Laser Flash Photolysis and Computational Study of Singlet Phenylnitrene

Laser Flash Photolysis and Computational Study of Singlet Phenylnitrene

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Abstract: Laser flash photolysis (LFP, Nd:YAG laser, 35 ps, 266 nm, 10 mJ) of phenyl azide (PA) releases open-shell singlet phenylnitrene (^{1}PN). ^{1}PN has a sharp absorption band at 350 nm and a very weak absorption band at 540 nm. These bands are assigned as n_z-n_y and a mixture of 52% $\pi-n_x$ and 28% $n_x-\pi^*$ transitions, respectively, on the basis of CASSCF and CASPT2 calculations. A CASPT2 calculation of the spectrum of triplet phenylnitrene (^{3}PN) is in very good agreement with the experimental spectrum. A sharp absorption band of ^{3}PN at 308 nm and a broad, structured band at 370 nm are assigned as n_z-n_y and $\pi-\pi$ transitions on the basis of CASSCF and CASPT2 calculations. The low intensity, long wavelength band of ^{3}PN tailing to 500 nm is assigned as a mixture of $\pi-n_x$, $n_x-\pi^*$ transitions. The decay of ^{1}PN in pentane was measured as a function of temperature to obtain observed rate constants of disappearance, k_{obs}. The rate constant k_{obs} is equal to $k_R + k_{ISC}$, where k_R is the absolute rate constant of rearrangement of ^{1}PN to benzazirine and k_{ISC} is the absolute rate constant of intersystem crossing to the lower energy triplet state (^{3}PN). When it is assumed that k_{ISC} is independent of temperature, k_{obs} can be dissected, and absolute values of k_R and k_{ISC} can be deduced. For ^{1}PN, $k_{ISC} = 3.2 \pm 0.3 \times 10^6$ s^{-1} and the Arrhenius parameters for k_R are found to be $E_a = 5.6 \pm 0.3$ kcal mol^{-1} and $A = 10^{13.1\pm0.3}$ s^{-1}.

Introduction

The intermediates produced upon thermal and photochemical decomposition of phenyl azide (PA) have long been a source of fascination to both organic and physical chemists.[1] These intermediates are of intrinsic interest but have many practical applications including lithography,[2] the preparation of electrically conducting polymers[3] and the photoaffinity labeling of biomolecules.[4]

Recently, two groups have simultaneously announced the direct detection of singlet phenylnitrene (^{1}PN).[5,6] The activation parameters to cyclization of ^{1}PN to benzazirine (*A*) were reported to be $E_a = 6.2 \pm 0.4$ kcal/mol and $A = 10^{13.6\pm0.4}$ s^{-1} in pentane.[6]
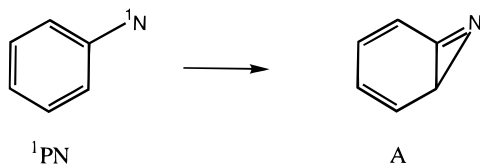
In our initial study,[6] it was not possible to directly measure the rate constant of intersystem crossing (k_{ISC}). This value was estimated, however, as 2.5×10^5 s^{-1}. Herein we are pleased to report an expanded study of the kinetics and spectroscopy of ^{1}PN. We now report revised activation parameters for cyclization of $E_a = 5.6 \pm 0.3$ kcal/mol^{-1} and $A = 10^{13.1\pm0.3}$. The absolute rate constant of ISC (k_{ISC}) has been directly determined for the first time and found to be $3.2 \pm 0.3 \times 10^6$ s^{-1}. Furthermore, the transient absorption spectrum of ^{1}PN is interpreted with the aid of modern computational methods.

Spectroscopy of Singlet Phenylnitrene

Laser flash photolysis (LFP, 266 nm, 35 ps, 10 mJ) of phenyl azide in pentane at 233 K produces the transient absorption spectra of Figure 1. Spectrum 1 (Figure 1) was measured, point by point, 2 ns after the laser pulse. Spectrum 2 was obtained with an optical multichannel analyzer 200 ns after a KrF laser pulse (249 nm, 12 ns, 50 mJ). We have previously assigned spectrum 1 to singlet phenylnitrene[6] in its lowest (open-shell)[7] electronic configuration (^{1}PN) and spectrum 2 to ketenimine K (Scheme 1).[8]

Spectrum 1 (Figure 1) was detected by measuring the kinetics of ^{1}PN using a low intensity (10 mJ) YAG laser. It depicts only the most intense absorption band of ^{1}PN. At temperatures below 170 K, the lifetime of ^{1}PN becomes sufficiently long that we can record the spectrum of this specie using a KrF laser (249

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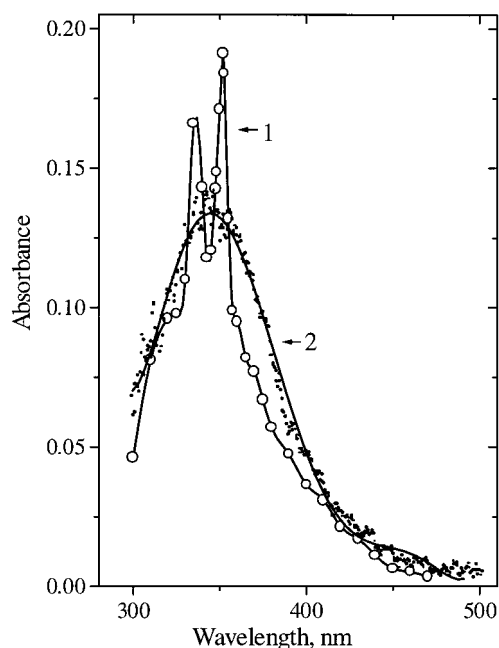
Figure 1. Transient spectra produced upon LFP of phenyl azide in pentane at 233 K. Spectrum 1 was recorded point by point, 2 ns after a laser pulse (Nd:YAG 266 nm, 35 ps, 10 mJ). Spectrum 2 was recorded with an OMA 200 ns after a laser pulse (KrF excimer, 249 nm, 12 ns, 50 mJ).

nm) and spectral averaging with an optical multichannel analyzer (OMA, Figure 2). Under these conditions (170 K, averaging), we were able to detect the strong band of Figure 1 (spectrum 1) and, in addition, a very weak, long wavelength absorption band at 540 nm. This absorption band, although weak, is reproducible and is unambiguously assigned to ^{1}PN because ^{3}PN, azepine A (Scheme 1), and the products of their reactions have no absorption at wavelengths above 500 nm.[1,9]

Quantum Chemical Calculations of the Absorption Spectra of Triplet and Singlet Phenylnitrene

The assignment of the transient absorption spectrum of Figure 1 to the open-shell singlet phenylnitrene (^{1}PN) is supported by the similarity of its spectrum to that of the longer-lived perfluorinated singlet arylnitrenes.[10] To support this assignment more strongly, we have also performed high level quantum chemical calculations of the ^{1}PN absorption spectrum.

Complete active space (CASSCF) calculations were undertaken to explore the vertical excitation spectra for singlet and triplet phenylnitrene. Additional electron correlation corrections to the CASSCF wave function (i.e., CASPT2) were also used. Twelve electrons in twelve orbitals were utilized for the CAS calculations, and the orbitals involved in the electronic transition are presented in Figure 3. The results of the CAS calculations are summarized in Table 1 (triplet PN) and Table 2 (singlet PN). We have also calculated the excited-state properties of triplet phenylnitrene, as the absorption spectrum of ^{3}PN is well-known.[8,11] These calculations will verify that our theoretical treatment is accurate and reasonable.

Triplet Phenylnitrene (^{3}PN). Wasserman and co-workers established by low-temperature EPR spectroscopy that the ground state of phenylnitrene has triplet multiplicity.[12] Figure

4 represents the electronic absorption spectrum of ^{3}PN in an EPA matrix at 77 K. 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.[8,11]

The π-system of ^{3}PN is closely related to that of the benzyl and anilino radicals. Thus, it is no surprise that the triplet absorption spectrum of ^{3}PN is very similar to the experimental spectra of the benzyl (C$_6$H$_5$CH$_2$) and anilino (C$_6$H$_5$NH) radicals.[13] Benzyl radical has a medium intensity feature at 316 nm and a very weak band at 452 nm. The anilino radical has a medium intensity band at 308 nm and a weak transition at 400 nm.

Kim et al.[7a] performed configuration interaction calculations with all single and double excitations, but they failed to reproduce the electronic absorption spectrum of triplet phenylnitrene quantitatively. Our calculations at the CASPT2[14] level predict that the vertical excitation energy to the first excited state (1^3B_1) will be at 432 nm (2.87 eV). This is in better agreement with the experimental data than that of Kim et. al. (321 nm).[7a] The improved correspondence is a result of the combination of an improved reference description and an adequate treatment of the dynamical electron correlation in the CASPT2 procedure. The calculated oscillator strength at the CASPT2 level is very small, which is also consistent with the known absorption spectrum of ^{3}PN (Figure 4). The transition consists principally of two electronic configurations. One component (49%) is the electron promotion from a π ($1a_2$) to an n_x ($3b_1$) orbital. Another contribution (25%) is the electron promotion from an n_x ($3b_1$) to a π_1* ($2a_2$) orbital.

The second excited state (T$_2$) is the 2^3A_2 state and has a vertical excitation energy of 393 nm (3.15 eV) which is associated with (47%) of $\pi(2b_1)-\pi(3b_1)$ and (27%) of $\pi(3b_1)-\pi$*($4b_1$) transitions. The excitation energy and oscillator strength are in good agreement with the experimental observations (Figure 4). Since the π system of ^{3}PN is closely related to that of the benzyl and anilino radicals, one would expect similar behavior of this T$_2$ state which is dominated by $\pi-\pi$ character. However, it should be noted that the intensity of the absorption band corresponding to the T$_2$ state is smaller in the benzyl and anilino radicals than that in ^{3}PN.[13]

^{3}PN also has a very strong absorption band in the UV region. The maximum of ^{3}PN at 308 nm exhibits a small blue shift relative to the benzyl and anilino radicals. The CASPT2 calculations predict that two states contribute to this absorption. The 2^3B_1 state has an excitation energy of 301 nm and an oscillator strengy of 0.013. The 3^3B_1 state has a transition energy of 299 nm and a larger oscillator strength (0.044). These results are in accord with the experimental spectrum. The composition of the electronic configurations for the 3^3B_1 state is the same as for the 1^3B_1 state, but the composition of the different configurations have changed considerably: 32% π ($1a_2$) to n_x ($3b_1$) and 47% from n_x ($3b_1$) to π* ($2a_2$). The transition to the 2^3B_1 state consists (79%) of electron promotion from the lone pair electron on nitrogen n_z($13a_1$) to an n_y($8b_2$) orbital. It is very

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Scheme 1

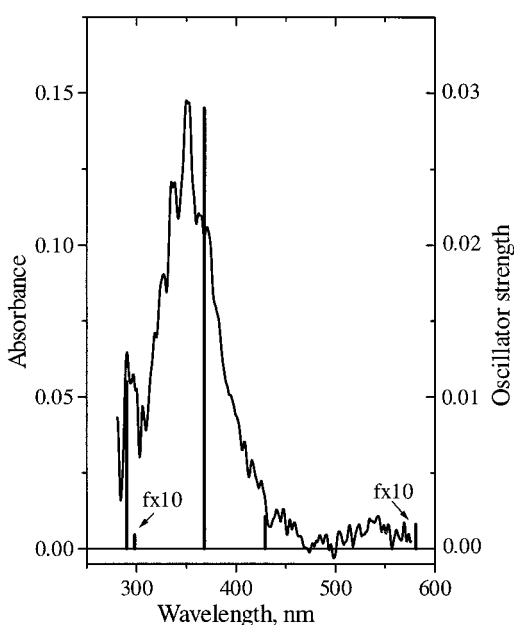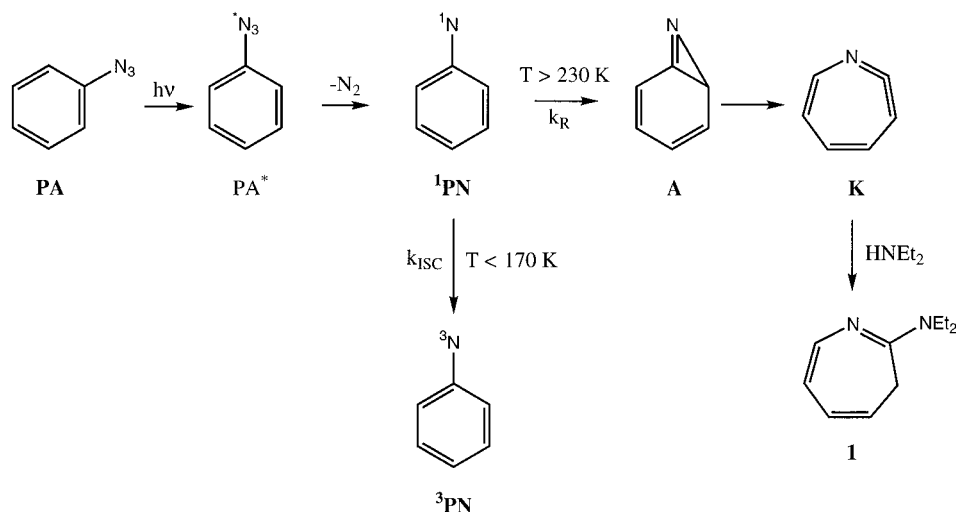**Figure 2.** The transient absorption spectrum of ^{1}PN in pentane obtained with an OMA at 150 K and averaged over six experiments. The spectrum was taken over a window of 100 ns immediately after the laser flash (KrF, 249 nm, 12 ns, 50 mJ). The calculated absorption spectrum (CASPT2) of ^{1}PN is depicted as solid vertical lines. The calculated oscillator strengths were used to depict the relative intensities of the different bands after normalization between the calculated band at 368 nm and the experimental band in that region.

similar to a transition observed with the parent nitrene, ^{3}NH, which has a 336 nm absorption band.[15] It is interesting that these two near degenerate states are largely separated in triplet perfluorophenylnitrene due to the fluorine substitution.[8,16]

In the benzyl radical there exists one absorption band between 250 and 280 nm.[13f] As we noted above, there is also a medium intensity feature at 316 nm and a very weak band at 452 nm for the benzyl radical, as well. CASPT2(11,9)[13g] calculations for the lowest 5 vertical excitation energies of the benzyl radical yield transition energies (with oscillator strengths in parentheses) of 432 (9×10^{-5}), 416 (6.5×10^{-4}), 317 (3.1×10^{-2}), 268

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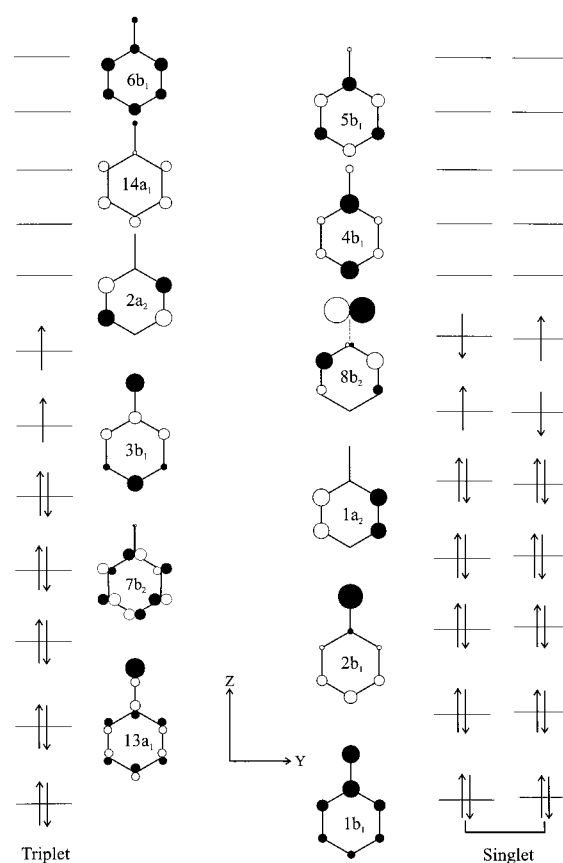

Figure 3. Orbitals involved in the electronic transitions of phenylnitrene.

(3.1×10^{-4}), and 241 nm (0.4).[13g] These data are in excellent agreement with the experimental absorption spectrum for the benzyl radical.[13]

Open-Shell Singlet Phenylnitrene (^{1}PN). The CASPT2 calculations of the absorption spectrum of ^{3}PN are in very good agreement with the experimental spectrum (Figure 4). This encouraged us to calculate the absorption spectrum of open-shell ^{1}PN in order to compare it to our experimental information. Calculations of ^{1}PN are more challenging than those of ^{3}PN because it is still an excited state of phenylnitrene relative to the triplet ground state.[7]

The orientation of electron spin has a large effect on the geometry of phenylnitrene. Via inspection of the bond lengths

Table 1. Vertical Excitation Energies of Triplet Phenylnitrene[a]

state	CASSCF, eV	CASPT2, eV	CASPT2, nm	w	osc. strength (f)
1^3A_2				0.76	
1^3B_1	3.77	2.87	432	0.75	3.4×10^{-4}
2^3A_2	3.33	3.15	393	0.74	9.4×10^{-3}
2^3B_1	4.97	4.12	301	0.76	1.3×10^{-2}
3^3B_1	6.40	4.15	299	0.67	4.4×10^{-2}
1^3A_1	5.10	4.43	280	0.76	0.0
1^3B_2	5.09	4.46	278	0.76	1.9×10^{-5}
3^3A_2	4.60	4.48	277	0.74	8.4×10^{-4}

[a] Using the CASSCF(8,8)/6-31G* geometry. Active space is (12,12)/[2262]. The basis set is a contracted ANO with N and C (4s3p1d) and H (2s1p). w is the weight of the CASSCF wave function. f is the calculated oscillator strength.

Table 2. Vertical Excitation Energies of Open Shell Singlet Phenylnitrene[a]

states	CASSCF, eV	CASPT2, eV	CASPT2, nm	w	osc. strength (f)
1^1A_2				0.76	
1^1A_1	1.19	0.77	1610	0.76	0.0
2^1A_1	2.20	1.62	765	0.76	0.0
1^1B_1	3.04	2.13	581	0.73	1.6×10^{-4}
2^1A_2	3.32	2.89	429	0.70	2.1×10^{-3}
2^1B_1	5.71	3.37	368	0.70	2.9×10^{-2}
1^1B_2	5.04	4.16	298	0.73	9.0×10^{-5}
3^1B_1	5.27	4.28	290	0.76	1.1×10^{-2}

[a] Using the CASSCF(8,8)/6-31G* geometry. Active space is (12,12)/[2262]. The basis set is a contracted ANO with N and C (4s3p1d) and H (2s1p). w is the weight of the CASSCF wave function. f is the calculated oscillator strength.
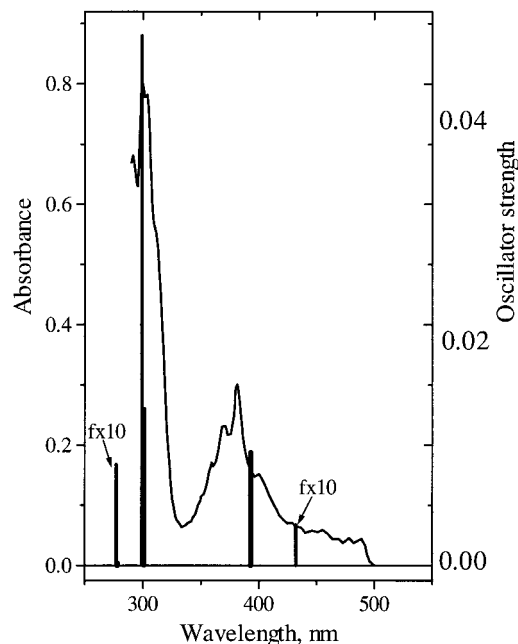

Figure 4. The absorption spectrum of ^{3}PN obtained in an EPA glass at 77 K.[8a] The calculated absorption spectrum (CASPT2) of ^{3}PN is depicted as solid vertical lines. The calculated oscillator strengths were used to depict the relative intensities of the different bands after normalization between the calculated band at 299 nm and the experimental band in that region.

of ^{3}PN and ^{1}PN,[7] we note that there is more delocalization in ^{3}PN than in ^{1}PN, as the C—C and C—N bond lengths are very similar to each other. However, the structure of ^{1}PN resembles a para-quinoidal biradical, since there is a relatively short C—N bond length and alternating long and short C—C bond lengths.

Figure 2 depicts the electronic absorption spectrum of the

1^1A_2 state of ^{1}PN. The first two electronically excited singlet states are both of A_1 symmetry (Table 2) and are calculated to be at 0.77 (1610) and 1.62 eV (765 nm). Neither of these transitions have been detected since both of these states have zero oscillator strength due to symmetry considerations, and they lie outside the wavelength range accessible to our spectrometer.

As shown above (Figure 2), the ^{1}PN absorption spectrum includes a very weak band with a maximum around 540 nm. The CASPT2 calculations (Table 2) predict an excited state (1^1B_1) with a vertical excitation energy of 581 nm (2.13 eV) and a very small oscillator strength (1.6×10^{-4}). This transition consists of 52% $\pi(1a_2)-n_x(3b_1)$ and 28% $n_x(3b_1)-\pi^*(2a_2)$. This excited state (1^1B_1) shows a large red shift (0.7 eV) as compared to the spectrum of ^{3}PN, since the configuration involved in this excited state is similar to that in ^{3}PN. This red shift is reasonable because if the configurations that compose the $^3B_1$ and $^1B_1$ states are similar, then the difference in excitation energies will simply reflect the singlet–triplet energy gap between the lowest singlet and lowest triplet states.

As in ^{3}PN, the next excited state in the singlet manifold is the 2^1A_2 state. This transition has a small oscillator strength (2.1×10^{-3}) and a 429 nm (2.89 eV) excitation energy. This corresponds to a 0.3 eV shift as compared to ^{3}PN. This electronic transition should manifest itself as a medium intensity band. In the experimental spectrum (Figure 2), however, this band seems to be a shoulder on the tail of a strong band at 350 nm.

In the ^{1}PN absorption spectrum, the only intense absorption band is localized around 350 nm (3.54 eV) which is a pronounced shift from the 308 nm band in ^{3}PN. This band has a long tail out to 450 nm and displays some fine structure that may be associated with the vibrations of the phenyl ring in ^{1}PN (Figure 1). The strongest absorption band in ^{1}PN, predicted by the CASPT2 method, is the transition to the 2^1B_1 exited state which has a 368 nm (3.37 eV) excitation energy. It is coincident with the spectroscopic observation (Figure 2). The main configuration (82%) involved in this transition is similar to the 2^3B_1 state and consists of electron promotion from an $n_z(13a_1)$ to an n_y (8b$_2$) orbital. The calculations predict that there is a large red shift (0.8 eV) in the absorption spectrum of ^{1}PN relative to ^{3}PN. The same argument advanced previously with the 1^1B_1 state might apply to this excited state as well. We should also note that there is a very large difference between the CASSCF and CASPT2 excitation energies for this state, and dynamical electron correlation is very important. The calculations indicate that the most intense absorption band is not $\pi-\pi$ in nature but instead it has n_z-n_y character. Therefore, we predict that singlet alkylnitrenes will have similar absorptions in the near UV spectral range.

The next transition with significant intensity involves the 3^1B_1 state. This transition is computed to have a large oscillator strength (1.1×10^{-2}) and a transition energy of 290 nm (4.28 eV). The contribution of the configurations is nearly identical to the 3^3B_1 state of ^{3}PN. The 3^1B_1 state has a much higher excitation energy than the 2^1B_1 state, and this feature differs from the 2^3B_1 and 3^3B_1 states.

If we compare the electronic absorption spectra of ^{1}PN and ^{3}PN, all of the calculated and experimental bands of ^{1}PN exhibit a red shift compared to those of ^{3}PN. The calculated vertical excitation energies of ^{3}PN are in excellent agreement with experiment, and the vertical energies for ^{1}PN are reasonable. The disagreement may be caused by a discrepancy between the theoretical and actual geometry of the singlet phenylnitrene. However, the agreement between the experimental and calcu-
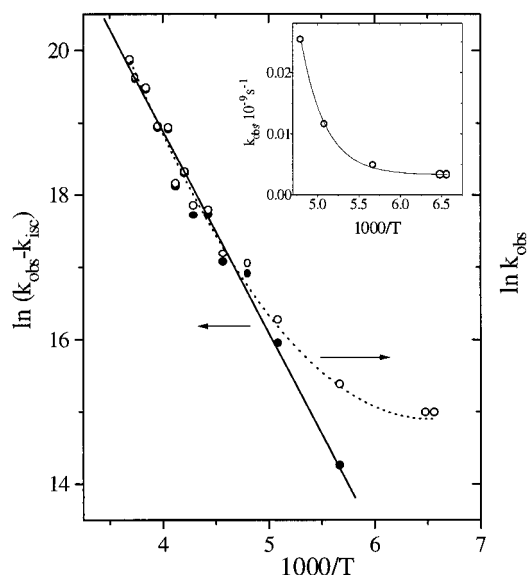
Figure 5. Arrhenius treatment of the k_{obs} data (open circles) and k_R data (filled circles) for singlet phenylnitrene deduced upon assuming that k_{ISC} is independent of temperature. Insert: temperature dependence of k_{obs} data.

lated spectra of ^{1}PN is still quite good and provides additional support of our assignment of the transient absorption spectrum (Figures 1 and 2) to ^{1}PN.

Kinetics of Singlet Phenylnitrene

Previously, the decay of ^{1}PN in pentane was monitored at 350 nm (the 540 nm band is too weak to be useful in this regard) over a temperature range of 220–270 K. We have been able to expand the range of temperature over which ^{1}PN can be studied to 150–270 K, which allows direct measurement of k_{ISC} and more accurate barriers to cyclization (vide infra). The disappearance of singlet phenylnitrene at 298 K was faster than the time resolution of the spectrometer. We estimate the lifetime (τ) of ^{1}PN to be ~1 ns under these conditions (vide infra). The lifetime of ^{1}PN is not sensitive to the presence of oxygen, in pentane, over this temperature range.

The decay of singlet phenylnitrene is exponential and can be analyzed to yield an observed rate constant k_{obs}. An Arrhenius treatment of the k_{obs} data (open circles), is presented in Figure 5. The magnitude of k_{obs} decreases with decreasing temperature until about 170 K, whereupon it reaches a value of about 3.2×10^6 s^{-1}. Below this temperature, k_{obs} remains constant.

The photochemistry of phenyl azide in the presence of diethylamine is temperature-dependent.[8] At temperatures above 230 K, ketenimine K is trapped to form azepine **1** (Scheme 1).[8,17] When phenyl azide is photolyzed below 180 K, the azepine product **1** is not produced. Instead, azobenzene **2** is formed, presumably as a result of the dimerization of triplet phenylnitrene.[1,8,17]

Given this background, it is natural for us now to identify the temperature-independent rate constant observed at low temperature as the rate constant of ISC to the triplet ground state (k_{ISC}). The rate constant k_{obs} is equal to $k_R + k_{ISC}$, where k_R is the absolute rate constant for rearrangement (see Scheme 1). As $k_{obs} = k_R + k_{ISC}$, it is possible to deduce values of k_R as a function of temperature and to obtain its associated Arrhenius parameters. The value of the temperature-independent limit was

estimated to be $k_{ISC} = 3.2 \pm 0.3 \times 10^6$ s^{-1}. An Arrhenius plot of $k_R = k_{obs} - k_{ISC}$ is linear (Figure 5, solid circles) and gives the activation energy for rearrangement $E_a = 5.6 \pm 0.3$ kcal mol^{-1} and preexponential factor $A = 10^{13.1 \pm 0.3}$ s^{-1}. The barrier to rearrangement (5.6 ± 0.3 kcal mol^{-1}) is slightly (within experimental error) smaller than the value we reported earlier (6.2 ± 0.4 kcal mol^{-1})[6] but remains in good agreement with the barrier to azirine formation calculated by Karney and Borden.[18]

The value of k_{ISC} is 3 orders of magnitude smaller than those for aryl carbenes.[19] There are at least three reasons why arylcarbenes can undergo ISC much faster than singlet phenylnitrene. The rate of a radiation-less transition increases as the energy separation between the two states goes to zero.[20] The gas-phase singlet–triplet splitting in phenylcarbene (PC) is ~4 kcal mol^{-1},[21] but it is about 18 kcal mol^{-1} in phenylnitrene.[7,18] Second, carbenes are divalent and have a bending mode with which to couple singlet and triplet surfaces, a vibration that is, of course, lacking in monovalent nitrenes. However, the most important factor is probably the electronic structure of the respective singlet intermediates. Singlet PC has a closed-shell electronic structure with one filled and one empty nonbonding orbital.[21] In such an "ionic" singlet, spin–orbit coupling (SOC) is a particularly effective mechanism of intersystem crossing.[22] Singlet phenylnitrene, on the other hand, is an open-shell singlet.[7] SOC is forbidden in this case and is ineffective in promoting ISC.

Conclusions

Laser flash photolysis (LFP, Nd:YAG laser, 35 ps, 266 nm, 10 mJ) of phenyl azide generates an intermediate with a strong, structured absorption band at 350 nm and a very weak band at 540 nm. CASPT2 calculations of the absorption spectrum of open-shell singlet phenylnitrene (^{1}PN) are in good agreement with the experimental spectrum of this intermediate. The agreement between the experimental and theoretical spectra supports our assignment of the transient absorption spectrum to ^{1}PN.

Singlet phenylnitrene (^{1}PN) decays in an exponential process which can be analyzed to yield an observed rate constant k_{obs}. The magnitude of k_{obs} decreases as the temperature is reduced, but it reaches a constant value of about 3.2×10^6 s^{-1} at temperatures below 170 K. Thus, the rearrangement (k_R) of ^{1}PN dominates at elevated temperatures, but intersystem crossing (k_{ISC}) is the preferred process at low temperature.[8,9] Therefore, k_{obs} (= $k_R + k_{ISC}$) can be dissected into k_R and k_{ISC}, assuming that ISC, a radiation-less process, is independent of temperature. Thus, we find an absolute rate constant of intersystem crossing (k_{ISC}) equal to $3.2 \pm 0.3 \times 10^6$ s^{-1} and the activation parameters are $E_a = 5.6 \pm 0.3$ kcal mol^{-1} and $A = 10^{13.1 \pm 0.3}$ s^{-1}, for rearrangement. This temperature dependence agrees with the predictions of Scheme 1 and provides additional support of our assignment of the transient as ^{1}PN.

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The excitation energies for the lowest excited valence states of ^{3}PN and ^{1}PN were computed by CASSCF and CASPT2 methods. The individual bands of the experimental spectra of ^{3}PN and ^{1}PN have been assigned on the basis of the theoretical calculations. We found that triplet phenylnitrene and ^{3}NH have similar excitation energies of their n_z–n_y transitions. This is the most intense absorption band in ^{3}PN, ^{1}PN, and ^{3}NH. Therefore, similar strong absorption bands in the near UV spectra can be predicted for singlet alkylnitrenes.

Experimental and Computational Details

Laser Flash Photolysis Methods. A Nd:YAG laser (Continuum, 35 ps, 10 mJ, 266 nm) was used as the excitation light source. The laser flash photolysis setup has previously been described in detail.[10] The time resolution of the spectrometer was about 1 ns.[10] Kinetics of transient absorption decay and growth were recorded in pentane at a temperature range 150−270 K. A typical solution was contained in a quartz cuvette which was placed in a quartz cryostat. Temperature was controlled by passing a thermostabilized nitrogen stream and kept to within ±1 K. The sample solutions were changed after every laser shot in order to avoid effects due to the accumulation of a photoproduct. Transient absorption spectra were recorded using a Nd:YAG laser source by detection kinetics in divisions of 0.5−10 nm from 300 to 500 nm. The absorption spectra of long-lived ($\tau \geq 300$ ns) intermediates were measured using an excimer KrF laser (Lumonics, 12 ns, 50 mJ, 249 nm) in conjunction with EG & G Princeton Applied Research model 1460 optical multichannel analyzer (OMA, minimal time gate of 100 ns).

Quantum Chemical Calculations. Optimized geometries of the two lowest electronic states of phenylnitrene (ground triplet state and open-shell singlet state) were taken from the CASSCF(8,8)/6-31G* study of Karney and Borden.[18] They reported an 18.5 kcal mol^{-1} (0.80 eV) T−S energy gap. Our CASPT2 calculations (using a different basis set) yield 18.7 kcal mol^{-1}.[18] The detailed orbital selection in the (8,8) active space is shown in their work.[18]

The excited-state energies for these two species were carried out by CASSCF and CASPT2 procedures in the MOLCAS program.[14] All energies are uncorrected for zero-point energy effects. The contracted basis set was an ANO basis with C and N of (4s3p1d) quality and H of (2s1p) quality. This basis set has demonstrated a satisfactory agreement with the experimental observation for the valence excited states. For the singlet and triplet states, a consistent active space (12,12)/[2,2,6,2] was chosen in the CASSCF and CASPT2 calculations where two a$_1$, two a$_2$, six b$_1$, and two b$_2$ orbitals were included (in C_{2v} symmetry). The active space was chosen in order to include the dynamical effect of the singly occupied and lone pair electrons, so that the in-plane 13a$_1$ and 7b$_2$ orbitals of phenylnitrene were involved in the active space.

CASSCF and CASPT2 calculations for the benzyl radical utilized the same basis set as above. The B3LYP/6-31G(d) procedure[23] was used to obtain the optimized geometry of the radical. The density functional theory calculations were performed with Gaussian 94.[24] Eleven electrons in nine orbitals were used for the CAS calculations which were performed with MOLCAS.

The state-averaged method was used in the CASSCF calculations for all of the excited states, and the CASPT2 calculations led to the first-order wave function and the second-order energy. The oscillator strengths (f) of the electronic transitions were obtained from the CASPT2 energy difference and CASSCF state interaction method.

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