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Identification and Chemistry of Phenylnitrene in Premixed Pyridine/Oxygen/Argon Flame with Tunable Synchrotron Photoionization[†]

Zhen-yu Tian, Tao Yuan, Jing Wang, Yu-yang Li, Tai-chang Zhang, Ai-guo Zhu, Fei Qi*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

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The triplet state phenylnitrene (PhN) species generated from the low-pressure (4.0 kPa) premixed laminar pyridine/oxygen/argon flame was detected and identified using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry techniques. The ionization energies of PhN were determined experimentally by photoionization efficiency spectra and theoretically by calculations. The results indicate that PhN has a 3A_2 ground state and its first and second adiabatic ionization energies are 8.04 and 9.15 ± 0.05 eV, respectively. Furthermore, the formation and consumption pathways of PhN are proposed according to the species detected in the present work. PhN is the first nitrogen-containing diradical detected in combustion chemistry, and so it should be added to the kinetic model of pyridine flames.

Key words: Pyridine, Phenylnitrene, Low-pressure premixed flame, Tunable vacuum ultraviolet photoionization, Molecular-beam mass spectrometry

I. INTRODUCTION

Experimental and theoretical studies of phenylnitrene (PhN) have been subjects of great interest to both organic and physical chemists over the past 40 years [1-6] because of its useful synthetic and industrial applications [7]. PhN is a diradical with C_{2v} symmetry, which is generally produced by pyrolysis or photolysis of phenyl azide [1,7-9]. Many previous investigations of PhN were related to spectroscopy studies [1,4,10,11]. In 1966, Reiser *et al.* reported the first electronic spectrum of PhN [1] and their studies were extended by subsequent researchers [2-4]. Porter and Ward assigned a UV absorption band of triplet PhN in 1968, which was supported by other groups [5,6,12]. In 1990, Hayes and Sheridan measured the vibrational frequencies of PhN from a mixture of PhN and dehydrozaepine [13]. The first singlet-triplet splitting energy of 18.0 kJ/mol was reported by Drzaic and Brauman from photodetachment spectroscopy experiments of the PhN anion [14,15]. According to experiments and computations by other investigators [7,16-18], this gap was small. Furthermore, there have been plenty of theoretical calculations of PhN [7,17-20]. However, literature studies on the ionization energies of PhN are scarce and only values determined by photoelectron spectrometry are available [8,21].

In this work, the isomeric identification of PhN was performed in the fuel-rich pyridine flame with molecular-beam mass spectrometry (MBMS) and tun-

able vacuum ultraviolet (VUV) synchrotron photoionization techniques [22-24]. The high resolution of photoionization mass spectrometry (PIMS) and the tunable photon energy from the synchrotron allow unambiguous identification of PhN. Furthermore, the experimental values are confirmed by theoretical calculations.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experimental method

The experiments were performed at the flame end-station of the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The experimental setup has been reported elsewhere [22,24-26] and a brief description is given here. The apparatus was composed of a flame chamber which contained a movable flat-flame burner (McKenna Burner) with 6 cm in diameter, a differentially pumped chamber with a molecular-beam sampling system, and a photoionization chamber combined with a reflectron time-of-flight mass spectrometer (RTOF-MS). Flame species were sampled by a quartz nozzle with a 40° included angle and a ~ 500 μm orifice at the tip. The sampled gas formed a molecular beam which then passed into a differentially pumped ionization region through a nickel skimmer. The molecular beam was crossed with the tunable VUV synchrotron light in the photoionization chamber and the photoions were collected and analyzed by the RTOF-MS with an approximate mass resolution of 1400. Then the ion signals were amplified by a pre-amplifier (VT120C, ORTEC, USA) and recorded using a multiscaler (FAST Comtec P7888, Germany) with a bin width of 2 ns. A digital delay generator (DG535, USA) was used to trigger a pulsed power supply and the multiscaler as well.

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*Author to whom correspondence should be addressed. E-mail: fqi@ustc.edu.cn, Tel: +86-551-3602125, Fax: +86-551-5141078

A 1 m Seya-Namioka monochromator was used to disperse synchrotron radiation from a bending magnet beamline of the 800 MeV electron storage ring. The energy resolution power $E/\Delta E$ (FWHM) is about 500 with the average photon flux of about 5×10^{10} photons/s. A lithium fluoride (LiF) window with 1.0-mm thickness was used to eliminate higher-order harmonic radiation from the monochromator when the wavelength was longer than 105.0 nm. The photon flux was monitored by a silicon photodiode SXUV-100 (International Radiation Detectors Inc., USA) to normalize the ion signals.

The pyridine sample was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. The purity of the pyridine was $\geq 99.5\%$ and no further purification was carried out. The equivalence ratios of the premixed flames were $\phi = 2.10$ (C/O/N=1:1.29:0.20) at pressure of 4.00 kPa. The flow rates for pyridine, O₂, and Ar were 0.895 mL/min (liquid at room temperature), 0.800 standard liter per minute (SLM), and 0.900 SLM, respectively. The cold gas velocity was 29.12 cm/s. Flow rates of O₂ and Ar were controlled by MKS mass flow controllers, and flow rate of pyridine was controlled by a syringe pump (ISCO 1000D, USA).

B. Computational method

In the present work, HF, MP2, CCSD(T), OVGF, and B3LYP methods of the neutral and ionic PhN with C_{2v} symmetry were employed for energetic calculations with the Gaussian 03 suite of programs. Structure optimizations were carried out using procedure. The adiabatic ionization energy was obtained from the difference in total energies between the neutral ground state molecule and the ion. The B3LYP/6-31G(d,p) harmonic frequencies, scaled by 0.9804, were used for correction of zero-point vibrational energies (ZPVE).

III. RESULTS AND DISCUSSION

A. Identification of PhN in pyridine flame

Figure 1 shows the partial photoionization mass spectra of the pyridine flame at the photon energies of 10.50, 10.00, and 9.00 eV, when the quartz nozzle was located at a distance of 7.5 mm from the burner surface. Some peaks which correspond to hydrocarbon, oxygenous, and nitrogenous species are observed. Because there are some isomers that may correspond to the same mass peak, and the number of possible chemical structures is increasing rapidly with increase of molecular weight, the isomeric identification of flame species is desired.

To obtain the PIE spectrum which contains precise information of ionization energies (*IE*s) of specific species, a series of mass spectra are measured with vari-

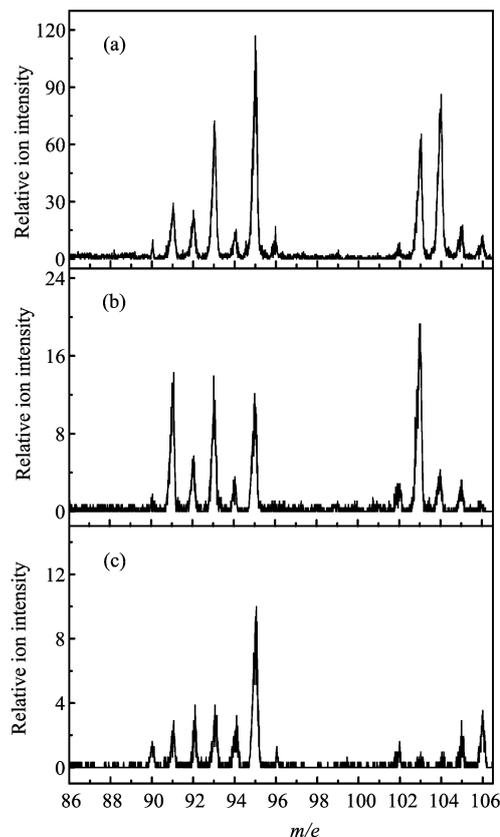


FIG. 1 Photoionization mass spectra of the pyridine/oxygen/argon flame at the photon energies of 10.50 eV (a), 10.00 eV, (b) and 9.00 eV, and (c) taken at the sampling nozzle position 7.5 mm from the burner surface.

ation of photon energy at the fixed burner position. The integrated ion intensities for a specified mass are normalized by the photon flux, and then plotted as a function of the photon energy, which yields the PIE spectra. Considering the cooling effect of the molecular beam, the experimental error for determining *IE* in this study is within 0.05 eV.

The tunability and high resolution of the synchrotron VUV light source allow measurement of PIE spectra for each observed mass. This work focuses on the identification of PhN by the measurement of PIE spectra of $m/e=91$ (C₆H₅N). As shown in Fig.2, two onsets at 8.04 and 9.15 eV are clearly observed, which correspond to ionization energies for different ionic states of PhN. Che *et al.* assigned the peak located at 8.21 eV to ionization of PhN (\tilde{X}^3A_2) to PhN⁺ (\tilde{X}^2B_2) in their photoelectron spectroscopy (PES) study [8]. The observed onset at 8.04 eV is in good agreement with the rising point of PES of PhN [8,21]. Kimura *et al.* concluded that the adiabatic ionization energy of PhN is close or equivalent to its vertical ionization energy. Thus, the first ionization energy of PhN is measured to be 8.04 eV in this study. Another onset at 9.15 eV corresponds to the second ionization

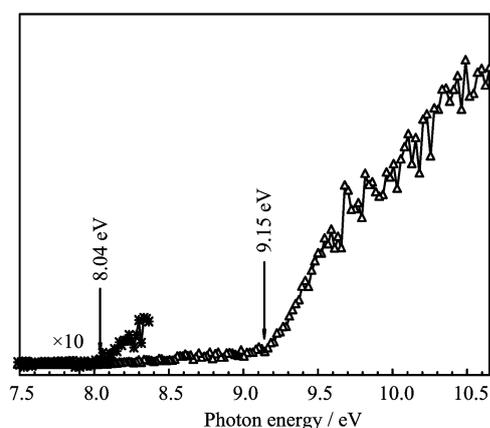


FIG. 2 The PIE spectra of $m/e=91$ (C_6H_5N) measured at the sampling nozzle position 7.5 mm from the burner surface from the premixed pyridine/ O_2 /Ar flame.

energy of PhN based on the theoretical calculation described in the following section. In the same way, $m/e=90, 92, 93, 94, 95, 96, 102, 103, 104, 105,$ and 106 in Fig.1 can be assigned to 5-ethynylidene-1,3-cyclopentadiene (C_7H_6), toluene (C_7H_8), aniline/picoline (C_6H_7N), phenol (C_6H_6O), pyridine oxide/2-pyridinol (C_5H_5NO), 1-methylcyclohex-1-ene (C_7H_{12}), phenylacetylene (C_8H_6), benzonitrile/benzonitrile (C_7H_5N), 3-pyridinecarbonitrile ($C_6H_4N_2$), 4-methylbenzyl radical (C_8H_9)/N-phenylmethanimine (C_7H_7N), and *p*-xylene (C_8H_{10}), respectively.

B. Geometries of PhN and PhN^+

PhN is composed of two states, singlet and triplet, both of which were previously observed in thermal decomposition and photodissociation of phenyl azide [27]. Previous calculations of PhN indicate that it has C_{2v} symmetry and an electron configuration of the valence shell [8,27]:

$$\sim(1b_1)^2(7b_2)^2(13a_1)^2(2b_1)^2(1a_2)^2(8b_2)^1(3b_1)^1$$

The results of low-temperature electron paramagnetic resonance (EPR) spectroscopy, reported by Wasserman *et al.*, indicated that the ground state of PhN has triplet multiplicity [28], which is in accordance with the point of Hund's Rule and supported by recent studies [8]. Based on the current calculations, the energy of singlet PhN is 1.441 eV higher than that of triplet PhN. This splitting energy is in good agreement with that previously obtained by DZ/SCF [7] and G2 method [8]. Hence, the ground state of PhN is triplet 3A_2 , in consensus with all previous work.

The geometries for the ground state and different ionic states of PhN were optimized by B3LYP method with the 6-31G(d,p) basis set. The optimized geometries are shown in Fig.3 and parameters for bond lengths and angles are listed in Table I. The N–C (1–2) bond length of the ground 3A_2 PhN is 1.328 Å, close to the

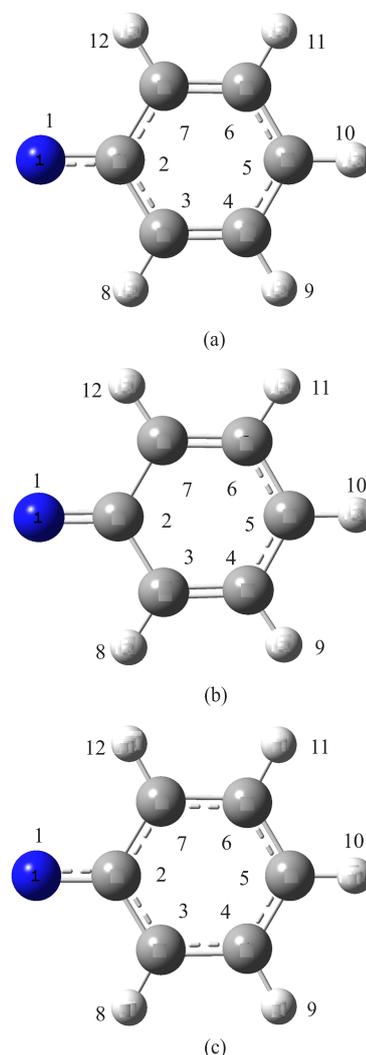


FIG. 3 The optimized geometries at B3LYP/6-31G(d,p) level for PhN (3A_2) diradical (a), PhN^+ (2B_2) (b), and PhN^+ (4A_1) (c).

1.338 Å optimized at CASSCF (8,8)/6-31G* [18]. It is 0.074 Å shorter than that calculated at DZ+d/SCF level since the latter did not take the electronic correlation effects into account [7]. The 1–2 bond length of 2B_2 PhN^+ is 0.006 Å longer than that of 1A_2 PhN (1.276 Å [18]), indicating this bond changes slightly between the singlet 1A_2 PhN and ionic state 2B_2 PhN^+ . The same happens to the triplet 3A_2 PhN and ionic state 4A_1 PhN^+ since the 1–2 bond length in the latter is 0.007 Å longer than that of the former. The 2–3 bond length of 3A_2 PhN is 1.435 Å, which is longer than that of previous calculations [7,16,18]. The 2–3 bond length of 2B_2 PhN^+ and 4A_1 PhN^+ are 1.467 and 1.428 Å, respectively. It can be seen that the alternative tendency of this value is opposite to that of 1–2 bond length by comparison with those in the singlet 1A_2 PhN and triplet 3A_2 PhN. The 3–4 and 4–5 bond length of 3A_2 PhN is almost the same as that of

TABLE I The optimized bond lengths and angles for the ground, doublet, and quadruplet ionic state of PhN using B3LYP/6-31G(d,p)

	PhN(\tilde{X}^3A_2)	PhN ⁺ (\tilde{X}^2B_2)	PhN ⁺ (\tilde{X}^4A_1)
Bond length/Å			
1–2	1.328	1.282	1.335
2–3	1.435	1.467	1.428
3–4	1.383	1.369	1.444
4–5	1.404	1.418	1.394
3–8	1.084	1.085	1.086
4–9	1.086	1.084	1.087
5–10	1.085	1.087	1.084
Bond angle/(°) ^a			
1–2–3	120.806	119.806	121.442
7–2–3	118.394	120.388	117.112
2–3–4	120.130	118.724	120.650
3–4–5	120.607	119.474	121.527
4–5–6	120.136	123.217	118.535
2–3–8	118.367	118.327	119.451
3–4–9	119.613	120.826	118.138
4–5–10	119.935	118.394	120.733

^a Atom 1 is N atom; Atoms 2 to 6 are C atoms; atoms 8 to 12 are H atoms; 1–2 stands for the bond length of atom 1 and 2, 1–2–3 for the angle of $\angle 1-2-3$.

CASSCF(8,8)/6-31G* calculations [18], while different from the result of Kim *et al.* [7]. In PhN, the B3LYP value of 1.085 ± 0.002 Å for C–H is close to the value of 1.082 Å obtained by the DZ+d/CISD method [7]. This value is a little longer than the C–H bond length of 1.083 Å in benzene [29], which indicates that the nitrogen substitution at benzene has little effect on the C–H distances.

According to the calculations of this study, the two spin-parallel electrons of 3A_2 PhN are located in 1–2–3–7 and 4–5–6 atoms. The electrons of 2B_2 PhN⁺ are located in 4–5–6 atoms, and electrons of 4A_1 PhN⁺ are located in 1 to 7 atoms, which could account for the alternation of bond lengths and bond angles. The 7–2–3 bond angle of 3A_2 PhN is 118.394° , which is about 2° smaller than the DZ/SCF, DZ+d/SCF, and DZ+d/CISD values [7]. The homologous angle of 2B_2 PhN⁺ and 4A_1 PhN⁺ are 120.388° and 117.112° , respectively. The 2–3–8 bond angle of 3A_2 PhN is 118.367° , which is about 1° smaller than the calculation result of Kim *et al.* [7]. The corresponding values of 2–3–8 in 2B_2 PhN⁺ and 4A_1 PhN⁺ are 118.327° and 119.451° , respectively. The 3–4–5 bond angle of 3A_2 PhN is 120.607° , a little larger than the SCF and CISD calculations [7]. When in doublet ionic state 2B_2 PhN⁺, this angle becomes 1.133° smaller. While in quadruplet ionic state 4A_1 PhN⁺, it is 0.920° larger than that of 3A_2 PhN. In addition, the 4–5–6 bond angle of 3A_2 PhN is in accordance with the result of Kim *et al.* [7].

The homologous angle of 2B_2 PhN⁺ and 4A_1 PhN⁺ are 123.217° and 118.535° , which results from the different occupation of electrons for these ionic states.

C. Ionization energy computations of PhN

The geometry of PhN is affected primarily by the orientation of electron spin. Different spin electrons occupy different orbitals, which make the ionization energies different. In this work, ionization energies of PhN are calculated with different methods including HF, MP2, OVGf, CCSD(T), and B3LYP based on the same basis set 6-31G(d,p). The theoretical and experimental energy differences between the neutral PhN and various ionic states PhN⁺ are listed in Table II. These values correspond to adiabatic ionization potentials at 0 K of the PhN diradical. By comparing the first onset on the PIE spectra of the PhN diradical with the calculated ionization energies, the experimental value (8.04 ± 0.05 eV) is in good agreement with the calculated adiabatic ionization potential value of 8.05 eV (the B3LYP method). Thus, the first adiabatic ionization energy of PhN is 8.04 ± 0.05 eV. It corresponds to ionization of electron from the $3b_1$ orbital. The second onset on the PIE spectra of PhN is 9.15 eV. Che *et al.* assigned a peak of PES at 9.30 eV to the removal of an electron of the $8b_2$ orbital [8]. However, the result of OVGf calculation indicates that the removal of a β spin electron of $1a_2$ (9.143 eV) is easier than the removal of a electron of $8b_2$ (9.407 eV). Moreover, 9.15 eV is in excellent agreement with the energy difference between PhN⁺ (\tilde{X}^4A_1) and PhN (\tilde{X}^3A_2) calculated by OVGf, CCSD(T) and B3LYP methods. Therefore, the second onset corresponds to ionization of a β spin electron of $1a_2$ orbital. To the authors' knowledge, no adiabatic ionization energy of PhN has been reported previously.

D. Formation and destruction of PhN

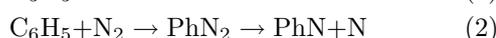
Although PhN is a common product originated from pyrolysis or photolysis experiments [1,7,8], it has never been reported in combustion chemistry previously. The formation pathways of PhN are still unclear and the authors will propose some possible channels in the following section which should be confirmed by theoretical calculations in the future.

By analogy to the formation of benzene via cyclopentadienyl (C_5H_5) and methyl [30–32], both of which are observed in the present work, PhN can be produced through the reaction of C_5H_5 and CN, as shown in formula (1). Fadden *et al.* pointed out that the phenoxy radical may be formed from the reaction of C_6H_5 and O_2 [33]. In the same way, PhN can be generated via the addition N_2 to C_6H_5 . Other species, e.g. N, HNO, and NCO, could also react with C_6H_5 , leading to the production of PhN. Moreover, it could result from the reaction of isocyanobenzene (C_6H_5NC) and an O atom.

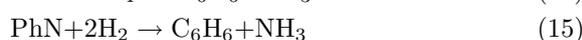
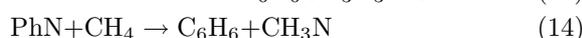
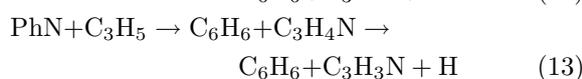
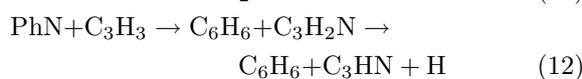
TABLE II Theoretical and experimental ionization energies of PhN. Computation is based on C_{2v} symmetry with different methods and the same basis set 6-31G(d,p) for PhN diradical

Methods	Computational and experimental ionization energies/eV		
	$\text{PhN}^+(\tilde{X}^2B_2) \leftarrow \text{PhN}(\tilde{X}^3A_2)$	$\text{PhN}^+(\tilde{X}^2A_1) \leftarrow \text{PhN}(\tilde{X}^3A_2)$	$\text{PhN}^+(\tilde{X}^4A_1) \leftarrow \text{PhN}(\tilde{X}^3A_2)$
HF			8.350
MP2			8.348
G2	8.356 [7]		
DFT	8.337 [7]	9.567 [7]	9.696 [7]
OVGF	8.551	9.407	9.143
CCSD(T)			9.152
B3LYP	8.05		9.27
PES	8.21 [7]	9.30 [7]	
Exp.	8.04		9.15

Most of these reactants are observed and identified in the present flame and their formation and consumption pathways have been discussed in the authors' previous work.



It was supposed that PhN could convert to 7-azabicyclo-[4.1.2]hepta-2,4,6-triene and 1-azacyclohepta-1,2,4,6-tetraene in *ab initio* study of its ring expansion. However, these species were not detected in the rich pyridine flame. According to the nitrogen-containing intermediates observed in the present work, PhN could be consumed by small radicals such as H/O/OH/CH₃ and mainly convert to benzene, NO and aniline (PhNH₂), as indicated in Eq.(7) to Eq.(10). Besides these radicals, C₃H₃ and C₃H₅ could react with PhN and C₆H₆ to form C₃HN and C₃H₃N. In addition, NH₃ and CH₃N may result from the reaction of PhN and CH₄/H₂, by analogy to the production of PH₃ and CH₃P from the reaction of C₆H₅P and CH₄/H₂ [34].



IV. CONCLUSION

The triplet state PhN was identified from a low-pressure premixed pyridine/oxygen/argon flame with equivalence ratio of 2.10 using tunable synchrotron photoionization and molecular-beam mass spectrometry techniques. Ionization energies of PhN were obtained by measurement of PIE spectra and calculated by various methods. The experimental and theoretical results agree well with each other and indicate that PhN has a ³A₂ ground state and its first and second adiabatic ionization energies are 8.04 and 9.15±0.05 eV, respectively. Moreover, the formation and consumption pathways of PhN are proposed.

V. ACKNOWLEDGMENTS

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