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A Laser Flash Photolysis and Computational Chemistry Study of 9-Anthrylnitrene

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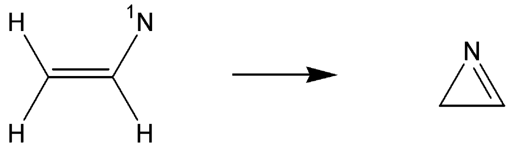
Laser flash photolysis (LFP) of 9-azidoanthracene produces singlet 9-anthrylnitrene (^{1}**AN**) with $\lambda_{max} = 331$, 344, and 412 nm. The lifetime of ^{1}**AN** is 17 ns at 77 K and is 27 ns at ambient temperature and is controlled by intersystem crossing (ISC) to the lower energy triplet state. The rapid rate of ISC of ^{1}**AN** relative to singlet phenylnitrene is due to the small (5.3 kcal/mol, CASPT2 (14,14)) calculated singlet−triplet separation of the large delocalized nitrene. There is no evidence of cyclization of ^{1}**AN** to form a bridgehead azirine (**AZ**) species. This observation is in agreement with calculations that indicate that the conversion of ^{1}**AN** to **AZ** is endothermic by 23 kcal/mol.

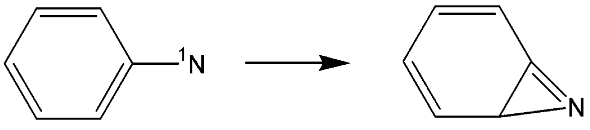
I. Introduction

Singlet vinylnitrene (^{1}**VN**) has never been directly detected and has no known bimolecular chemistry. It is not clear if ^{1}**VN** is a species with a finite lifetime or whether it cyclizes to azirine in a barrierless process.[1]



^{1}**VN**

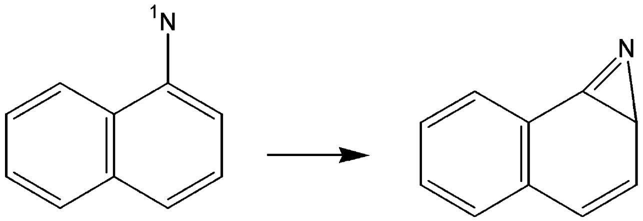
Singlet phenylnitrene (^{1}**PN**) has a lifetime of 1 ns at ambient temperature. ^{1}**PN** decays by cyclization to benzazirine over a barrier of 5.6 kcal/mol.[2]



^{1}**PN**

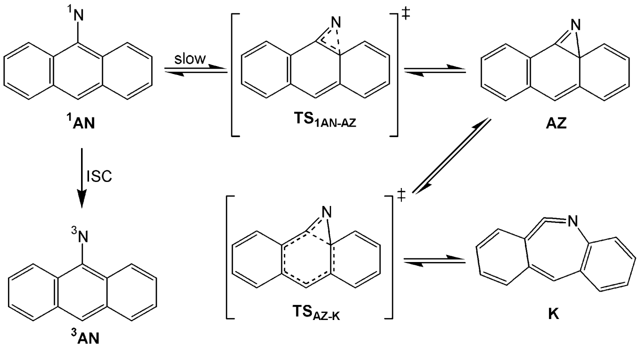
The barrier in ^{1}**PN** is due to the greater strain in benzazirine relative to azirine which lowers the exothermicity of the reaction. Cyclization of ^{1}**PN** also leads to loss of aromaticity in the six-membered ring.

One can extend this reasoning to the 1- and 2-naphthylnitrenes (^{1}**NN**). As the aromaticity of a naphthylnitrene, per ring, is less than that of a benzene ring, one predicts that 1- and 2-^{1}**NN** will cyclize at a rate intermediate between ^{1}**VN** and ^{1}**PN**.



^{1}**NN**

SCHEME 1



Cyclization of singlet 9-anthrylnitrene (^{1}**AN**), however, must proceed at a bridgehead position and dearomatize two rings when forming azirine **AZ** (Scheme 1). Thus, intuition suggests that ^{1}**AN** may cyclize rather slowly.

Our studies of the naphthylnitrenes will be reported elsewhere. Herein, we are pleased to report our studies of 9-anthrylnitrene and direct observation of this singlet nitrene.

II. Experimental Section

Laser Flash Photolysis. A Nd:YAG laser (Spectra Physics LAB-150-10, 266 nm, 5 ns, 50 mJ) was used as the excitation light source. The spectrometer has been described in detail elsewhere.[3] Typically, solutions were prepared in dry spectroscopic grade solvents to an optical density (OD) of about 1.5−2.0 at the excitation wavelength (266 nm). For low-temperature LFP experiments, the temperature was maintained at 77 K by suspending the sample in boiling liquid nitrogen. In these experiments, a quartz cuvette was placed in a quartz cryostat. The sample solutions were changed after every laser shot, unless otherwise indicated.

Computational Chemistry. To estimate the singlet−triplet splitting of 9-anthrylnitrene, the geometries of the singlet and triplet states of this nitrene were fully optimized using the CASSCF method[4] with the standard 6-31G* (5D) basis set.[5] A (14,14) or (12,12) active space was employed. This consists of one 2p AO of the nitrogen atom and all π-MOs except the first or first two lowest π-MOs and highest π^*-MOs, respectively. The effects of including dynamic electron correlation were

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determined by CASPT2/6-31G* (5D) calculations[6] for CASSCF optimized geometries with CASSCF wave functions as a reference.

To compute the potential energy surfaces for the ring-expansion of singlet 9-anthracenylnitrene ^{1}**AN**, geometries of the stationary points involved were fully optimized using the B3LYP[7] method with the 6-31G* (6D) basis set. Vibrational frequencies were calculated to analyze the nature of stationary points (minimum or transition state) and were used to account for ZPE differences. Single-point energies were then calculated using the B3LYP/6-311+G(2d,p) method[8] with B3LYP/6-31G* optimized geometries. The broken symmetry DFT calculations (UB3LYP method with mixed HOMO and LUMO to destroy the spatial symmetry) were initially used for the calculations of the transition state ($\mathbf{TS_{1AN-AZ}}$) connecting an open-shell singlet nitrene (^{1}**AN**) and a closed-shell intermediate (**AZ**). These TS calculations, performed with the STQN (QST2) method,[9] are the same as those employed in the related calculations for ring-closure of singlet phenylnitrene (^{1}**PN**).[10] However, unlike the calculations for ring-closure of ^{1}**PN** whose TS has significant open-shell character ($\langle S^2\rangle = 0.24$),[10] the wave function for $\mathbf{TS_{1AN-AZ}}$ reverted to restricted DFT in the midpoint of the QST2 transition state search and the $\langle S^2\rangle$ value was 0.00. Note that an internal instability can be tested for the DFT wave function of the closed-shell $\mathbf{TS_{1AN-AZ}}$.

Due to the open-shell character of singlet 9-anthrylnitrene ^{1}**AN**, the DFT method failed to correctly estimate its chemical properties. Thus, the following method was used to obtain the full potential energy surface for the rearrangement of ^{1}**AN**. At first, the DFT energies for those stationary structures relative to triplet 9-anthrylnitrene ^{3}**AN**, denoted as ΔE_{DFT}, were computed at the (U)B3LYP/6-311+G(2d,p)//(U)B3LYP/6-31G* level with the correction of unscaled (U)B3LYP/6-31G* ZPE differences. The calculated energies for the stationary structures relative to singlet 9-anthrylnitrene ^{1}**AN**, denoted as $\Delta E_{\mathrm{DFT/CASPT2}}$, were derived by subtracting ΔE_{ST} from ΔE_{DFT}.

Time-dependent DFT (TD-DFT) calculations[11] of ^{3}**AN**, azirine **AZ**, and ketenimine **K** were performed at the B3LYP/6-31G* level of theory.

Both CASSCF and CASPT2 calculations were carried out with MOLCAS version 5.0,[12] while the B3LYP calculations were carried out with GAUSSIAN 98.[9]

Materials. Pentane, 3-methylpentane, and pyridine (Aldrich) are spectroscopic grade and were used as received. Diethyl ether and *n*-butyl lithium in hexane solution were used as received. THF was refluxed over sodium and distilled under argon prior to use. Commercially available 9-aminoanthracene (Aldrich) was used without further purification. *p*-Toluenesulfonyl azide was prepared as described in the literature.[13]

9-Azidoanthracene.[14,15] 1.135 g (5.88 mmol) of 9-aminoanthracene was added to a predried two-necked round-bottom flask and dissolved in 20 mL of anhydrous THF. The solution was cooled in an ice bath and purged with argon. A 4.0 mL solution of 1.5 M *n*-butyl lithium (6.0 mmol) in *n*-hexane was slowly added to the THF solution and was stirred for an additional period of 10 min (dark-red color solution). An amount of 1.161 g (5.88 mmol) of *p*-toluenesulfonyl azide was dissolved in 20 mL of dry THF and was slowly added to the reaction solution. The reaction mixture was stirred with cooling with an ice bath for 1 h (green mixture), and then brought to room temperature. After addition of 50 mL of water, the mixture was extracted with 100 mL of diethyl ether. The ethereal extract was washed successively with 2 N HCl and water. The dry ethereal solution was concentrated under reduced pressure to remove the solvent, the residue was purified by passage through a silica gel column with hexane, and the product was recrystallized in methanol under dry ice to give 135 mg (10% yield) of 9-azidoanthracene as a yellow solid: mp 53−54 °C; IR (CCl_4, BaF_2) 2117.4 cm^{-1}.

TABLE 1: Calculated Absolute Energies (Hartrees) of Triplet 9-Anthracenylnitrene ^{3}AN and Singlet−Triplet Energy Gap (ΔE_{ST}, kcal/mol) of This Nitrene by CASSCF and CASPT2 Methods with the 6-31G* Basis Set

method[a]	^{3}**AN**	ΔE_{ST}
CASSCF(12,12)//CASSCF(12,12)	−589.936419	7.45
CASSCF(14,14)//CASSCF(12,12)	−589.957544	9.02
CASSCF(14,14)//CASSCF(14,14)	−589.959416	9.41
CASPT2(12,12)//CASSCF(12,12)	−591.725975	5.97
CASPT2(14,14)//CASSCF(12,12)	−591.732172	5.82
CASPT2(14,14)//CASSCF(14,14)	−591.731654	5.27

[a] The reference weights of the CASSCF wave functions for all CASPT2 calculations are found to be 0.61−0.62.

III. Results and Discussion

III.1. Computational Results. 1-, 2-, and 9-anthracenylnitrenes have triplet ground states as do phenylnitrene and the naphthylnitrenes. This was demonstrated by recording the electronic spectra[14,16−19] and EPR spectra[14,20] of triplet 1-, 2-, and 9-anthracenylnitrenes in organic matrixes at 77 K. The D parameters of these nitrenes were determined to be 0.65, 0.75, and 0.47 for 1-, 2-, and 9-anthracenylnitrenes, respectively. Compared to the *D* values of phenylnitrene (1.00) and 1- and 2-naphthylnitrene (0.79, 0.89−0.93), the smaller *D* value of anthracenylnitrenes demonstrates the increased delocalization and average separation of the two unpaired electrons.[14,20] The 9-isomer has the smallest *D* value of the three anthracenylnitrenes, demonstrating that the 9-position is the better conjugating position.

Singlet anthracenylnitrenes are expected to intersystem cross to their ground triplet states and to cyclize to form azirines much like the singlet naphthylnitrenes. Thus, it is no surprise that the product distributions observed upon photolysis of 2-azidoanthracene in the presence of nucleophiles resemble those formed upon photolysis of 2-azidonaphthalene[21,22] and provide evidence for the intermediary of azirine and triplet nitrenes. To our knowledge, the photochemistry of 9-azidoanthracene in solution has not been explored by chemical analysis of reaction mixtures. Hypothetical cyclization of singlet 9-anthracenylnitrene ^{1}**AN** must involve a bridgehead carbon to form an azirine intermediate **AZ** with a particularly high energy (Scheme 1).

The singlet−triplet splitting (ΔE_{ST}) of 9-anthracenylnitrene was predicted by the CASSCF and CASPT2 methods with the 6-31G* basis set. In principle, these calculations should have been performed with an active space of (16,16), which consists of 15 π MOs plus one in-plane 2p MO on the nitrogen atom. However, this calculation is too large to perform with our resources. In practice, active spaces of (14,14) and (12,12) were employed, for which the first or first two highest π* and lowest π MOs were excluded, respectively. The calculated values of ΔE_{ST} obtained in this manner are given in Table 1.

Inspection of the data in Table 1 reveals that the CASSCF ΔE_{ST} calculated values are very sensitive to the size of the active space; however, the ΔE_{ST} from corresponding CASPT2 calculations agree well with one another. Thus, multireference perturbation theory (CASPT2) is able to correct for some deficiencies associated with an incomplete active space and the CASPT2 ΔE_{ST} value can be considered to be reliable.

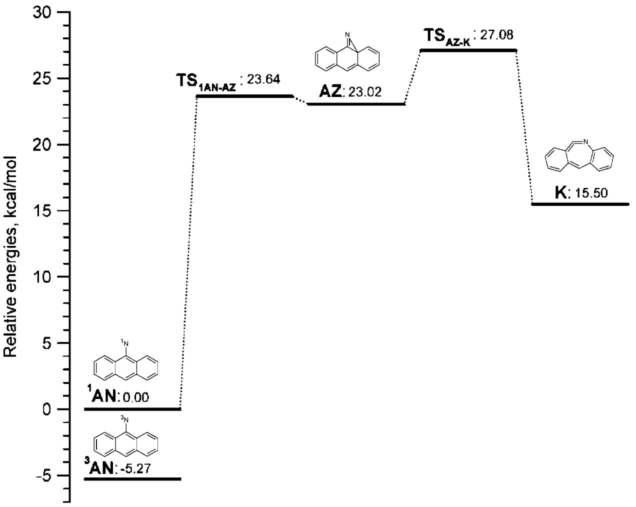

Figure 1. DFT/CASPT2 energies relative to singlet 9-anthrylnitrene **^{1}AN** for species involved in the rearrangement of **^{1}AN**.

TABLE 2: Calculated CASPT2, DFT, and DFT/CASPT2 Relative Energies (kcal/mol) for Singlet 9-Anthrylnitrene ^{1}AN, Triplet 9-Anthrylnitrene ^{3}AN, and Stationary Species Involved in the Ring-Expansion Reactions of ^{1}AN

species	ΔE_{CASPT2}[a]	ΔE_{DFT}[b]	$\Delta E_{DFT/CASPT2}$[c]
^{1}AN	0.00		0.00
^{3}AN	−5.27	0.00	−5.27
TS_{1AN-AZ}		28.91	23.64
AZ		28.29	23.02
TS_{AZ-K}		32.35	27.08
K		20.77	15.50

[a] CASPT2(14,14)/6-31G*//CASSCF(14,14)/6-31G* relative energy. [b] (U)B3LYP/6-311+G(2d,p)//(U)B3LYP/6-31G* + ZPE energies relative to **^{3}AN**. [c] $\Delta E_{DFT/CASPT2} = \Delta E_{DFT} - \Delta E_{ST}$.

The best value of ΔE_{ST} of 9-anthracenylnitrene is 5.3 kcal/mol which is obtained from CASPT2(14,14) calculations. The magnitude of ΔE_{ST} of 9-anthracenylnitrene is less than one-third of that calculated for phenylnitrene (19.5 kcal/mol) and less than one-half of that of 1-naphthylnitrene (13.9 kcal/mol).[23] The smaller ΔE_{ST} value calculated for 9-anthracenylnitrene is most likely due to a greater delocalization of one of the singly occupied MOs of **^{1}AN** relative to the smaller **^{1}PN** and **^{1}NN** systems, and consequently reduced electron−electron repulsion which results from enlarging the π system.

For comparison purposes, ΔE_{ST} of 9-anthracenylnitrene was also studied by DFT at the UB3LYP/6-311+G(2d,p)//UB3LYP/6-31G* level. The broken symmetry calculations of singlet nitrene **^{1}AN** was found to have an $\langle S^2 \rangle$ value of ~1.0 and its energy ($E_{50:50}$) is best interpreted as a 50:50 mixture of triplet E_T and singlet E_S.[10,24] Thus, the UB3LYP ΔE_{ST} can be deduced from eq 1 by doubling the energy difference between **^{3}AN** and a broken symmetry **^{1}AN**. This led to a UB3LYP ΔE_{ST} value of 7.2 kcal/mol (Supporting Information). The UB3LYP method overestimates the ΔE_{ST} of 9-anthracenylnitrene by 1.9 kcal/mol relative to the CASPT2 calculations.

$$\Delta E_{ST} = \Delta E_T - \Delta E_S = 2(E_T - E_{50:50}) \qquad (1)$$

where $E_{50:50} = (E_T + E_S)/2$

The potential energy surface of the rearrangement of singlet 9-anthracenylnitrene **^{1}AN** was estimated using DFT methods combined with CASPT2 ΔE_{ST} as described in the Experimental Section. The DFT and DFT/CASPT2 relative energies for stationary species involved in the rearrangement of **^{1}AN** are given in Table 2, and the calculated potential energy surface is illustrated in Figure 1.

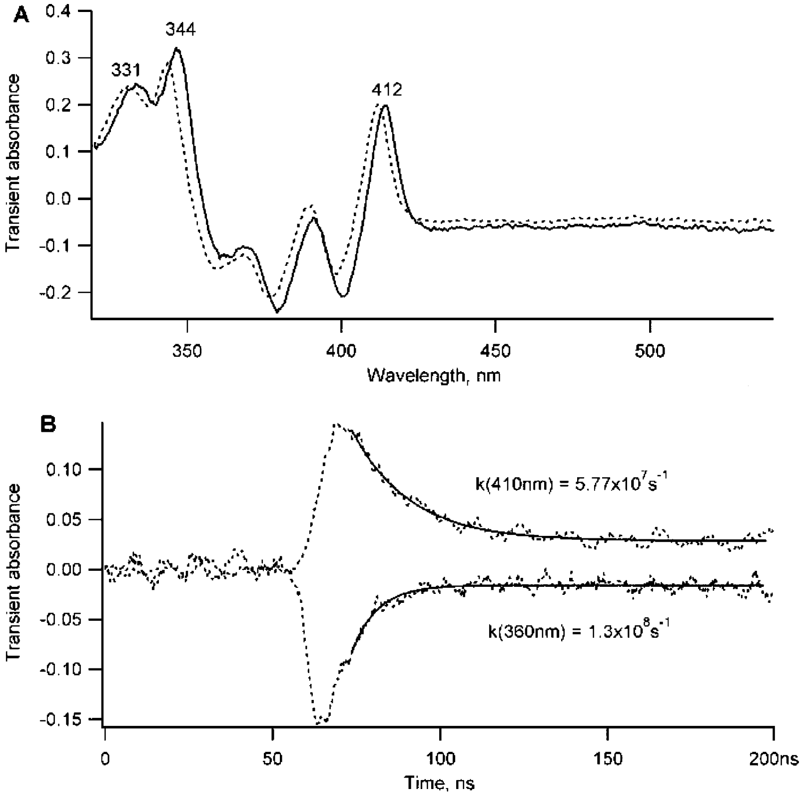

Figure 2. (A) Transient absorption spectra detected over a window of 20 ns following LFP (266 nm) of 9-azidoanthracene in glassy 3-methylpentane at 77 K just after (solid line) and 1 μs after (dashed line) the laser pulse; (B) kinetic traces for the disappearance of singlet 9-anthracenylnitrene **^{1}AN** monitored at 410 nm and the recovery of transient absorption at 360 nm.

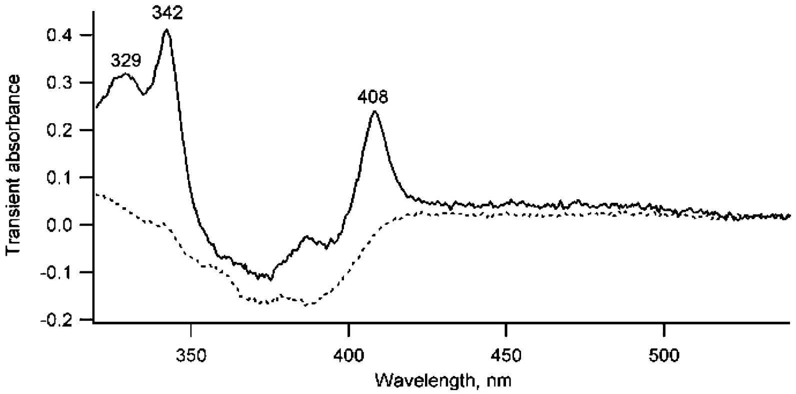

Figure 3. Transient absorption spectra detected over a window of 10 ns following LFP (266 nm) of 9-azidoanthracene in pentane at ambient temperature immediately after (solid line) and 20 μs after (dashed line) the laser pulse.

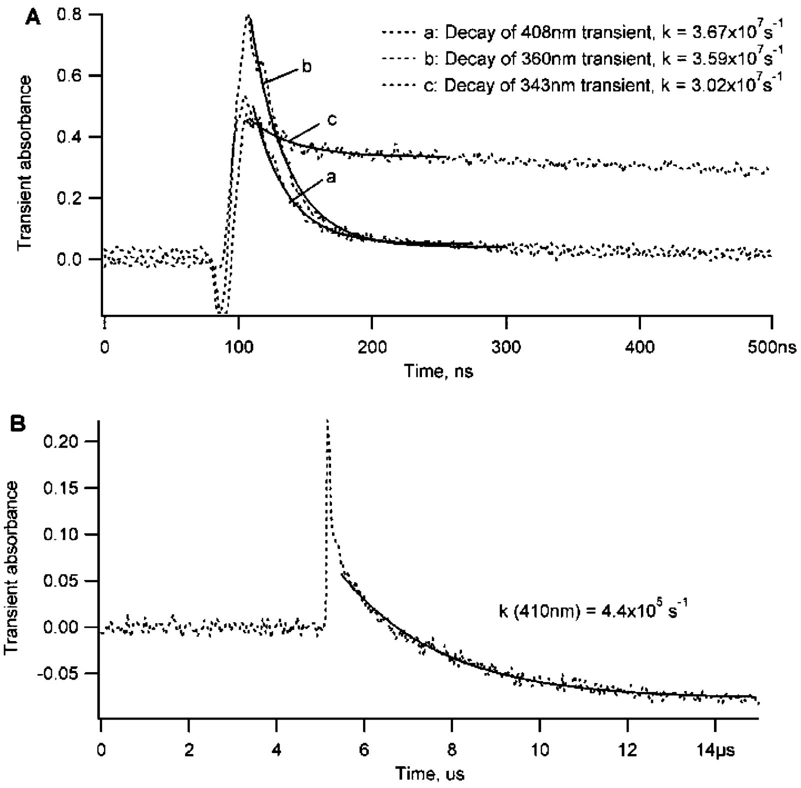

Figure 4. Changes in transient absorption as a function of time (A) at 408, 360, and 343 nm on the nanosecond time scale, and (B) at 410 nm on the microsecond time scale, following LFP (266 nm) of 9-azidoanthracene in pentane at ambient temperature.

Theory predicts that the cyclization of singlet 9-anthracenylnitrene ^{1}**AN** to form azirine **AZ** is endothermic by 23 kcal/mol, and the barrier to cyclization of ^{1}**AN** is 23.6 kcal/mol. This is just what one would expect from naive extrapolation of the chemistry of 1-naphthylnitrene and its cyclization toward its bridgehead carbon.[23] Anthrylazirine **AZ**, once formed, is predicted to revert back to singlet nitrene ^{1}**AN** over a negligible (0.6 kcal/mol) barrier, in preference to the ring-expansion reaction to form ketenimine **K**, a process with a calculated barrier of 4 kcal/mol. Ketenimine **K** is not likely to be formed as it is 15.5 kcal/mol higher in energy than singlet nitrene ^{1}**AN**.

III.2. LFP Results. Laser flash photolysis (LFP, 266 nm, 5 ns, 50 mJ) of 9-azidoanthracene in glassy 3-methylpentane at 77 K produces the transient absorption spectra of Figure 2A. The observed transient spectra exhibit absorption maxima at 412, 344, and 331 nm, at various delays after the laser pulse. The transient absorption, monitored at 410 nm (Figure 2B), decays exponentially with a time constant of about 17 ns. The spectrum observed 1 μs after the laser pulse is consistent with the persistent spectrum of ^{3}**AN** recorded by Alvarado et al.,[14] in ethanol−ether glass at 77 K. Since triplet 9-anthrylnitrene is known to be a persistent species under the conditions of this study,[14] the observation of a decay trace most likely corresponds to intersystem crossing from singlet to triplet 9-anthrylnitrene at 77 K. Thus, we conclude that $k_{ISC} = (5.8 \pm 0.1) \times 10^7$ s^{-1} for 9-anthrylnitrene at 77 K. Singlet 9-anthrylnitrene ^{1}**AN** must have a UV−Vis absorption spectrum similar to, but with larger molar extinction coefficients (ϵ), at 340 and 410 nm relative to the triplet nitrene ^{3}**AN**.

Singlet and triplet phenylnitrenes are reported to have strong absorption bands at 350 and 308 nm, respectively,[2] and the absorption maxima of 1-naphthylnitrene have been observed at

397, 383, and 362 nm for the singlet nitrene, and 362 and 347 nm for the triplet nitrene.[23] The longest wavelength absorption maxima of 9-anthrylnitrene is longer than that of 1-naphthylnitrene and phenylnitrene, which demonstrates the effect of conjugation of the extended π system.

Rapid recovery of the transient absorption at 360 nm was observed at 77 K (Figure 2B). This process takes place within the time resolution of the instrument, and is attributed to luminescence.

The rapid rate of ISC of ^{3}**AN** is similar to that of singlet 1-pyrenylnitrene,[25] ($\tau = 22$ ns, benzene, ambient temperature; 34 ns, 77 K, 1:1 methylcycohexane/isopentane), another highly delocalized nitrene.

At ambient temperature, transient absorption bands are observed around 410, 340, and 330 nm (Figure 3). The decay of the transient absorption monitored at 410 nm was biphasic. The faster process has a first-order rate constant of 3.6×10^7 s^{-1}, and the slower process has a first-order rate constant of 4.4×10^5 s^{-1} (Figure 4). The former process can be attributed to intersystem crossing, which is a little slower, but still close to the value observed at 77 K in a rigid environment. The lifetime of ^{1}**AN** at ambient temperature is 27 ns. The slow process is assigned to the disappearance of triplet nitrene ^{3}**AN**, which also absorbs at 410 nm. On the basis of Rigaudy's studies[21,22] of triplet 2-anthrylnitrene, we expect that triplet nitrene ^{3}**AN** decay produces 9-aminoanthracene and the corresponding azo dimer.

LFP studies of phenyl azide provided direct observation of the corresponding ketenimine species, which has a characteristic broad and intense UV−vis absorption at 340 nm.[2] In the case of 9-azidoanthracene, the TD-DFT calculations predict that ketenimine **K** will absorb UV−vis light strongly at 545, 393, 325, and 321 nm, and azirine **AZ** will have strong UV−vis absorption at 436, 390, and 313 nm (Supporting Information). However, the LFP experiments involving 9-azidoanthracene provide no evidence of the formation of azirine or ketenimine intermediates. This is consistent with theoretical predictions of a very high barrier to cyclization of singlet 9-anthracenylnitrene ^{1}**AN**.

Singlet nitrene ^{1}**AN** has a short lifetime because it rapidly undergoes intersystem crossing (ISC) to its ground triplet state ^{3}**AN**. ISC in ^{1}**AN** is much faster than in ^{1}**NN** (1.1×10^7 M^{-1} s^{-1}) and ^{1}**PN** (3.8×10^6 M^{-1} s^{-1}) at 77 K.[23] This is attributed to the small singlet−triplet energy gap (~5.3 kcal/mol) of anthracenylnitrene relative to ^{1}**NN** (13.9 kcal/mol)[23] and ^{1}**PN** (19.5 kcal/mol) calculated at the same level of theory[23,26] which results from the extensive delocalization of one of the singly occupied MOs and a reduction in the electron−electron repulsion of the two unpaired electrons which contributes to the singlet−triplet energy separation. Finally, we note that laser flash photolysis of 9-azidoanthracene in the presence of pyridine did not produce detectable transient absorption of a pyridine−nitrene ylide.

IV. Conclusions

As predicted by extrapolation of the properties of the naphthylnitrenes,[23] the barrier to cyclization of singlet 9-anthracenylnitrene ^{1}**AN** is computed to be very large. The lifetime of ^{1}**AN** is ~27 ns in pentane at ambient temperature, corresponding to intersystem-crossing (k_{ISC}) to the lower energy triplet state. The larger rate constant of intersystem crossing (k_{ISC}) of 9-anthracenylnitrene relative to phenylnitrene and the naphthylnitrenes is due to the much smaller singlet−triplet splitting (5.3 kcal/mol) of 9-anthrylnitrene which reflects the extensive delocalization of the nitrene π system and consequently, reduced electron−electron repulsion.

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Supporting Information Available: Computational data including Cartesian coordinates of optimized geometries, electronic and zero-point vibrational energies, vibrational frequencies and TD-DFT absorption maxima and oscillator strengths.

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