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A Matrix Isolation Spectroscopy and Laser Flash Photolysis Study of 2-Pyrimidylnitrene

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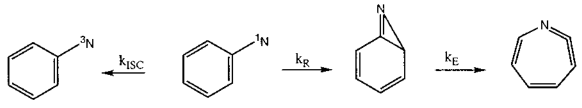
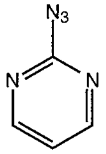
Photolysis (254 nm) of 2-azidopyrimidine (AP) in glassy ethanol (EtOH) at 77 K produces the EPR spectrum of 2-pyrimidylnitrene ($D = 1.15$ cm^{-1}) in its triplet ground state. Photolysis (254 nm) of AP in EtOH at 77 K leads to bleaching of the absorption of the azide ($\lambda_{max} = 242$ nm) and formation of a broad absorption band between 300 and 400 nm and a highly structured band between 400 and 450 nm. A more highly resolved but similar spectrum was observed by photolysis of AP in argon at 14 K. The appearance of these bands in argon is accompanied by the formation of a series of IR transitions. The experimentally observed IR spectrum was consistent with the spectrum of triplet 2-pyrimidylnitrene (^{3}PN) predicted by density functional theory with the 6-31G* basis set. The UV−vis spectrum is attributed to ^{3}PN based on the IR and EPR results. Laser flash photolysis (LFP) of AP in dichloromethane at ambient temperature produced ^{3}PN with its characteristic structured absorption between 400 and 450 nm. The triplet nitrene was formed in an exponential process ($k_{OBS} = 8 \pm 2 \times 10^7$ s^{-1}, $\tau \sim 13$ ns, $\lambda_{max} = 429$ nm) following the laser flash. The transient absorption observed at 455 nm decays with the same time constant and is attributed to singlet 2-pyrimdylnitrene (^{1}PN). Simple expectations based on anti-aromaticity arguments and density functional theory calculations agree that cyclization of singlet 2-pyrimidylnitrene to form a 1H-benzodiazirine is more endothermic than the corresponding process in unsubstituted singlet phenylnitrene if the singlet−triplet gaps of the two nitrenes are comparable. The rate constant of intersystem crossing of ^{1}PN is more than 200 times faster than that of parent singlet phenylnitrene. Cyclization of ^{1}PN to the benzo 1H-diazirine is not observed, and the hypothetical process is at least 13 times slower than that of singlet phenylnitrene to a benzazirine at ambient temperature. ^{3}PN decays over tens of microseconds in a second order process, presumably to form the azo dimer, and reacts with molecular oxygen.

I. Introduction

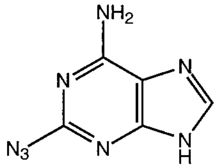
In solution at ambient temperature, singlet phenylnitrene has a lifetime, which is controlled by cyclization to benzazirine, of ~1 ns.[1,2] The experimentally determined barrier to cyclization is 5.6 ± 0.2 kcal/mol[3], in good agreement with the earlier prediction of Karney and Borden.[4] Singlet phenylnitrene relaxes to the lower energy triplet state with $k_{ISC} = 3 \times 10^6$ s^{-1}.[3] This process is unimportant at ambient temperature and becomes faster than cyclization only at temperatures below 180 K.[5]



Pyrimidines are heterocyclic building blocks of nucleic acids. Thus, it is not surprising that 2-azidopyrimidine (AP) and the closely related species 2-azidoadenine (AA) and their derivatives have been studied as photoaffinity labeling reagents.[6]

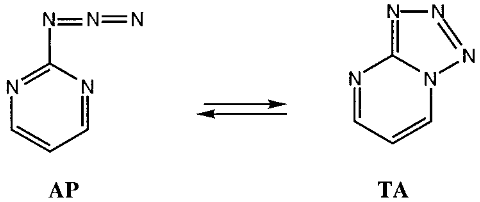


AP



AA

2-Azidopyrimidines and adenines are both in equilibrium with bicyclic heterocyclic, tetrazole (TA) compounds.[7] It occurred to us that singlet 2-pyrimidylnitrene (^{1}PN) might cyclize slowly because the 1H diazirine reaction product (AZ) is antiaromatic (Scheme 1). This might lead to an unusually long-lived singlet arylnitrene and bountiful bimolecular chemistry. This, in fact, has been observed with the closely related species 3,5 dimethylpyrimidyl nitrene.[8] Wentrup has studied the related carbodiimides by matrix spectroscopy.[9]



AP **TA**

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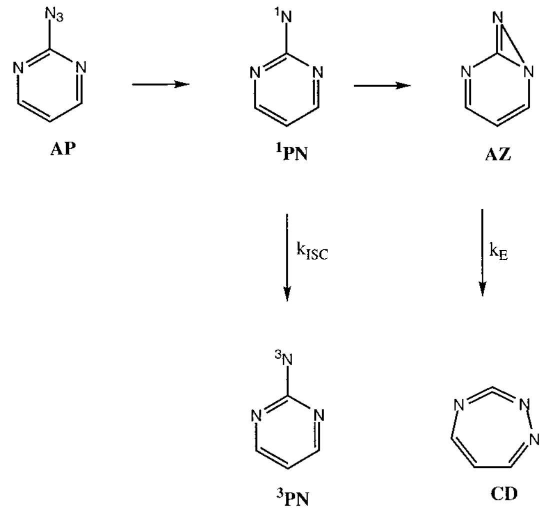
SCHEME 1



Herein we report the study of 2-pyrimidylnitrene by matrix spectroscopy and laser flash photolysis techniques. It will be shown that unlike singlet phenylnitrene, the predominant relaxation mechanism of ^{1}PN is ISC, even at ambient temperature, and that cyclization of the singlet nitrene is at least an order of magnitude slower than that of singlet phenylnitrene.

II. Experimental Section

Spectroscopy in Argon Matrix. A gaseous mixture of 2-azidopyrimidine AP (in equilibrium with tetrazole TA) and argon was directly deposited on the surface of a CsI window of a closed-cycle cryogenic system cooled by helium (Air Products). The mixture of gaseous sample was prepared by heating the solid 2-azidopyrimidine-tetrazole mixture to 60 °C in a glass U shaped tube. It is known that azide−tetrazole equilibrium favors the tetrazole in the solid phase and favors the azide form in the gas phase.[7a,c] Equilibration is complete only on the time scale of hours.[7c] Therefore, the sample deposited in the argon matrix is enriched in the tetrazole form, which has low light sensitivity.[7a,c]

The argon matrix formed was maintained at 14 K during the entire experiment. The UV−vis spectra were measured with a Lambda 6 UV−vis spectrophotometer, and the IR spectra were recorded with an FIT-IR 2000 Perkin-Elmer spectrometer with 2 cm^{-1} resolution. Ray-o-Net 254 nm lamps were used to photolyze the samples. The resulting IR and UV−vis spectra were recorded at the same time in each step.

Spectroscopy in Glassy Matrix. Solutions (5×10^{-3} M) of 2-azidopyridine in ethanol were kept at room temperature for 4−5 h prior to study to allow the azide−tetrazole mixture to come to equilibrium.[7a,c] Samples were placed in thin-walled 2 mm quartz cuvettes for UV−vis spectroscopy or into cylindrical round quartz tubes with a 4 mm diameter for EPR spectroscopy. The samples were cooled to 77 K by immersion in boiling nitrogen. Ray-o-Net 254 nm lamps were used to photolyze the samples. The photolysis of the samples and the recording of UV−vis spectra were performed in a quartz cryostat with plane-parallel windows containing liquid nitrogen. UV−vis spectra were recorded with a Lambda 6 UV−vis spectrophotometer. EPR spectra were recorded with a Bruker EMX spectrometer.

Laser Flash Photolysis. A KrF excimer laser (Lumonix, 12 ns, 50 mJ, 248 nm) was used as the excitation light source. The laser apparatus system at The Ohio State University has previously been described in detail.[10] Solutions were kept at room temperature for 4−5 h before analysis to allow the azide-tetrazole mixture to achieve equilibrium.[7a,c] A typical solution was contained in a quartz cuvette and deoxygenated prior to photolysis by purging with argon. Temperature was varied in the range of 220−295 K by passing a thermostated nitrogen stream over the sample and kept to within ±1 K. In these experiments a quartz cuvette was placed in a quartz cryostat. The sample solutions were changed after every laser shot in order to avoid effects due to the accumulation of photoproducts. The transient absorption spectra were measured using an excimer KrF laser in conjunction with an optical multichannel analyzer (EG & G Princeton Applied Research Model 1460). All spectra were averaged over 10−15 experiments.

Computational Details. The geometries of the intermediates (triplet 2-nitrenopyrimidine, diazirine, and carbodiimide) were fully optimized at the B3LYP[11] level of theory using the 6-31G* basis set. For the triplet state, an unrestricted method was utilized. The C_{2v} symmetry was maintained during the optimization of the triplet nitrene. The harmonic frequencies were calculated at the B3LYP/6-31G* level, and no imaginary frequencies were found. All calculations were performed using the GAUSSIAN 98 program.[12]

Synthesis. 2-Azidopyrimidine was prepared from 2-aminopyrimidine by the procedure of Simchen et al., developed for a related pyrimidine.[13] The azide was characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and the spectra were in agreement with those reported previously in the literature.[7c] Spectroscopic grade ethanol was used as received, but methylene chloride was purified by passage through a column of alumina and was stored over molecular sieves.

III. Results

III.1. Spectroscopy in Glassy Ethanol at 77 K. *III.1.1. EPR Spectroscopy*. 2-Azidopyrimidine (5×10^{-3} M) was dissolved in ethanol (EtOH) and the sample was cooled to 77 K by immersion in boiling nitrogen. After exposure of the sample to light (254 nm), a new resonance was observed at 7220 G, characteristic of a triplet arylnitrene[14] with $|D| = 1.15$ cm^{-1} (Figure 1). The spectrum disappeared upon warming and softening the glass.

III.1.2. UV−Vis Spectroscopy. The UV spectrum of 2-azido pyrimidine in glassy EtOH at 77 K is progressively bleached upon exposure to 254 nm radiation. As the azide spectrum disappears, a broad absorption band grows between 300 and 400 nm and a structured band appears between 400 and 450 nm (Figure 2). The newly formed spectrum disappears upon warming and softening the glass.

III.2. Argon Matrix Spectroscopy. Azido pyrimidine was deposited in an argon matrix at 14 K. The tetrazole has $\lambda_{max} =$ 270 nm; the azide has a much stronger absorption maximum at 242 nm with a shoulder at 270 nm. Thus, one cannot use argon matrix UV spectroscopy to analyze the ratio of azide to tetrazole present in the sample. The sample contains at least 10−20% azide. Typically, the azide form is more sensitive to light than the tetrazole form.[7] Brief exposure (30 s) of the matrix to 254 nm light induced changes in the UV−vis and IR spectra of the sample. The changes in the UV spectra were entirely consistent with that observed in glassy EtOH, although the resolution was superior in argon at 14 K (Figure 3).

Exposure of the sample to 254 nm light for 30 s led to the partial depletion (~50%) of the IR spectrum of azide AP and the appearance of the IR spectrum of photoproducts (Figure 4A). Because of the sensitivity of ^{3}PN to light, it was not

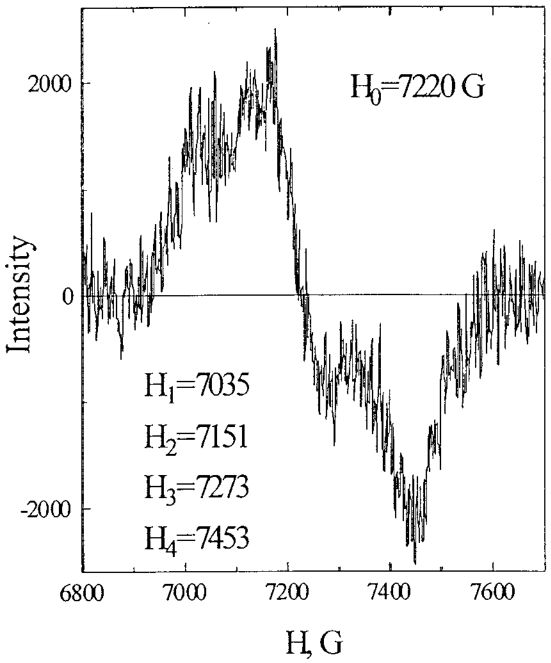


Figure 1. The EPR spectrum of ^{3}PN produced upon 254 nm photolysis of AP in glassy ethanol at 77 K.

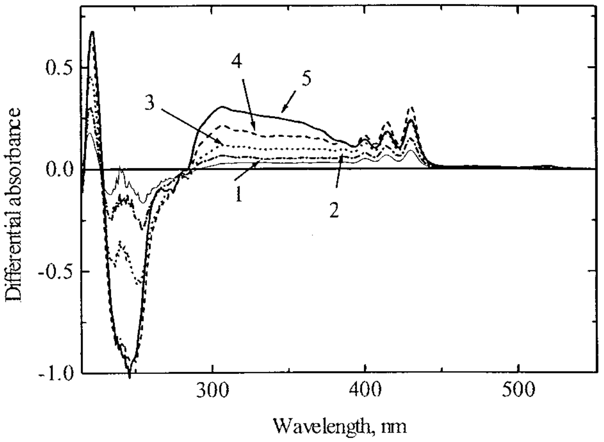


Figure 2. Changes in the UV−vis spectrum induced upon 254 nm photolysis of PA in glassy EtOH at 77 K: (1) 10 s, (2) 20 s, (3) 40 s, (4) 80 s, and (5) 180 s of photolysis.

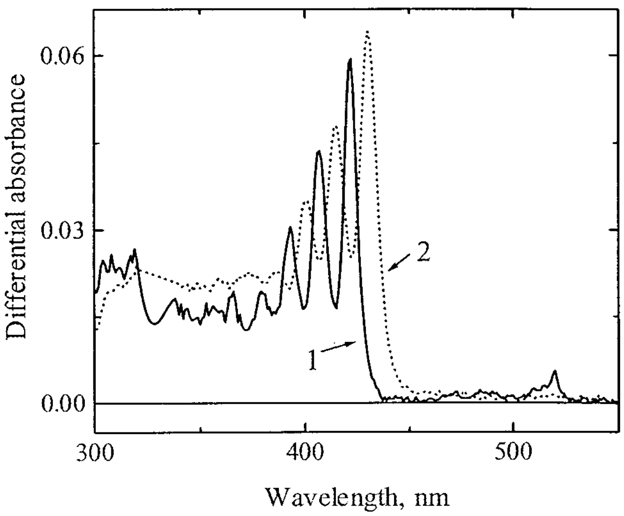


Figure 3. The differential absorption spectra of ^{3}PN obtained by 254 nm photolysis of AP in (1) argon 14 K for 30 s and (2) glassy EtOH at 77 K for 10 s.

possible to completely convert azidopyrimidine to the triplet nitrene. Density functional theory (DFT) calculations on ^{3}PN utilizing the 6-31G* basis set predict the spectrum shown in Figure 4B. The IR spectrum of ^{3}PN, calculated at this level is in excellent agreement with the experimental spectrum, after scaling by 0.97. The bands observed at 1593, 1720, and 1970 cm^{-1} are not attributed to ^{3}PN and are presently unassigned. These peaks are not consistent with the calculated spectrum of the corresponding benzo 1H-diazirine. The currently unassigned IR bands in Figure 4A may be related to the heterocyclic tetrazole (TA), which is in equilibrium with 2-azidopyrimidine, or to its photoproducts.

Upon continued exposure of ^{3}PN to 254 nm light, the IR spectrum of the triplet nitrene and the unidentified species disappear and a new band appears at 2045 cm^{-1}, which is assigned to carbodiimide (CD, Scheme 1, Figure 5, inset) on the basis of DFT calculations and by analogy to Wentrup's studies.[9] According to the B3LYP/6-31G* calculations, the most intense band in the IR spectrum of CD should be observed at 2046 cm^{-1}, in very good agreement with experiment. As the 2045 cm^{-1} IR band is formed, a broad UV band with $\lambda_{max} = 350$ nm is formed concurrently (Figure 5) which is also attributed to carbodiimide CD.

III.4. Laser Flash Photolysis. Laser flash photolysis of AP produces the transient spectrum shown in Figure 6 (spectrum 1). The transient spectrum bears obvious resemblance to the spectrum recorded in EtOH at 77 K (Figure 6, spectrum 2) and is attributed to ^{3}PN.

Transient absorption at 429 nm grows exponentially following the laser pulse (Figure 7, curve 1). Analysis of the exponential growth yields $k_{OBS} = 8 \pm 2 \times 10^7$ s^{-1} at 295 K and $k_{OBS} = 3 \pm 1 \times 10^7$ s^{-1} at 220 K. There is a decay of transient absorption at 455 nm (Figure 7, curve 2) following the laser pulse. The species absorbing at 455 nm decays with the same observed rate constant as the growth of the species absorbing at 429 nm (Figure 7).

The species absorbing at 429 nm decays over hundreds of microseconds (Figure 8) in a nonexponential process. Its decay is accelerated by the presence of oxygen (Figure 9). A very rough estimation of the triplet nitrene absolute rate constant of reaction with oxygen is $k_{O2} \sim 3 \times 10^6$ M^{-1} s^{-1}. The identity of the weakly absorbing species that is formed and then decays at 480 nm is not known.

IV. Discussion

EPR spectroscopy demonstrates that 2-pyrimidylnitrene (PN), as per parent phenylnitrene, has a triplet ground state. This is not surprising considering the large (18 kcal/mol)[15−17] singlet−triplet splitting of phenylnitrene. Several peaks in the IR spectrum obtained in argon at 14 K are confidently assigned to ^{3}PN on the basis of the agreement of the experimental and calculated IR spectra. The minimum energy geometries of ^{3}PN, AZ, and CD calculated by DFT theory and their relative energies are given in the Supporting Information. The geometry of AZ is particularly interesting. To avoid an anti-aromatic electronic structure, the N−N bond of the diazirine is extremely long (1.749 Å).

As the UV−vis spectrum between 400 and 500 nm is observed under the same conditions as the EPR and IR studies; the carrier of this spectrum is also assigned to ^{3}PN. The structured absorption between 400 and 500 nm of ^{3}PN is considerably more prominent than absorption bands of triplet phenylnitrene in the visible region of the spectrum.

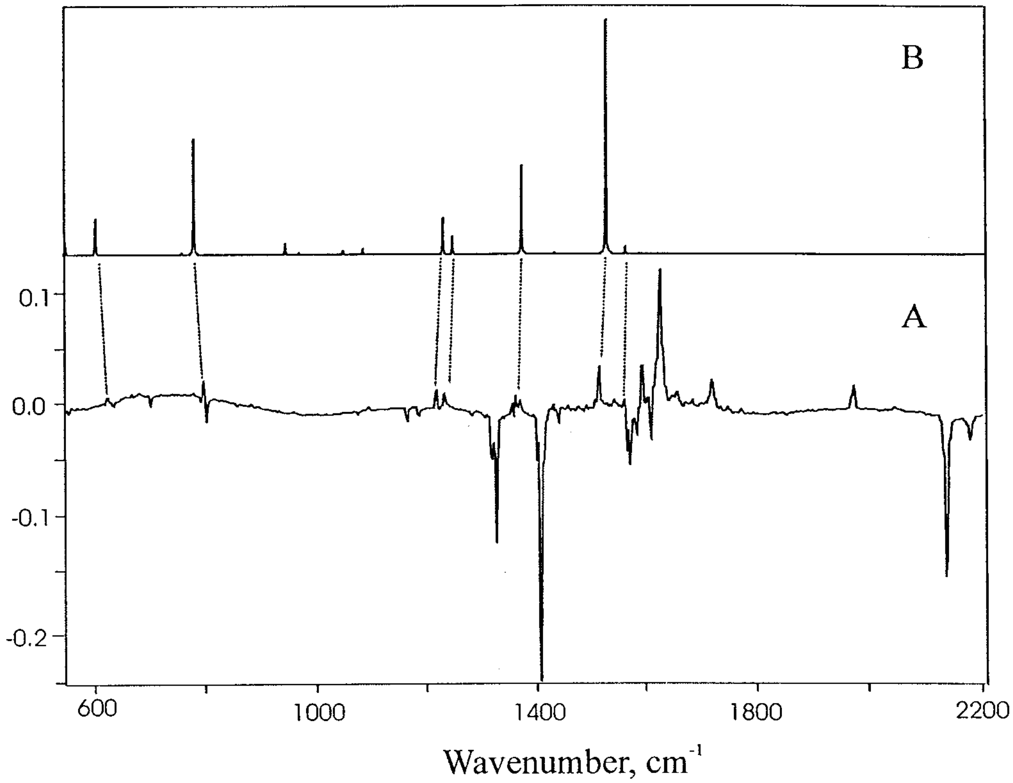


Figure 4. The differential IR spectrum produced by exposure of AP in argon at 14 K to 254 nm light for 30 s (A). Negative peaks are due to the disappearance of the azide. Positive peaks are due to photoproducts. The IR spectrum of ^{3}PN is calculated (B) using density functional theory.

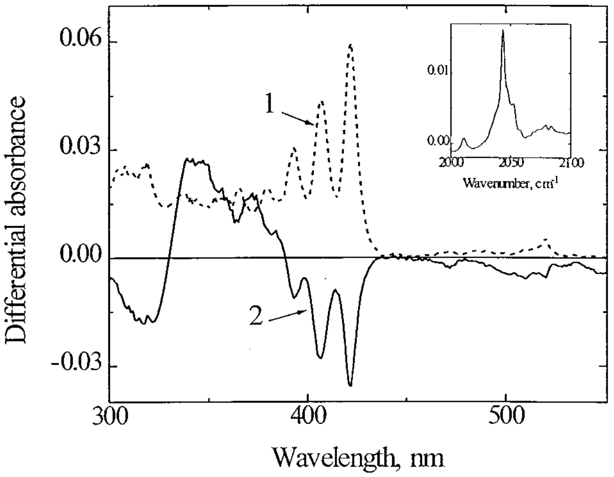


Figure 5. Differential electronic absorption spectrum obtained after 30 s irradiation (1) and difference between spectra after 2 and 1 min (2) of irradiation of 2-azidopyrimidine in an argon matrix at 14 K. Inset: differential IR spectrum for the same conditions as (2).

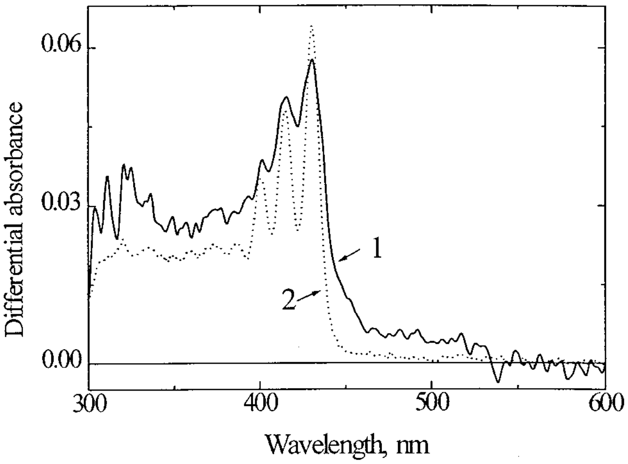


Figure 6. (1) The transient spectrum produced by LFP of AP recorded 50 ns after the laser pulse over a 200 ns window and (2) the spectrum of ^{3}PN in glassy EtOH at 77 K.

Laser flash photolysis (LFP) of 2-azidopyrimidine generates transient absorption between 400 and 500 nm which is assigned to triplet pyrimidylnitrene (^{3}PN) on the basis of matrix spectroscopy. As expected, the triplet nitrene decays in solution by a second order process, most likely dimerization, to form an azo compound. The triplet nitrene also reacts with oxygen. Triplet PN reacts a thousand times more slowly with oxygen than does a triplet carbene. This effect has been noted before[18] and can be attributed to the influence of lone pair-lone pair repulsion between the nitrene nitrogen and molecular oxygen.

Transient absorption at 455 nm decays with the same observed rate constant as the formation of triplet PN at 429 nm. Thus, the 455 nm transient is assigned to singlet PN. We have noted previously that the spectra of singlet and triplet phenylnitrene are similar because they have the same open shell electron configurations.[3] The absorption maximum of singlet phenylnitrene (350 nm) is shifted to a wavelength 42 nm longer than the absorption maximum of triplet phenylnitrene (308 nm).[3] Thus, the fact that singlet PN absorbs at a wavelength 26 nm longer than triplet PN is not surprising.

We originally predicted that singlet pyrimidylnitrene would cyclize more slowly than singlet phenylnitrene due to the antiaromaticity of the diazirine product AZ, (Scheme 1) expected in the former case. DFT calculations (B3LYP/6-31G*) quantitatively confirm this. The benzazirine derived from cyclization of phenylnitrene is calculated to be 19.6 kcal/mol higher in energy than triplet phenylnitrene. The 1H-benzodiazirine obtained by cyclization of 2-pyrimidylnitrene is calculated to be 28.7 kcal/mol above triplet PN. The calculations predict that

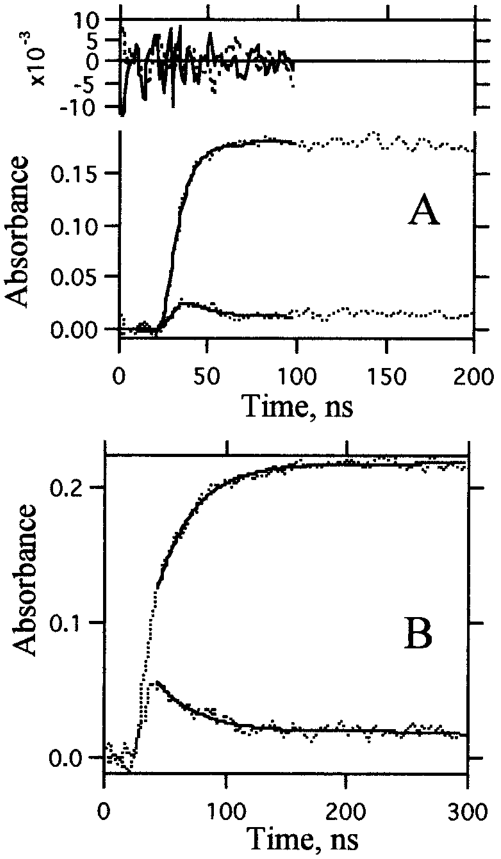


Figure 7. Kinetic traces obtained by LFP of AP at (A) 295 K and (B) 220 K. Growth curves were measured at 429 nm and decay curves were measured at 455 nm.

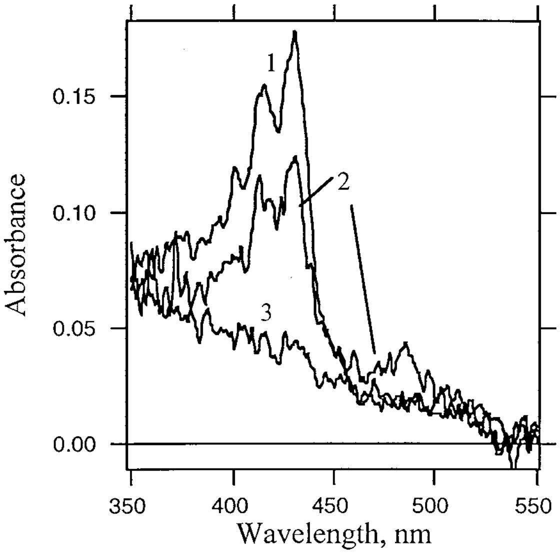


Figure 8. Transient absorption produced by LFP of AP in CH_2Cl_2 at 295 K (1) 50 ns (2) 1 μs and (3) 50 μs after the laser pulse.

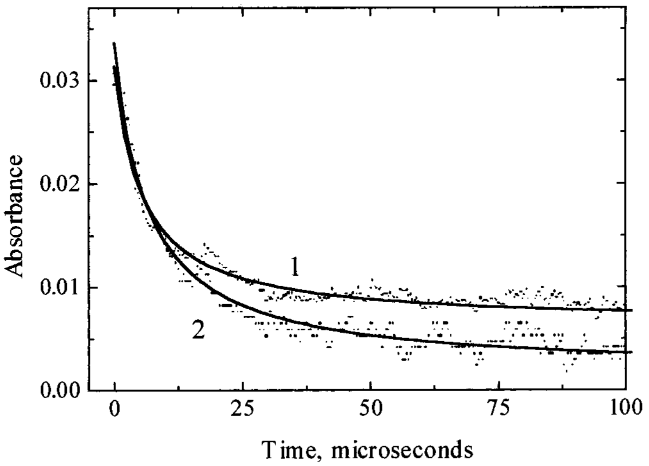
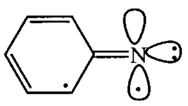
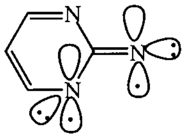


Figure 9. The decay of transient absorption measured at 429 nm in the (1) absence and (2) the presence (~2 × 10^{-3} M) of oxygen. The sample was flashed with 248 nm light in CH_2Cl_2 at 295 K. Solid lines are the best fit using equations for bimolecular reaction 1 and bimolecular and monomolecular reactions 2.

cyclization of ^{1}PN will be more endothermic than that of parent singlet phenylnitrene if the singlet−triplet gaps of phenyl and pyrimidylnitrene are comparable. This will clearly lengthen the singlet nitrene lifetime and explains why pyrimidylnitrenes can be trapped in solution[8] and singlet phenylnitrene cannot.[1,2,19] The rate retardation is at least a factor of 13 at ambient temperature. The rate factor is surely much greater than 13 as we cannot measure the rate of the cyclization process, which is too slow to compete with ISC, the dominant process in methylene chloride solution. The intersystem crossing rate of singlet pyrimidyl nitrene is 200 times faster than that of singlet phenylnitrene.[3] We have found previously that electron donating groups greatly accelerate ISC in singlet arylnitrenes but electron accepting groups provide only modest enhancement of ISC.[20] Normally, the pyrimidyl nitrogens will be considered an electron attracting substituent, thus an acceleration of ISC was not anticipated.

Singlet phenylnitrene has a quinoidal biradical structure.





The analogous singlet PN structure will place considerable spin density on the pyrimidyl ring nitrogens. We speculate that enhanced spin−orbit coupling of pyrimidyl nitrogen (relative to carbon) due to its greater nuclear charge, and the ^{14}N hyperfine interaction may contribute to the increased rate of ISC in this nitrene.

Experiments are in progress with pyridyl nitrenes to examine the effect of a single nitrogen, and its position, on the rate of ISC of the corresponding singlet nitrene.

V. Conclusions

Photolysis (254 nm) of 2-azidopyrimidine (AP) in glassy ethanol at 77 K produces the EPR spectrum of 2 pyrimidyl nitrene ($D = 1.15$ cm^{-1}) in its triplet ground state. Photolysis (254 nm) of AP in ethanol at 77 K leads to bleaching of the absorption of the azide ($\lambda_{max} = 242$ nm) and formation of a broad absorption band between 300 and 400 nm and a highly structured band between 400 and 450 nm. A more highly resolved spectrum was observed by photolysis (30s) of AP in argon at 14 K. The appearance of these bands in argon is accompanied by the formation of a series of IR transitions. The experimentally observed IR spectrum was consistent with the spectrum of triplet 2-pyrimidylnitrene predicted by density functional theory with the 6-31G* basis set. The UV−vis spectrum is attributed to ^{3}PN based on the IR and EPR results. Laser flash photolysis (LFP) of AP in dichloromethane at ambient temperature produced ^{3}PN with its characteristic structured absorption between 400 and 450 nm. The triplet nitrene was formed in an exponential process ($k = 8 \pm 2 \times 10^7$ s^{-1}, $\tau \sim 13$ ns, $\lambda = 429$ nm) following the laser flash. Transient absorption observed at 455 nm decays with the same time constant and is attributed to singlet 2-pyrimidylnitrene (^{1}PN). The rate constant of intersystem crossing of ^{1}PN is more than 200 times faster than that of parent singlet phenylnitrene. ^{3}PN decays over tens of microseconds in a second order process, presumably to form the azo dimer, and reacts with oxygen.

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Supporting Information Available: The geometries of ^{3}PN, AZ, and CD calculated by DFT at the B3LYP level are provided along with the relative energies of these species. This material is available free of charge via the Internet at http://pubs.acs.org.

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