated here.

respectively. Experimental and theoretical investigations of PAHs and graphene have revealed the profound influence of edge topology on electronic and structural properties of the species.^{22–26} Both acridine and phenanthridine have received considerable attention in the past,^{19,27} but their precise dissociation mechanisms are poorly characterized.

In this work we determine the molecular structures of the products formed after HCN-loss from the PANHs through their IRMPD spectra. Unambiguous identifications are made by comparing the IRMPD spectra of the dissociation products with spectra of possibly formed products. The chemical pathways leading to these products are characterized by quantum-chemical computations of the potential energy surfaces (PES).

2 Methods

2.1 Experimental

The experiments have been performed on an ion trap mass spectrometer coupled to the free electron laser for infrared experiments (FELIX) at Radboud University.²⁸ The experimental apparatus has been described in detail previously^{12,29} and a brief description is provided below.

The apparatus consists of a radio-frequency quadrupole ion trap (QIT) assembly (R. M. Jordan Co.) mounted inside a vacuum chamber that is pumped by a turbopump to a pressure of $\leq 10^{-7}$ mbar. A flow of helium is supplied to the ion trap and raises the pressure to $\sim 5 \times 10^{-5}$ mbar. This reduces the size of the ion-cloud, resulting in improved mass resolution and better overlap with the focused IR laser beam from the free electron laser.

Acridine and phenanthridine (Sigma-Aldrich, 97 and 98%, respectively) are placed in a pyrex tube that is positioned inside the vacuum chamber in a ceramic oven heated to ~ 45 °C. The $C_{12}H_8$ species (acenaphthylene (ACN), biphenylene (BPh), 1-ethynyl-naphthalene (1EN), 2-ethynyl-naphthalene (2EN) – Sigma-Aldrich, 99, 99, 99, and 97%, respectively) are more volatile and are connected on the outside of the vacuum chamber and introduced effusively *via* a dosing valve.

An ArF excimer laser (193 nm) with a pulse energy of ~ 3.5 mJ is focused in the center of the ion trap through a MgF_2 lens to (dissociatively) ionize the species under investigation. The three electrodes of the trap are kept at ground potential and a 1 MHz radio-frequency (RF) signal with a peak-peak amplitude of ~ 1375 V is supplied to the ring-electrode. Ions generated in the focus of the laser are captured in the RF-field, provided their mass-to-charge ratio (m/z) has a stable trajectory in the ion trap.

Mass selection of the ions is achieved by applying an 80 ms long stored waveform inverse Fourier transform (SWIFT) pulse to the repeller endcap electrode.³⁰ The SWIFT pulses have been constructed following the method described by Doroshenko and Cotter,³¹ using quadratic phase modulation for the frequency components.³² The SWIFT pulse excites the mass-selective axial secular frequencies of all ions inside the trap except for the ion of interest, thereby ejecting unwanted species from the trap while leaving the species under investigation unaffected.

Ions are ejected from the trap through a hole in the extractor endcap by simultaneously applying high voltage pulses of +800 and –800 V to the repeller and extractor endcap electrodes, respectively. After the ions exit the trap they are further accelerated into a time-of-flight (TOF) mass spectrometer by an extraction grid biased at –2375 V. The 40 cm long TOF tube contains a concentric liner biased at the same negative potential as the extraction grid. The field free flight tube is terminated by the front grid of the Z-gap microchannel plate detector that is also kept at the same potential. This configuration yields a mass resolution of $m/\Delta m \approx 300$.

Mid-IR spectra have been recorded by measuring the fragmentation yield induced by the intense radiation from FELIX as a function of IR laser wavelength.³³ The fragmentation yield is defined as the total integrated intensity of IR-induced fragment ions divided by the total integrated ion intensity, *i.e.* the sum of the fragment and precursor ion intensities. Typical FELIX macropulse energies range from 50 to 70 mJ with a spectral resolution that is Fourier limited by the duration of the FELIX micropulse and amounts to about 0.5% of the central wavelength.²⁸ The IR radiation is tightly focused into the center of the ion trap in a double-pass configuration created by two concave mirrors with a focal length of 7.5 cm. The experiment is operated at a repetition rate of 10 Hz that is provided by FELIX. Further details on the measurement cycle are given in Fig. S1 of the ESI.†

2.2 Computational

Density functional theory (DFT) calculations have been performed with the Gaussian09 software package³⁴ employing the B3LYP functional.^{35,36} Reaction coordinates have been scanned at the 6-31+G* level of theory to locate transition states and intermediates. The identified structures have been re-optimized with the 6-311++G(2d,p) basis set to obtain more accurate energies. Vibrational frequencies of the possible reaction product structures have also been computed at the B3LYP/6-311++G(2d,p) level of theory. The frequencies of the computed spectra are scaled uniformly with a factor of 0.96 to correct for anharmonicities and are subsequently convoluted with a Gaussian line shape with a full width at half maximum (FWHM) of 30 cm^{-1} to facilitate comparison between the experimental and computational spectra.

3 Results

3.1 Mass spectrometry

The mass spectrum resulting from the UV multiphoton dissociative ionization of phenanthridine is shown in Fig. 2A.

Mass peaks are observed at $m/z = 180, 179, 152, 151$ and 150 . The peak at $m/z = 179$ is attributed to the phenanthridine radical cation. The intense peak at $m/z = 180$ is likely due to protonated phenanthridine that is formed by a self-protonation reaction of the radical cation $\text{Phe}^{\bullet+}$ with neutral phenanthridine present as a background vapor:³⁷

The very weak signal observed at $m/z = 153$ corresponds to C_2H_2 -loss from phenanthridine and contains a contribution of the ^{13}C component of the product at $m/z = 152$. The mass peak observed at $m/z = 152$ is clearly more intense and corresponds primarily to the HCN -loss channel:

This signal also possibly contains a small contribution of a product formed through C_2H_2 -loss accompanied by dehydrogenation, as was observed in high mass resolution experiments.²⁷ Mass peaks at $m/z = 151$ and 150 represent (further) dehydrogenation of products formed from HCN - and/or C_2H_2 -loss.

The middle trace in Fig. 2 shows the normalized mass spectrum that is recorded after applying the SWIFT-pulse to the repeller endcap of the ion trap. SWIFT excitation results in a clean isolation of the product at $m/z = 152$, with only a small fraction of the initial (protonated) phenanthridine left in the trap. Finally, the bottom trace in Fig. 2 shows the normalized mass spectrum that is obtained when FELIX is tuned to 750 cm^{-1} , which is resonant with a vibrational transition in the $m/z = 152$ fragment. Fragments induced by IRMPD are detected at $m/z = 151$ and 150 corresponding to H - and H_2 -loss. Mass spectra recorded for dissociative ionization of acridine result the same fragments and isolation is achieved in a similar fashion. The effect of the trapping time on the ion signal intensities is investigated and discussed in detail in Fig. S2 of the ESI†

Fig. 2 Mass spectra of (A) phenanthridine after dissociative ionization at 193 nm , (B) the mass-isolated HCN -loss fragment peak at $m/z = 152$ and (C) the isolated fragment after being dissociated resonantly at 750 cm^{-1} by the intense IR-radiation generated by FELIX. The arrow points to the H - and H_2 -loss channels induced by infrared multiphoton dissociation (IRMPD).

3.2 IRMPD spectroscopy

3.2.1 $\text{C}_{12}\text{H}_8^{\bullet+}$ isomers. A number of isomeric forms of the $\text{C}_{12}\text{H}_8^{\bullet+}$ species are conceivable that could potentially represent the molecular structures of the fragments formed in the dissociative ionization of phenanthridine and acridine. Reference IRMPD spectra were recorded for the radical cations of four candidate structures that are commercially available: acenaphthylene ($\text{AcN}^{\bullet+}$), 2-ethynylnaphthalene ($2\text{EN}^{\bullet+}$), 1-ethynylnaphthalene ($1\text{EN}^{\bullet+}$) and biphenylene ($\text{BPh}^{\bullet+}$). These spectra, shown in Fig. 3, are corrected for fluctuations in the mid infrared laser pulse energies emitted by the FEL by scaling the IRMPD induced fragment ion intensities to the measured FEL pulse energy (see Fig. S3 of the ESI†).

The bottom panels in Fig. 3 show the vibrational spectra of these compounds computed at the B3LYP/6-311++G(2d,p) level of theory (stick diagram). A uniform frequency scaling factor of 0.96 is applied and the spectra are convoluted with a Gaussian line shape with a full width at half maximum (FWHM) of 30 cm^{-1} . Generally, the recorded IRMPD spectra match the calculated spectra very well, although relative intensities of the calculated spectra exhibit deviations from the measured intensities, which is not uncommon for IRMPD spectra. Summaries of calculated and measured frequencies and the assignments of the vibrational modes are listed in Tables S1–S4 in the ESI† Fig. 4 presents the theoretical spectrum of another $\text{C}_{12}\text{H}_8^{\bullet+}$ isomer of interest, benzopentalene ($\text{BP}^{\bullet+}$), computed at the B3LYP/6-311++G(2d,p) level of theory. An experimental spectrum could not be recorded because this compound is not available. Similar to the other computed spectra, this spectrum is convoluted with a 30 cm^{-1} Gaussian line shape function and the harmonic frequencies have been uniformly scaled by a factor of 0.96 .

3.2.2 HCN -loss fragments. The IRMPD spectra of the HCN loss fragments of acridine and phenanthridine have been recorded and are displayed in Fig. 5. A comparison of the fragment ion spectra with those of the five possible C_{12}H_8 structures is shown in Fig. S4 of the ESI† The IR spectrum of the $[\text{M}-27]^{\bullet+}$ fragment from acridine (Fig. 5A) shows the best match with the computed spectrum of $\text{BP}^{\bullet+}$ that is overplotted in green onto the acridine fragment spectrum in panel (A). While the band at 752 cm^{-1} matches reasonably well with the mode at 742 cm^{-1} in the spectrum of $\text{BPh}^{\bullet+}$ in Fig. 3B, the small mismatch in peak position combined with the absence of the other $\text{BPh}^{\bullet+}$ features around 970 and 1490 cm^{-1} rule out $\text{BPh}^{\bullet+}$ as the product ion structure. Although the positions of the bands at $752, 1097$ and 1343 cm^{-1} in the spectrum of the acridine $[\text{M}-27]^{\bullet+}$ fragment match reasonably well with features in the spectrum of $\text{AcN}^{\bullet+}$ (Fig. 3A), the relative intensities do not match. Furthermore, other $\text{AcN}^{\bullet+}$ resonances, specifically the strong mode at 834 cm^{-1} , are not clearly present in the spectrum of the acridine fragment, ruling out this species as a main contributor. The IR spectra of $1\text{EN}^{\bullet+}$ and $2\text{EN}^{\bullet+}$ do not appear to match at all with that of the acridine $m/z\ 152$ fragment, leaving $\text{BP}^{\bullet+}$ as the only candidate structure, yet a small contribution of $\text{AcN}^{\bullet+}$ cannot be excluded entirely. The three main resonances and two weaker transitions observed in the experimental spectrum closely resemble the bands in the computed $\text{BP}^{\bullet+}$ spectrum.

Fig. 3 IR spectra of (A) acenaphthylene $\bullet^+$, (B) biphenylene $\bullet^+$, (C) 1-ethynyl-naphthalene $\bullet^+$ and (D) 2-ethynyl-naphthalene $\bullet^+$. The top panels show experimental IRMPD spectra normalized to the power of FELIX, and the bottom panels represent harmonic frequency calculations at the DFT level (B3LYP/6-311++G(2d,p)) scaled by a factor of 0.96 to correct for anharmonicities. The red stick-plot lines represent the calculated intensities and the black line is a convolution with a 30 cm^{-1} FWHM Gaussian line shape function.

Fig. 4 Spectrum of benzopentalene $\bullet^+$ computed at the (B3LYP/6-311++G(2d,p)) and scaled by a factor of 0.96 to correct for anharmonicities. The red stick-plot lines show the calculated intensities and the black line is a convolution with a 30 cm^{-1} FWHM Gaussian line shape function.

The computed feature at 1560 cm^{-1} is not observed in the experimental spectrum, which is likely caused by reduced FEL

pulse energies towards the high-frequency end of the spectrum (see Fig. S3 in the ESI†), as has also been observed for pentalene $\bullet^+$.¹²

The spectrum of the $[\text{M}-27]\bullet^+$ fragment from phenanthridine shown in Fig. 5B exhibits the same features as the acridine fragment spectrum in panel A (bands marked with a “*”), but is complemented by additional resonances superimposed on a broad absorption stretching from 900 to 1400 cm^{-1} . The presence of all bands that are observed in the spectrum of the acridine fragment suggests that $\text{BP}\bullet^+$ is also a primary dissociation product of phenanthridine. The slightly weaker bands at 835 and 1180 cm^{-1} match perfectly with two of the strongest features in the spectrum of $\text{AcN}\bullet^+$ shown in Fig. 3A and plotted in green onto the fragment spectrum in Fig. 5B to facilitate the comparison. Close inspection reveals that $\text{AcN}\bullet^+$ can also explain the broad structure between 900 and 1400 cm^{-1} . We thus conclude that the dissociative ionization of phenanthridine proceeds along two parallel pathways yielding $\text{BP}\bullet^+$ and $\text{AcN}\bullet^+$. A branching ratio between the two products cannot be determined from the present experiment, as IRMPD involves a non-linear process.

3.3 Potential energy surface

The $\text{C}_{13}\text{H}_9\text{N}\bullet^+$ potential energy surface has been explored computationally to provide insight into possible reaction

Fig. 5 IRMPD spectra of the $[M-27]^+$ fragments of (A) acridine and (B) phenanthridine. The spectrum of benzopentalene $^{•+}$ is overplotted on panel (A) to facilitate comparison. Similarly, the spectrum of acenaphthylene $^{•+}$ is overplotted on panel (B). The stars (*) in panel (B) mark the features of this spectrum that are attributed to benzopentalene $^{•+}$.

pathways leading to the $C_{12}H_8^{•+}$ products. A summary of the PES containing only the rate limiting transition states connecting acridine $^{•+}$ and phenanthridine $^{•+}$ to the $C_{12}H_8^{•+}$ products is

shown in Fig. 6. The energies in this PES (in eV) are indicated relative to that of the acridine radical cation. The detailed computed PES of the individual steps are available from Fig. S6–S10 of the ESI†. The computed barrier of 4.58 eV involved in the isomerization of acridine $^{•+}$ to phenanthridine $^{•+}$ is slightly lower than the value of 4.76 eV reported by Johansson *et al.*¹⁹ The transition state for the formation of BPh $^{•+}$ from phenanthridine $^{•+}$ is in good agreement with their computations. However, where from the study by Johansson *et al.*¹⁹ it appears that the formation of BPh $^{•+}$ is the lowest energy product channel, the full potential energy surface as investigated here suggests that the formation of BP $^{•+}$ is lowest in energy, followed by AcN $^{•+}$ and 1EN $^{•+}$. The path leading to BPh $^{•+}$ is in fact highest in energy with a rate limiting barrier at 4.95 eV. The spectroscopic experiments described in the previous section support our computed PES, showing that the observed product ion structures (BP $^{•+}$ and AcN $^{•+}$) are indeed those accessible over the lowest energy transition states.

For both acridine $^{•+}$ and phenanthridine $^{•+}$, the path with the lowest barrier (4.31 and 3.78 eV, respectively) leads to BP $^{•+}$ via a 6–6 to 5–7 ring conversion (see Fig. S7 and S8 of ESI†). The formation of AcN $^{•+}$ and 1EN $^{•+}$ share the same rate limiting transition state at 4.95 eV. However, the formation of 1EN $^{•+}$ requires an additional step with a submerged barrier at 4.71 eV, which is unlikely to compete with the submerged barrier at 3.5 eV that leads to the AcN $^{•+}$ (see Fig. S9 and S10 of ESI†).

The reaction pathway from phenanthridine $^{•+}$ to BPh $^{•+}$ has a rate limiting barrier at 5.27 eV. Acridine $^{•+}$ and phenanthridine $^{•+}$ are found to be connected by a transition state located at 4.58 eV. No path connecting acridine or phenanthridine to 2EN $^{•+}$ has

Fig. 6 Summary of the $C_{13}H_9N^+$ potential energy surface showing the rate limiting transition states for each reaction path. Energies are given in eV.

been identified. For acridine $\bullet^+$ to reach $\text{AcN}^{\bullet+}$ or $1\text{EN}^{\bullet+}$ isomerization to phenanthridine $\bullet^+$ is required according to the computed PES, causing this dissociation channel to be kinetically unfavorable compared to the reaction leading to $\text{BP}^{\bullet+}$, which requires fewer steps and is substantially lower in energy. Moreover, even if isomerization to phenanthridine $\bullet^+$ were to occur, dissociation to $\text{BP}^{\bullet+} + \text{HCN}$ would still be the lowest energy dissociation channel.

4 Discussion and conclusion

The ionization potentials of acridine and phenanthridine are 8.1 eV³⁸ and 8.3 eV,³⁹ respectively. Upon ionization with two 193 nm photons ($2 \times 6.42 = 12.84$ eV) an excess energy of ~ 4.74 and 4.54 eV is available for dissociation of the metastable acridine and phenanthridine radical cations, respectively. In both cases this is sufficient to form $\text{BP}^{\bullet+}$ via HCN-loss, which is computed to require 4.30 and 3.78 eV (see Fig. 6). Although the experiments are performed at room temperature, the ions in the trap may be substantially hotter (± 800 °C),⁴⁰ undergo collisions with the background helium gas and are excited by the SWIFT isolation pulse. It is therefore not unlikely that the path leading from phenanthridine $\bullet^+$ to $\text{AcN}^{\bullet+}$ and $1\text{EN}^{\bullet+}$ also opens up, as the internal energy due to UV excitation is only 0.21 and 0.14 eV below the rate-limiting barrier leading to these products, respectively.

For phenanthridine $\bullet^+$ the path that leads to $\text{AcN}^{\bullet+}$ (see Fig. S9 and S10 of the ESI†) contains about twice as many steps as the path leading to $\text{BP}^{\bullet+}$ (Fig. S9 of ESI†). This dissociation channel thus appears kinetically less favorable, however, $\text{AcN}^{\bullet+}$ is detected experimentally and thus competes with the formation of $\text{BP}^{\bullet+}$. Possibly, a lower energy pathway leading to $\text{AcN}^{\bullet+}$ exists that is not identified in the present calculations, or the measurement is somewhat more sensitive towards $\text{AcN}^{\bullet+}$. A full Rice–Ramsperger–Kassel–Marcus⁴¹ (RRKM) model of the potential energy surface may also provide more detailed insight into the observed products and their branching fractions as a function of internal energy of the parent ion.

The molecular structures of the reaction products of HCN-expulsion from a zigzag and armchair PANH have been resolved on the basis of their IR spectra. The formation of benzopentalene $\bullet^+$ and acenaphthylene $\bullet^+$ upon UV-induced dissociation of acridine and phenanthridine is in good agreement with potential energy surface calculations. The established reaction pathways are believed to be generic and similar chemical pathways leading to pentagon-containing products are conceivable for C_2H_2 -loss from zigzag- and armchair-edged PAHs. Various recent experimental^{9,11,12,20,42,43} and theoretical^{10,44} studies have indeed suggested that pentagon formation occurs in PAH breakdown. The present study confirms those indications based on firm spectroscopic evidence.

The facile formation of 5-membered rings upon energetic processing of polyaromatic species suggests that PA(N)Hs with a mixed pentagon/hexagon structure may be abundant in photo-dominated regions of the interstellar medium, or in regions where thermal processing of polyaromatics occurs.

The facile formation of pentagons in the breakdown of pure hexagonal species also strongly supports indications that fullerene-like species be formed in the energetic processing of larger PAHs.

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