

The Interplay of Theory and Experiment in the Study of Phenylnitrene

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Received December 2, 1999

ABSTRACT

The intra- and intermolecular chemistry of phenylnitrene (**PhN**), its singlet–triplet energy separation, and its electronic spectra are interpreted with the aid of *ab initio* molecular orbital theory. The key to understanding singlet **PhN** is the recognition that this species has an open-shell electronic structure, in contrast to the related species, phenylcarbene, which has a closed-shell electronic structure. The thermodynamics of nitrenes, benzazirines, dehydroazepines, aminyl radicals, and their hydrocarbon analogues are also discussed.

I. Introduction

Traditionally the characterization of a metastable intermediate begins with chemical analysis of the stable products that it forms upon reaction. However, attempted generation of singlet phenylnitrene (C_6H_5N , **PhN**) usually produces intractable polymeric tars instead of informative bimolecular adducts.¹ Thus, for decades progress in the

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chemistry of arylnitrenes was less rapid than in that of arylcarbenes,² which do give useful and informative reaction products with many trapping reagents.

In the 1990s, there was a rapid increase in our understanding of the chemistry and spectroscopy of phenylnitrene, primarily as a result of the application of two tools: laser flash photolysis (LFP) and high-level *ab initio* molecular orbital (MO) calculations. It is the purpose of this Account to review this progress and to illustrate the synergism between theory and experiment in this research.

II. Summary of Experimental Findings

II.1. Solution Phase Chemistry. Carbenes are generated in many ways, including the decomposition of diazirines and diazo compounds. Typically, singlet carbenes react rapidly (bimolecular rate constants of 10^7 – 10^9 $M^{-1} s^{-1}$) with most functional groups (alcohols, aromatics, alkenes, and even the normally unreactive C–H bonds of alkanes)³ to form stable adducts.² The intermolecular reactions of phenylcarbene (C_6H_5CH , **PhCH**) are those of a typical carbene.

At ambient temperatures the reactivity of phenylnitrene (**PhN**) bears little resemblance to that of **PhCH**.^{1,2} When nitrogen is extruded from phenyl azide (**PhN₃**) in alcohol or hydrocarbon solvents, adducts similar to those observed from **PhCH** are not formed in appreciable yields; instead, a polymeric tar is produced.⁴ If a highly dilute solution of **PhN₃** is photolyzed in a hydrocarbon solvent,

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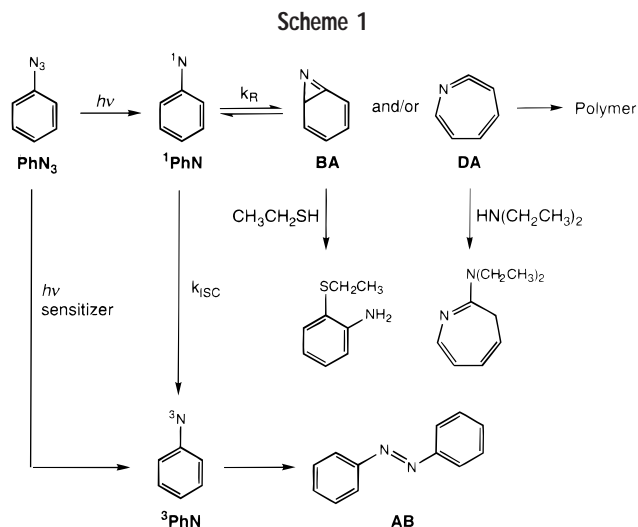
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then azobenzene (**AB**), the product of **PhN** dimerization, is formed (Scheme 1).^{1,5,6}

Simple adducts with ethanethiol⁷ or diethylamine⁸ are formed upon photolysis of **PhN₃**, but these trapping products do not arise from reaction with singlet **PhN** itself. Instead, these adducts are derived from benzazirine (**BA**) and dehydroazepine (**DA**), rearrangement products of singlet **PhN** (Scheme 1). The **DA** intermediate has been observed (IR and UV-vis) in solution^{5,6} and in an argon matrix,⁹ but the putative **BA** intermediate has not yet been detected by spectroscopic methods, although analogous species have been detected.¹⁰

It is possible to “freeze out” the nitrene rearrangement and subsequent diethylamine trapping reaction. Below 170 K, only azobenzene (**AB**) is formed from photolysis of **PhN₃** in the presence of diethylamine.¹¹ EPR spectroscopy has convincingly demonstrated that the triplet states of **PhN**¹² and **PhCH**¹³ are lower in energy than the corresponding singlet states, and thawing frozen solutions of triplet **PhN** produces **AB**. Thus, this product is usually assumed to be formed by the dimerization of triplet phenyl nitrene (**³PhN**).¹¹

Triplet-sensitized photolysis of **PhN₃** at ambient temperatures in the presence of diethylamine gives largely azobenzene, and the yield of the **DA** trapping product is greatly reduced.^{5,14} Thus, once formed, **³PhN** does not appear to revert readily to singlet phenyl nitrene (**¹PhN**), which is the source of the **BA** and **DA** rearrangement products.

The inferences that emerge from these observations are summarized in Scheme 1.^{1,5,11} Photolysis of **PhN₃** in solution releases singlet **¹PhN**, which isomerizes to **BA** and/or **DA**. The rearrangement of **¹PhN** is fast in comparison to intersystem crossing, reaction with solvent, and reaction with reagents which readily trap carbenes.

Unlike **¹PhN**, **¹PhCH** is easy to trap chemically, but it has been difficult to observe its isomerization products—bicyclo[4.1.0]heptatriene and cycloheptatetraene—in solution. Recently, Warmuth and Marvel have obtained the NMR spectrum of cycloheptatetraene, formed by pho-

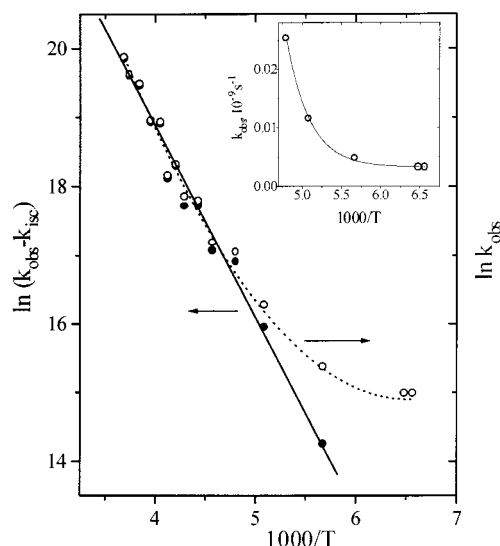


FIGURE 1. Arrhenius treatment of the observed rate constant (k_{obs}) of decay of **¹PhN** and of the rate constant for its rearrangement ($k_r = k_{\text{obs}} - k_{\text{ISC}}$).

tolysis of **³PhCH** inside a deuterated hemicarcerand at 77 K.¹⁵ However, the thermal rearrangement of **¹PhCH** is known only in the gas phase at elevated temperatures.¹⁶ The differences between the inter- and intramolecular reactivities of **¹PhCH** and **¹PhN** indicate that **¹PhCH** rearranges more slowly than **¹PhN**, and/or the intermolecular reactions of **¹PhCH** are much faster than those of **¹PhN**.

The **BA**¹⁰ and/or **DA**⁹ intermediates formed from **¹PhN** polymerize in solution,^{1,4} unless they are trapped by nucleophiles. However, in dilute solutions in hydrocarbon solvents, derivatives of **BA** and/or **DA** apparently form triplet nitrenes, presumably via the intermediacy of the corresponding singlet nitrenes.¹⁷ The reversibility of the rearrangement of certain singlet aryl nitrenes implies that the singlet nitrene and its rearrangement products are close in energy.

In contrast, conversion of **¹PhN** to **³PhN** appears to be an irreversible process, indicating that the singlet–triplet energy gap (ΔE_{ST}) must be large enough that the singlet is not thermally populated. However, in **PhCH** the singlet and triplet states interconvert very rapidly,² which has been taken to be indicative of a small singlet–triplet energy gap ($\Delta E_{\text{ST}} = 2\text{--}3$ kcal/mol).^{18,19}

II.2. Time-Resolved Spectroscopy. Upon laser flash photolysis (LFP) of **PhN₃** at ambient temperature with a 20 ns or longer pulse, **DA** is observed by either time-resolved UV (320–380 nm, broad)^{5,11} or IR (1890 cm^{-1}) spectroscopy.⁶ The rate constant for the reaction of **DA** with diethylamine was found to be $6.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.⁶

In 1997, with improved time resolution, two groups detected a short-lived intermediate upon flash photolysis of **PhN₃** or phenyl isocyanate ($\text{C}_6\text{H}_5\text{NCO}$).^{20,21} This transient species has a strong, sharp absorption at 350 nm and a lifetime of ca. 1 ns at ambient temperature, which is independent of the concentration of oxygen. The observed rate constant for decay (k_{obs}) was measured as a function of temperature in pentane (Figure 1).²²

The Arrhenius plot has two distinct regions. At high-temperature $A = 10^{13.1 \pm 0.3} \text{ s}^{-1}$ and $E_a = 5.6 \pm 0.3 \text{ kcal/mol}$. However, between 150 and 180 K the decay of the transient is independent of temperature, and $k_{\text{obs}} = (3.2 \pm 0.3) \times 10^6 \text{ s}^{-1}$. The breakpoint in the Arrhenius plot is around 180–200 K. This is the same temperature range in which the solution phase chemistry changes from the trapping of **DA** with diethylamine to the dimerization of triplet **PhN**.¹¹ Thus, the low-temperature data of Figure 1 were associated with k_{ISC} , the rate constant for intersystem crossing of ¹PhN to ³PhN, and the high-temperature data with k_r , the rate constant for rearrangement of ¹PhN (Scheme 1).

Scheme 1 predicts that $k_{\text{obs}} = k_r + k_{\text{ISC}}$, and a plot of $\ln(k_{\text{obs}} - k_{\text{ISC}})$ versus $1/T$ (Figure 1) is, in fact, linear. Based on ab initio calculations, described in the next section, we deduce that k_r is the rate constant for rearrangement of ¹PhN by cyclization to form **BA**, which in a subsequent, faster step undergoes electrocyclic ring opening to give **DA**.

III. What Accounts for the Differences between PhN and PhCH?

The many dissimilarities between the chemistries of **PhN** and **PhCH**²³ suggest that there is a fundamental difference between the electronic structures of these two species. Despite the fact that the nitrene and the carbene differ only by replacement of a lone pair on nitrogen in the former by a C–H bond in the latter, this apparently small difference has profound consequences. The key to understanding the differences in reactivity between **PhN** and **PhCH** is to understand first the general differences between the electronic structures of carbenes and nitrenes and then how these differences are affected by the presence of a phenyl substituent.

III.1. Electronic Structures of Carbenes and Nitrenes.

A feature common to both carbenes and nitrenes is that they each have two valence electrons which must be distributed between two nonbonding molecular orbitals (NBMOs). As shown in Figure 2, in a carbene these two orbitals are a pure $2p-\pi$ AO and a hybridized σ orbital. The amount of $2s$ character in the latter NBMO depends on whether this orbital is occupied by one or two electrons. Nevertheless, the $2s$ character in the σ NBMO always makes it substantially lower in energy than the $2p-\pi$ NBMO.

Consequently, in carbenes the configuration in which both nonbonding electrons occupy the σ NBMO is a good representation of the lowest singlet state. This singlet state is considerably lower in energy than the singlet state in which one electron occupies each of the NBMOs (with antiparallel spins) and far lower in energy than the singlet state in which both electrons occupy the $2p-\pi$ AO. However, the ground state of the parent carbene (CH_2) is a triplet, due to the lower Coulombic repulsion between the nonbonding electrons, which results from their occupying different orbitals with parallel spins. The energy difference between the lowest singlet and the triplet

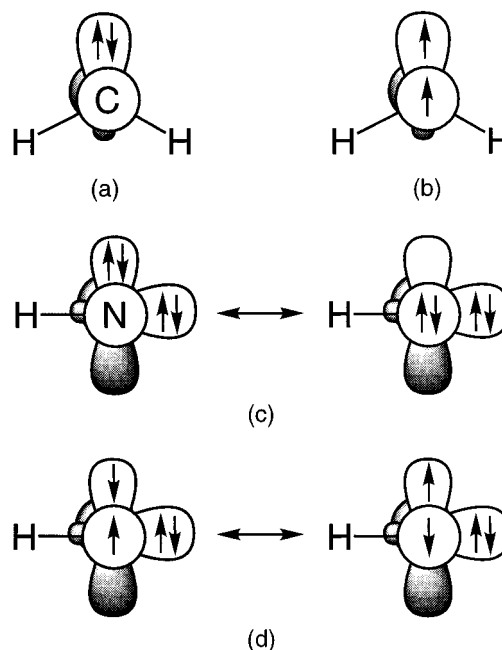


FIGURE 2. Schematic depictions of the lowest (a) singlet and (b) triplet states of methylene and of the (c) "closed-shell" and (d) "open-shell" components of the lowest singlet state (¹Δ) of nitrene.

ground state of CH_2 is $\Delta E_{\text{ST}} = 9 \text{ kcal/mol}$.²⁴ This energy difference is small enough that substituents which can donate a lone pair of electrons into the $2p-\pi$ NBMO, the orbital that is empty in the lowest singlet state, can make this state the ground state.²⁵ Methyl²⁶ and phenyl^{18,19} substituents also selectively stabilize the lowest singlet, reducing ΔE_{ST} to 2–4 kcal/mol, but the triplet remains the ground state of methylcarbene and of **PhCH**.

In the parent nitrene (NH), the lone pair of electrons on nitrogen that replaces one of the C–H bonds in CH_2 occupies a hybrid AO with a very large amount of $2s$ character. The other two electrons in nonbonding orbitals occupy AOs on nitrogen that are both pure $2p$ orbitals. The degeneracy or near-degeneracy of these two orbitals is the primary reason nitrenes are very different from carbenes.

Unlike the case in a carbene, in a nitrene the two configurations in which both electrons occupy the same NBMO are usually either degenerate or have nearly the same energies. Therefore, as shown in Figure 2, the "closed-shell" configuration for the lowest singlet state in CH_2 must be replaced by a linear combination of two configurations in NH. However, it is misleading to call the resulting singlet state of NH "closed-shell", because it is easy to show²⁷ that this singlet has one electron in each of two $2p$ AOs that are rotated 45° from the $2p$ AOs shown in Figure 2. Consequently, in NH, the "closed-shell" singlet and the "open-shell" singlet, in which one electron occupies each of the $2p$ AOs, have exactly the same energy and form the two components of a ¹Δ state.

In NH the lower Coulombic repulsion energy of the triplet is unmitigated by the energetic advantage in CH_2 of having both nonbonding electrons in the hybridized σ NBMO. Therefore, the value of $\Delta E_{\text{ST}} = 36 \text{ kcal/mol}$ in NH ²⁸ is 4 times larger than the value of $\Delta E_{\text{ST}} = 9 \text{ kcal/mol}$ in

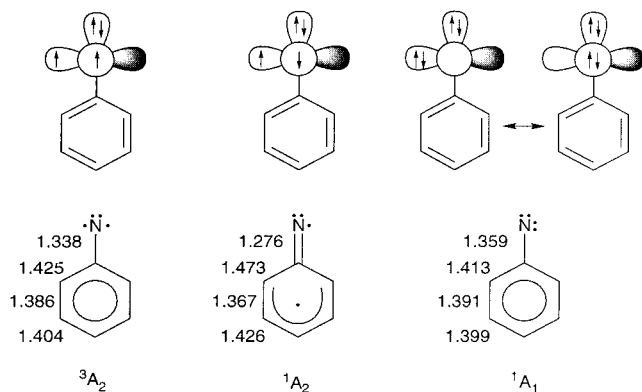


FIGURE 3. Calculated bond lengths (Å) in the triplet and in the lowest and first-excited singlet states of **PhN**.^{30b}

CH_2 .²⁴ As in the case of the carbene, replacement of hydrogen in NH by a methyl substituent has a relatively small effect on the singlet–triplet splitting, reducing it by 5 kcal/mol to $\Delta E_{\text{ST}} = 31$ kcal/mol.²⁹ However, surprisingly, but as predicted by calculations,³⁰ a phenyl substituent has been found to lower the singlet–triplet splitting from $\Delta E_{\text{ST}} = 36$ kcal/mol in NH, to a value of $\Delta E_{\text{ST}} = 18$ kcal/mol in **PhN**.³¹

III.2. Electronic Structure of PhN. Calculations³⁰ and experiments³¹ both give $\Delta E_{\text{ST}} = 18$ kcal/mol for **PhN**, but the calculations have the advantage of providing the opportunity to understand why the phenyl group has such a large effect on reducing ΔE_{ST} from its value in NH. The phenyl substituent in **PhN** obviously lifts the degeneracy between the nitrogen 2p orbital that interacts with the π orbitals of the benzene ring and the nitrogen 2p orbital that lies in the plane of the ring. Therefore, it would be reasonable to suppose that phenyl substitution selectively stabilizes the “closed-shell” (1A_1) singlet state of **PhN** by selectively stabilizing one of the two configurations that contribute to this state.

However, the calculations show that this supposition is incorrect and that it is, instead, the open-shell (1A_2) state which is selectively stabilized.³⁰ In addition, as shown in Figure 3, the calculations reveal that the geometry of this state is very different from that of the triplet (3A_2), despite the orbital occupancy being the same in both states. In the 1A_2 state, the electron in the π NBMO is almost completely localized in the benzene ring, so that this state of **PhN** resembles an iminyl radical attached to C-6 of a cyclohexadienyl radical.

In 1A_2 , unlike the case in 3A_2 , the σ and π electrons have opposite spin; hence, they are not correlated by the Pauli exclusion principle. Localizing electrons of opposite spin to different regions of space—in this case the σ NBMO on nitrogen and the π NBMO of the cyclohexadienyl radical—minimizes their mutual Coulombic repulsion energy.²⁷ Thus, ΔE_{ST} is much lower in **PhN**^{30,31} than in NH ²⁸ or CH_3N ²⁹ because the benzene ring allows the π electron in the 1A_2 state of **PhN** to become localized in a region of space that is disjoint from the region of space that is occupied by the σ electron.^{30b}

III.3. Consequences of the Differences between the Electronic Structures of PhCH and PhN. The fact that

the lowest singlet of **PhCH** is a closed-shell (1A) electronic state, whereas the lowest singlet of **PhN** is an open-shell (1A_2) state, is responsible for many of the differences between these two reactive intermediates. For example, although the much smaller value of ΔE_{ST} in the carbene contributes to its $>10^3$ -fold faster rate of intersystem crossing (ISC), the difference between the orbital occupancies in the lowest singlet states of **PhCH** and **PhN** also plays a role. When spin–orbit coupling provides the mechanism for intersystem crossing, a change in orbital angular momentum facilitates the change in spin angular momentum that is associated with crossing from a singlet to a triplet.³² Such a change in orbital angular momentum occurs in **PhCH**, where the σ^2 configuration of the nonbonding electrons in the singlet is transformed into $\sigma\pi$ in the triplet.

However, since the lowest singlet and triplet states of **PhN** both have the same $\sigma\pi$ orbital occupancy, to a first approximation, ISC in **PhN** is not facilitated by a change in orbital angular momentum. Vibronic mixing between the open-shell singlet (1A_2) state and the higher energy closed-shell singlet (1A_1) may provide a second-order mechanism for spin–orbit coupling in **PhN**. The modulation of both the energy difference between 1A_2 and 1A_1 and the weight of the σ^2 configuration in the latter can explain qualitatively the effects of both π electron-donating substituents on the benzene ring^{33,34} and polar, hydroxylic solvents³⁵ on accelerating the rate of intersystem crossing in **PhN**.³⁶

The difference between the reactivities of the lowest singlet states of **PhCH** and **PhN** can also be explained by the difference between their electronic configurations.³⁷ As in other carbenes, the empty π NBMO in the lowest singlet state of **PhCH** facilitates the electrophilic insertion and addition reactions of this reactive intermediate.³⁸ In contrast, singlet **PhN** does not undergo these reactions readily, because its π NBMO is not empty but is occupied by an electron.

Hydrogen atom abstraction or addition to π bonds by the singly occupied σ NBMO on nitrogen is a possible reaction for both the lowest singlet and triplet states of **PhN**. These reactions are not observed for the singlet, perhaps because its intramolecular rearrangement is so fast that these intermolecular reactions cannot compete. However, hydrogen abstraction by triplet **PhN** is very slow—so slow that abstraction competes with dimerization under the conditions of the LFP experiments only in polystyrene matrixes, where the latter reaction is retarded.³⁹ In contrast, triplet **PhCH** undergoes hydrogen atom abstraction reactions readily. This difference between **PhN** and **PhCH** in reactivity toward hydrogen abstraction can be attributed to the smaller thermodynamic driving force in **PhN** than in **PhCH**, due to the much weaker bond formed to hydrogen in an abstraction reaction by a nitrene than by a carbene.⁴⁰

The difference between the strengths of the N–H and C–H bonds formed by hydrogen atom abstraction reactions of the triplet ground states of **PhN** and **PhCH** with suitable hydrogen donors is calculated to be 22–24 kcal/

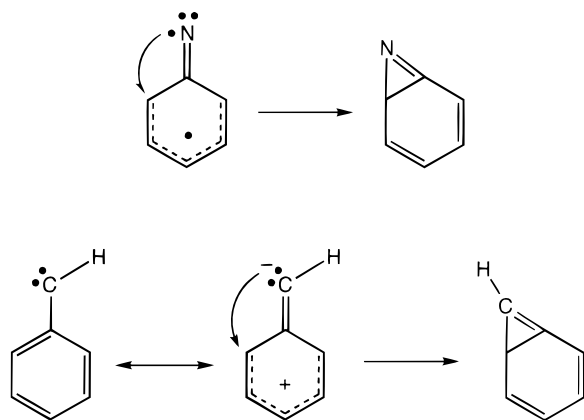


FIGURE 4. Schematic depiction of the difference between the cyclization of the open-shell singlet state of **PhN** and the closed-shell singlet state of **PhCH**.

mol, a difference in bond strengths that is similar to but 3–5 kcal/mol larger than the difference between the strengths of the bonds to hydrogen formed by the triplet ground states of CH_2 and NH .⁴⁰ The fact that the bonds formed in abstraction of hydrogen by triplet nitrenes are much weaker than those formed in abstraction of hydrogen by triplet carbenes has been attributed to the rehybridization of the nitrogen lone pair from nominally sp in a triplet nitrene to sp^2 in the resulting aminyl radical. The substantially greater amount of $2s$ character in the orbital occupied by the σ lone pair in a nitrene compared to that in an aminyl radical stabilizes the former, relative to the latter. Not only is the nominal change in hybridization smaller in going from a triplet carbene to an alkyl radical, but the electrons affected are all shared pairs in the bonds to carbon, rather than an unshared pair of electrons, localized on the atom that rehybridizes.

The large amount of $2s$ character in the lone pair orbital on nitrogen makes triplet nitrenes more thermodynamically stable than triplet carbenes.⁴⁰ This difference in thermodynamic stabilities is manifested experimentally not only in the weaker bonds formed in the bimolecular reactions of triplet nitrenes than in those of triplet carbenes but also in the rearrangement of all three pyridylcarbenes to **PhN** on heating.^{41a,b} This difference is also responsible for the finding that the ring expansion of **PhN** is readily reversible, whereas the ring expansion of **PhCH** is not.^{41c}

III.4. Why Is Ring Expansion Faster for PhN than PhCH? It seems paradoxical that **¹PhN** undergoes *intermolecular* reactions much more slowly than **¹PhCH**, but that the order of *intramolecular* reactivity is reversed. In agreement with the experimental evidence described above, calculations show that cyclization to the corresponding bicyclo[4.1.0]heptatriene is rate limiting in the ring expansion reactions of both **PhN** and **PhCH**.³⁷ Also in excellent agreement with experiment²² is the calculated barrier of 6 kcal/mol for the cyclization of **¹PhN** to **BA**.³⁷ However, the barrier to cyclization of **¹PhCH** is computed to be much higher, in the range of 13–15 kcal/mol.^{18,37} What accounts for this large difference in barrier heights?

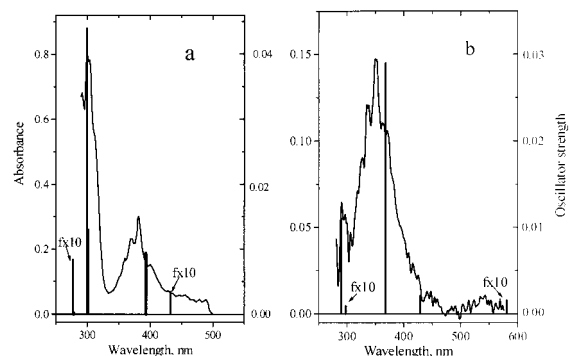


FIGURE 5. Experimental absorption spectra of (a) triplet and (b) singlet **PhN**. The computed positions and oscillator strengths (f , right-hand axes) of the absorption bands are depicted as solid vertical lines. For very small computed oscillator strengths, values multiplied by 10 are presented ($f \times 10$).

As shown in Figure 4, cyclization of singlet **PhN** requires only that the nitrogen bend out of the molecular plane, so that the singly occupied σ NBMO on it can interact with the singly occupied π NBMO.³⁷ In contrast, as also depicted in Figure 4, cyclization of **PhCH** requires changes in its electronic structure. A double bond to the exocyclic ring carbon must be created, and this requires some charge separation in the transition structure, which is energetically costly. A population analysis finds that the negative charge on the exocyclic carbon increases by $0.07e$ on going from **¹PhCH** to the transition structure for its cyclization. In contrast, the negative charge on nitrogen actually decreases by $0.02e$ between **¹PhN** and the transition structure for its cyclization.

IV. Electronic Absorption Spectra of Singlet and Triplet **PhN**

The electronic absorption spectrum of **³PhN** in low-temperature matrixes is well known.^{11,42} There is a strong sharp band at 308 nm, a broad structured band at 370 nm, and a broad unstructured feature which tails out to 500 nm (Figure 5a). The spectrum of **¹PhN** was first detected only in 1997.^{20,21} The spectrum of **¹PhN** has a sharp absorption band at 350 nm and a very weak absorption around 540 nm (Figure 5b).²² The electronic absorption spectra of **¹PhN** and **³PhN** are rather similar, but all of the bands of **¹PhN** exhibit a red-shift compared to those of **³PhN**.

The electronic absorption spectrum of **³PhN** has been computed using the semiempirical INDO method¹¹ and by *ab initio* configuration interaction calculations, with inclusion of all single and double excitations.^{30a} However, neither of these computational studies succeeded in reproducing the spectrum of **³PhN** quantitatively.

Recently, the individual absorption bands in the spectra of **¹PhN** and **³PhN** have been assigned on the basis of the CASSCF and CASPT2 calculations.²² The computed positions and intensities of the absorptions are shown in Figure 5. The agreement between the experimental and calculated spectra of **¹PhN** provides support for the assignment of the transient absorption spectrum and for the open-shell electronic structure of **¹PhN**.

The spectra of both ^1PhN and ^3PhN exhibit a strong absorption band in the near-UV region around 350 nm. Two transitions ($1^3\text{A}_2 \rightarrow 2^3\text{B}_1$ and $1^3\text{A}_2 \rightarrow 3^3\text{B}_1$) contribute to this absorption in the case of ^3PhN , but only one transition ($1^1\text{A}_2 \rightarrow 2^1\text{B}_1$) contributes to the strongest absorption band of ^1PhN . The main configurations involved in the $1^1\text{A}_2 \rightarrow 2^1\text{B}_1$ and the $1^3\text{A}_2 \rightarrow 2^3\text{B}_1$ transitions are the same and consist of excitation of an electron from the lone pair orbital on nitrogen to the singly occupied nitrogen 2p orbital that lies in the molecular plane. These transitions around 300 nm are very similar to those observed from the triplet ground states of the parent NH (336 nm),⁴³ methylnitrene (315 nm),⁴⁴ and 1-norbornylnitrene (298 nm).⁴⁵

V. Conclusions

Calculations have proven to be an important partner to experiments in the study of the chemistry of ^1PhN . For example, knowing that ^1PhN has an open-shell electronic structure is essential in order to understand the many differences between ^1PhN and $^1\text{PhCH}$. In the absence of the results of ab initio calculations on ^1PhN , it is not at all clear how the nature of the lowest singlet state would have been established.

In addition to providing explanations of known facts, calculations performed at the University of Washington have also allowed us to make predictions, which, in turn, have stimulated new experiments at The Ohio State University. For example, LFP investigations of the effects of substituents on the barrier to ^1PhN cyclizations^{34,46,47} have been undertaken to test experimentally the computational predictions⁴⁸ regarding these effects.

On the other hand, without the stimulus of the intriguing experimental differences between ^1PhN and $^1\text{PhCH}$, plus a certain amount of patient nagging from the experimentalists at OSU, it is unlikely that calculations on the electronic structure and chemistry of ^1PhN would ever have been undertaken by the computational chemists at UW. The research described in this Account thus provides an example of not only the interplay of theory and experiment but also of the synergistic interaction between computational and experimental chemists.

The research described in this Account was supported by generous grants from the National Science Foundation. N.G. acknowledges the support of the Russian Foundation for Basic Research.

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AR990030A