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Flash Photolysis of the Naphthyl Azides with UV−Vis and IR Detection of Intermediates

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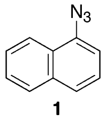
Laser flash photolysis (LFP) of 1-naphthyl azide in glassy 3-methylpentane at 77 K produces singlet 1-naphthylnitrene (362, 383, 397 nm), which relaxes to the lower energy triplet nitrene with $k_{isc} = (1.1 \pm 0.1) \times 10^7$ s^{-1}. LFP of 2-naphthyl azide under the same conditions fails to produce the corresponding singlet nitrene presumably due to rapid ($k \geq 10^8$ s^{-1}, 77 K) isomerization to an azirine. LFP of 1- and 2-naphthyl azides at ambient temperature produces the expected azirines which were detected by time-resolved infrared spectroscopy (1728 cm^{-1} from 1-naphthylnitrene; 1724 cm^{-1} from 2-naphthylnitrene) with lifetimes of 3.2 and 150 μs, respectively. Absolute bimolecular rate constants of reaction of the azirines with diethylamine in solution at ambient temperature were determined.

I. Introduction

Naphthylnitrenes can be generated by thermolysis or photolysis of the appropriate azide.[1,2]



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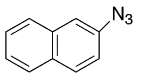

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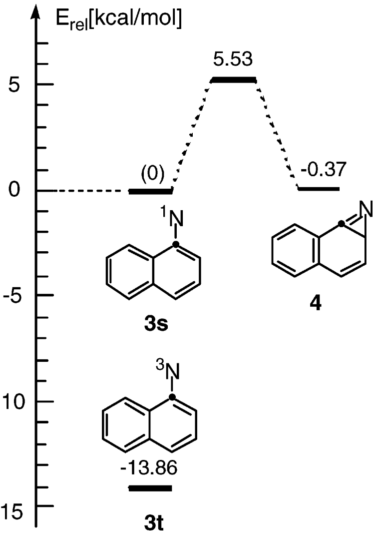
Upon extrapolation of the chemistry of phenylnitrene, one expects that singlet naphthylnitrenes can intersystem cross (ISC) to their ground triplet states or undergo cyclization reactions to form azirines (Schemes 1 and 2). However, the kinetic and thermodynamic properties of these intermediates, relative to their analogues generated from phenyl azide, are altered due to the extended aromatic ring in the naphthyl system.

Like phenylnitrene, the ground states of 1- and 2-naphthylnitrenes have triplet multiplicity. This was demonstrated by the observation of the EPR spectra of triplet 1- and 2-naphthylnitrene in organic matrixes at liquid-nitrogen temperature.[3] The *D* parameter of 1-naphthylnitrene (0.789 cm^{-1}) is much smaller than that of phenylnitrene (0.998 cm^{-1}). The originally reported *D* value of 2-naphthylnitrene (1.0083 cm^{-1}) seems rather high. More recent values of 0.89 and 0.925 cm^{-1} are more reasonable.[3] These results are consistent with the increased delocalization of one of the two unpaired electrons into the π electronic system of triplet naphthylnitrene, relative to phenylnitrene. The persistent UV−vis spectrum of triplet nitrene **3t** was first obtained by Reiser and co-workers upon photolysis of 1-naphthyl azide **1** in an organic matrix at 77 K.[4,5] This group reported that the electronic spectrum of **3t** has absorption maxima at 321 ($\epsilon = 4.0$) and 536 ($\epsilon = 3.2$) nm. The matrix UV−vis spectrum of **3t** is very similar to the absorption spectrum of the 1-naphthylaminyl radical,[6] presumably due to the similarity of the π-system of **3t** to that of the 1-naphthylaminyl radical. The Reiser group subsequently measured the quantum yield ($\phi = 0.95$ at 77 K) of photolysis of **1** and reported absolute rates of the dimerization and hydrogen-abstraction reactions of **3t**.[7] It was reported that the dimerization of **3t** was close to diffusion-controlled with a bimolecular rate constant of ~5×10^8 M^{-1} s^{-1} in solvents such as cyclohexane, benzene, and ethanol. In contrast, the hydrogen-abstraction reaction of **3t** was found to be a comparatively slow process. For example, the observed rate constant of this process with a tertiary C−H bond is only 3×10^3 M^{-1} s^{-1}.

SCHEME 1: CASPT2//CASSCF(12,12)/6-31G* Energies Relative to 3s Corrected with the CASSCF Zero-Point Vibrational Energy Differences[17]



The products obtained upon pyrolysis and photolysis of the naphthyl azides were first reported in the 1970s and 1980s.[8−14] In 1974, the Suschitzky group discovered that the thermal decomposition of 1- and 2-naphthyl azides (**1** and **2**) in bromobenzene yields significant amount of dibenzo[*a*,*h*]phenazine. The photolytic decomposition of 2-naphthyl azide **2** in diethylamine (DEA) leads to a diamine product, but photolysis of 1-naphthyl azide **1** in DEA produces mostly azonaphthalene and aminonaphthalene in low yields[8] and a very low yield of diamine adduct.[11] In 1975, Carroll et al. found that the yield of diamine product is sensitive to the photolysis time. A drastic

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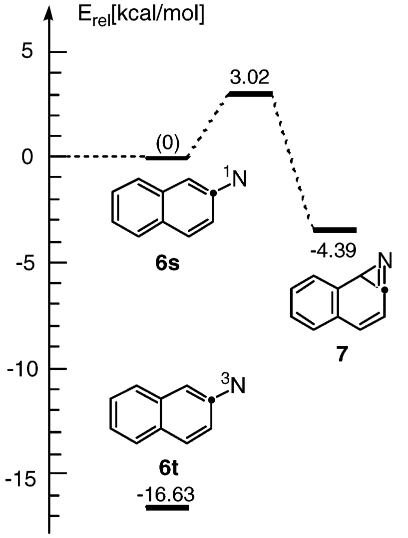
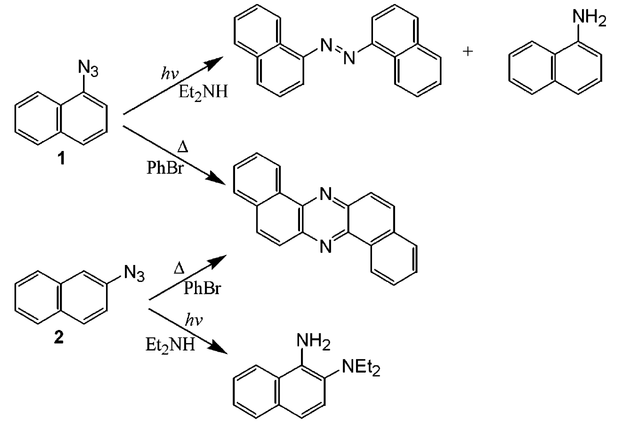
SCHEME 2: CASPT2//CASSCF(12,12)/6-31G* Energies Relative to 6s Corrected with the CASSCF Zero-Point Vibrational Energy Differences[17]



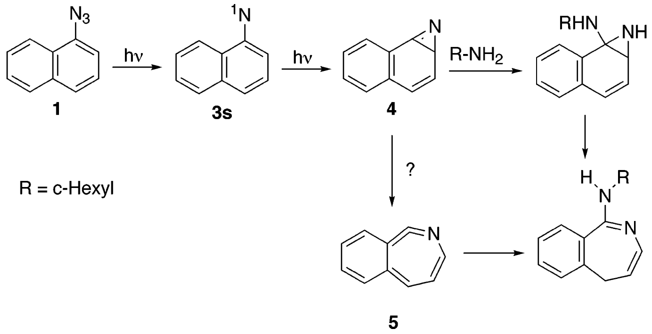
reduction in photolysis time leads to a much-improved yield of the diamine.[9]



In 1977, Suschitzky's group[10] discovered that the yield of diamine products formed on photolysis of the naphthyl azides can also be significantly influenced by the presence of (Me$_2$NCH$_2$)$_2$ (TMEDA) as cosolvent. TMEDA was found to improve the yield of diamine adducts upon photolysis of both **1** and **2** in piperidine, presumably due to the formation of a coordinated complex of TMEDA and singlet nitrene.[10] It was proposed that this complex suppresses intersystem crossing to the triplet nitrene and equilibrates with the corresponding singlet nitrene which leads to the formation of singlet derived products. Interestingly, TMEDA apparently catalyzes the isomerization of azirine **4** to **7**, the azirine derived from singlet 2-naphthylnitrene **6s**.

Leyva and Platz demonstrated that reaction temperature plays an important role as well in the photochemistry of 1-naphthyl azide.[11] Moderate yields of adducts were observed by simply lowering the temperature of the photolysis of **1** with DEA.

Although photolysis of **1** and **2** in the presence of secondary amine did not lead to detectable azepine products, a formal azepine adduct was observed (12% yield) upon photolysis of **1** in cyclohexylamine, a primary amine.[13] However, the putative azepine **5** has never been observed and it has been suggested that this product is obtained by the trapping of **4** followed by rearrangement of the initially formed adduct.[14]



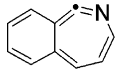
The photoproduct studies mentioned above suggest the intermediacies of azirines and didehydroazepines in the photochemistry of 1- and 2-naphthyl azides. Additional evidence of these intermediates were provided by the observations of adducts in the photolysis of 2-naphthyl azide with ethylthiol[12] and with methanolic methoxide.[14]

In 1980, Dunkin and Thomson obtained infrared evidence for azirines and didehydroazepines by UV-irradiation (λ > 330 nm) of 1- and 2-naphthyl azides in nitrogen or argon matrixes at 12 K.[15] The IR bands at 1708−1736 cm^{-1} formed on initial photolysis were assigned to tricyclic azirines, and the IR bands at 1910−1930 cm^{-1}, formed on secondary photolysis of the tricyclic azirines, were attributed to didehydroazepine intermediates.

In 1984, Schrock and Schuster comprehensively examined the photochemistry of the naphthyl azides using a combination of product analysis, low-temperature spectroscopy, and LFP methodology.[16] In the case of 1-naphthyl azide, no transient absorption above 350 nm was observed immediately after the laser flash. However, the transient absorption spectrum of triplet nitrene **3t** (λ_{max} = 370 nm) was observed a few microseconds after the laser pulse. The intensity of the transient absorption of the triplet nitrene increased exponentially with a time constant of 2.8 μs in benzene at ambient temperature. Triplet nitrene **3t** disappeared within 100 μs accompanied by the concurrent formation of 1,1′-azonaphthalene, which absorbs strongly at 420 nm. The formation of the azo compound exhibits second-order kinetics with a rate constant of 1×10^9 M^{-1} s^{-1}. The precursor to triplet nitrene **3t** was assigned to tricyclic azirine **4** (Scheme 1), a species that serves as a reservoir for singlet 1-naphthylnitrene **3s**. However, the latter species was not directly observed in this study.

Similar results were obtained from the photolysis of 2-naphthyl azide, **2**, except that in this case the transient absorption of triplet nitrene **6t** was too weak to permit its direct observation and the formation of 2,2′-azonaphthalene was found to be approximately 20 times slower than that of 1,1′-azonaphthalene. Thus, it was concluded that the corresponding azirine **7** (Scheme 2) formed upon photolysis of 2-naphthyl azide **2** has a much longer lifetime than the azirine **4** produced by photolysis of 1-naphthyl azide **1**, and that the difference in the lifetimes of these azirines is the key to understanding the profound difference in the photochemistry between 1- and 2-naphthyl azides.[16]

Very recently, Maltsev et al. reinvestigated the photochemistry of 1- and 2-naphthyl azides in Ar matrixes.[17] This study allowed them to assign the UV−vis and IR spectra of triplet nitrenes, **3t** and **6t**, the azirines **4** and **7**, and those of novel ring expansion products, the cyclic ylides derived from **5** and **8**.



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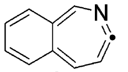

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These authors also provided a comprehensive study of the potential energy surfaces on which the above compounds undergo their rearrangements. The part of the CASSCF/CASPT2 calculations that are relevant to the present work is reproduced in Schemes **1** and **2**. Singlet nitrene **3s** cyclizes selectively at the β carbon. The azirine derived from cyclization at carbon 9 is predicted to be very high in energy.[17] Thus, the azirine isomerization process proposed by Carroll et al.[10] more reasonably explains the product mixture than the mechanism posited by Leyva and Platz.[11]

In this work, we are pleased to report the first detection of singlet 1-naphthylnitrene **3s** by laser flash photolysis (LFP) of azide **1** at 77 K with UV−vis detection, and direct measurement of the intersystem crossing rate constant k_{isc}. We also report the first spectroscopic observation of azirines **4** and **7** in solution by LFP of the naphthyl azides with IR detection.

II. Experimental and Computational Methods

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 laser spectrometer is described elsewhere.[18] 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 means of 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.

Time-Resolved Infrared (TRIR) Studies. A Nd:YAG laser (Coherent Infinity XPO/OPO, 266 nm, 40 Hz repetition rate, 0.6−0.9 mJ/pulse) was used as the excitation light source, and a reservoir of sample solution (10 mL of a 5 mM solution of 1-naphthyl azide **1** or 2-naphthyl azide **2** in acetonitrile with or without diethylamine) was continually circulated between two calcium fluoride salt plates with a 0.5 mm path length. The TRIR spectrometer is described in detail elsewhere.[19]

Materials. 3-Methylpentane and acetonitrile (Aldrich) are spectroscopic grade and were used as received. Diethylamine (DEA) was refluxed over calcium hydride and distilled under argon prior to use. Commercially available 1- and 2-aminonaphthalene (Aldrich) were used without further purification. 1-Naphthyl azide (**1**) and 2-naphthyl azide (**2**) were prepared by decomposition of the corresponding diazonium chlorides with sodium azide.[16,20,21]

Theoretical Calculations. Geometries of singlet naphthylnitrenes **3s** and **6s** and triplet naphthylnitrenes **3t** and **6t** were fully optimized at the CASSCF(12,12)/6-31G* level of theory.[22] The (12,12) active space included eleven π and π^* MOs plus the in-plane 2p AO of the nitrogen atom. On the basis of these CASSCF/6-31G* optimized geometries, the vertical excitation energies of the naphthylnitrenes were computed using the CASSCF and CASPT2 procedures[23] with the ANO−S basis set (4s3p1d for N and C and 2s1p for H).[24] These excited-state calculations involved nine A″ and five A′ transitions. The state-averaged method was used in the CASSCF calculations for all of the excited states, and the oscillator strengths (*f*) of the electronic transition were computed from the CASPT2 energy difference and CASSCF state interaction method. To eliminate intruder states in the CASPT2 calculations of the excited states, a level shift of 0.3 h had to be applied.[25] These computational results are summarized in Tables S1−S4 in the Supporting Information. All CASSCF and CASPT2 calculations were performed with the MOLCAS 5.0 suite of programs.[26]

III. Results and Discussion

1-Naphthylnitrene. The cyclization of 1-naphthylnitrene **3s** toward the β-carbon to form azirine **4** is predicted to be slightly exothermic (−0.37 kcal/mol), and to involve a barrier of 5.53 kcal/mol, according to CASPT2 calculations. However, CASPT2[23] calculations were found to overestimate the barrier to cyclization of phenylnitrene by ∼3 kcal/mol.[27] If one assumes that the calculations on the naphthylnitrenes suffer from a similar error, then the barrier to cyclization of **3s** can be estimated to be 2.5 kcal/mol.[27] The barrier for cyclization of 1-naphthylnitrene would then be significantly smaller than that determined by analogous LFP experiments with singlet phenylnitrene (5.8 kcal/mol).[28]

Calculations predict that singlet 1-naphthylnitrene **3s** will have weak absorptions at 593 and 534 nm, and intense absorptions at 400, 371, 348, 342, and 315 nm (See Supporting Information Table S1). All of the intense bands involve $\pi-\pi^*$ excitations. The absorption spectrum of triplet nitrene **3t** has strong absorption bands at 536 and 321 nm.[4,5,17]

Laser flash photolysis (LFP, 266 nm, 5 ns, 50 mJ) of 1-naphthyl azide **1** in glassy 3-methylpentane at 77 K produces the transient absorption spectra of Figure 1A. A short-lived species absorbing strongly at 397, 383, and 362 nm was observed immediately after the laser flash. The spectrum was recorded over a time window of 10 ns. After a few hundreds of nanoseconds, the transient absorption of this short-lived species disappeared and a second very long-lived absorption spectrum emerged with maximum absorption at 362 and 347 nm. The decay of the transient absorption at 397, 383, and 362 nm and the growth of the transient absorption at 347 nm follow a first-order rate law (Figures 1B and 2). Upon fitting to an exponential equation, the observed rate constants (k_{obs}) of these kinetic traces are deduced and found to be equal within experimental error ($(1.1 \pm 0.1) \times 10^7$ s^{-1}).

The long-lived species can be assigned to the triplet state of 1-naphthylnitrene **3t** because its transient spectrum is equivalent to the persistent spectrum produced by photolysis of **1** at low temperatures.[4,17] Conversely, the short-lived transient species is attributed to singlet 1-naphthylnitrene **3s** on the basis of the conversion of the carrier of the transient absorption to triplet nitrene **3t** at 77 K. The observed rate constant of $(1.1 \pm 0.1) \times 10^7$ s^{-1} corresponds, therefore, to the rate of intersystem crossing (k_{isc}) of singlet 1-naphthylnitrene. Furthermore, calculations of the UV−vis spectrum of singlet nitrene **3s** (Table S1) are in satisfactory agreement with the experimental observation of Figure 1A. Note that both singlet and triplet 1-naphthylnitrene absorb light of 362 nm. However, the singlet nitrene must have a larger molar extinction coefficient (ϵ) at 362 nm than the triplet nitrene so that the transient absorption at 362 nm exhibits a net decay curve but does not decay to the baseline (Figure 2B).

The above experiments reveal that k_{c} (the rate constant of nitrene cyclization) is slower than k_{isc} at 77 K. Assuming a normal *A* factor of 10^{13} s^{-1}, this result indicates that the barrier to cyclicization of the singlet nitrene must be greater than 2.1 kcal/mol.[28] This is consistent with the 2.51 kcal/mol barrier for this process calculated by CASPT2 after correction by 3 kcal/mol (see above).[27,28]

At ambient temperature, singlet 1-naphthylnitrene **3s** is too short-lived to be detected. In 1984, Schrock and Schuster determined the lifetime of azirine **4** to be 2.8 ± 0.2 μs by

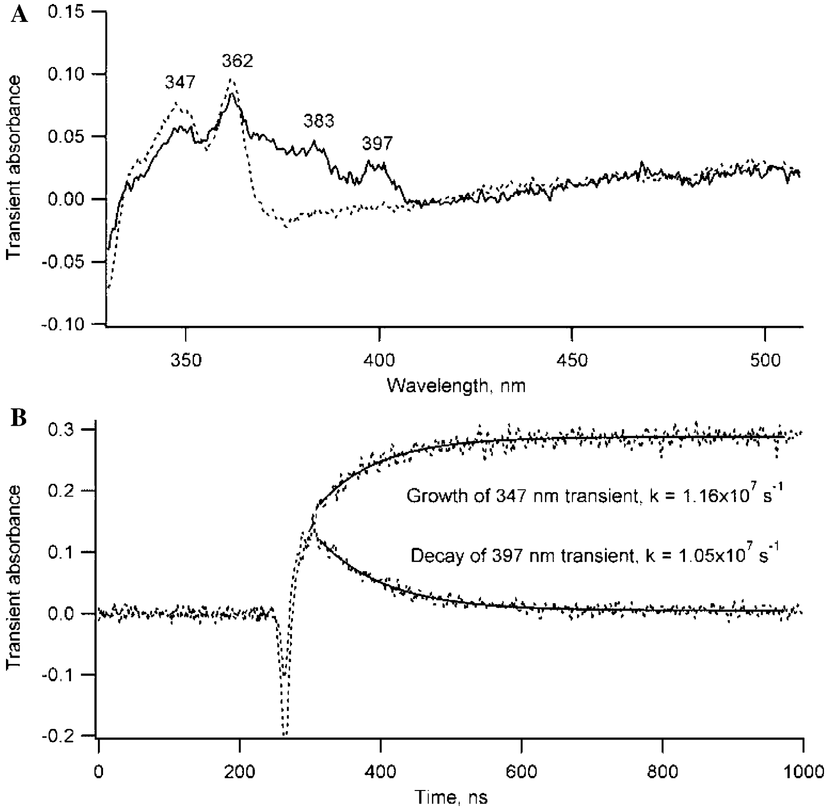


Figure 1. (A) Transient absorption spectra detected over a window of 10 ns following LFP (266 nm) of 1-naphthyl azide **1** in glassy 3-methylpentane at 77 K within 20 ns of the laser pulse (solid line) and 200 ns after (dashed line) the laser pulse. (B) Kinetic traces for the disappearance of singlet 1-naphthylnitrene **3s** monitored at 397 nm and the growth of triplet 1-naphthylnitrene **3t** monitored at 347 nm.

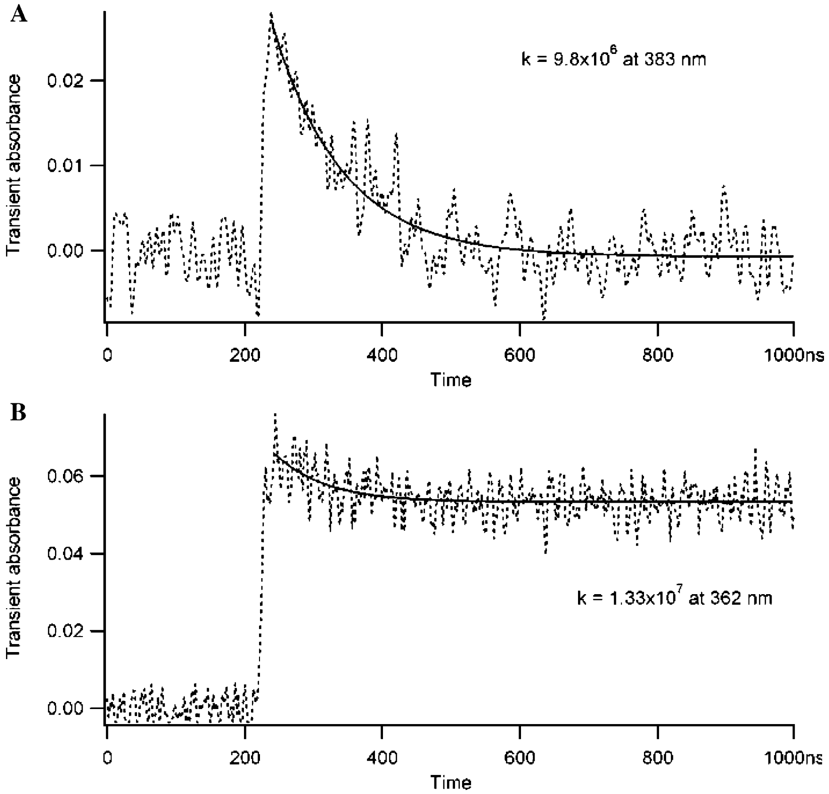


Figure 2. Kinetic traces for the disappearance of singlet 1-naphthylnitrene **3s** monitored at (A) 383 nm and (B) 362 nm produced by LFP (266 nm) of 1-naphthyl azide **1** in glassy 3-methylpentane at 77K.

measuring the growth rate of triplet 1-naphthylnitrene **3t** produced by LFP of 1-naphthyl azide **1** in benzene. Azirine **4** was not observed because it does not absorb strongly at wavelengths greater than 300 nm.[16,17]

Azirine **4** has a characteristic IR absorption involving the C═N stretching mode at 1730 cm^{-1}.[17] Figure 3A demonstrates the transient IR absorption produced by LFP of 1-naphthyl azide **1** in acetonitrile at ambient temperature. This spectrum has its

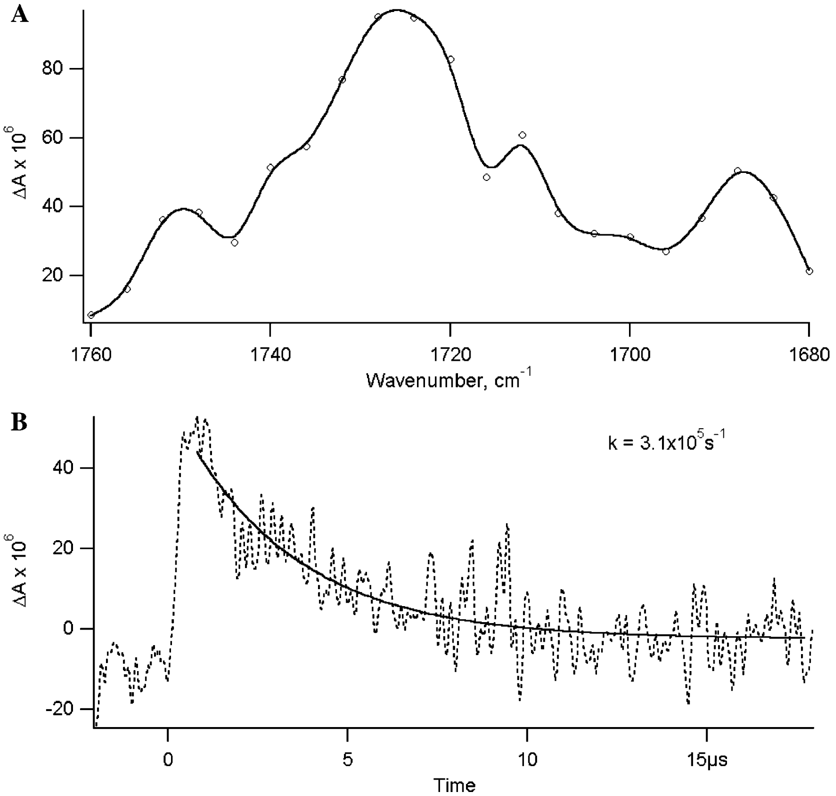
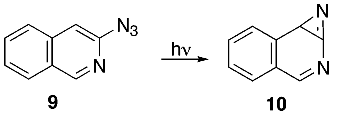


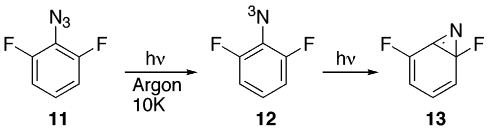
Figure 3. (A) Transient IR spectra detected over a window of 1 μs following LFP (266 nm) of 1-naphthyl azide **1** in acetonitrile at ambient temperature immediately after the laser pulse. (B) Kinetic traces for the disappearance of naphthazirine **4** monitored at 1728 cm^{-1}.

maximum absorption at ~1728 cm^{-1} and is attributed to azirine **4** on the basis of its similarity to the matrix IR spectrum.[17]

In addition to the azirines formed upon photolysis of the naphthyl azides, two other azirine intermediates have been detected previously in matrix isolation studies. Wentrup[29] reports that photolysis of 3-azidoisoquinoline **9** (320 nm, argon 12 K) produces azirine **10** with a vibrational frequency of 1725 cm^{-1} in excellent agreement with Maltsev et al.[17] and our own TRIR studies.



Morawietz and Sander[30] report that photolysis of 2,6-difluorophenyl azide **11** produces the corresponding triplet nitrene **12**, which can subsequently photoisomerize to azirine **13**. Their observations are summarized below. Note that the vibrational frequency of **13** (1679 cm^{-1}) is rather different from the other examples cited.



By monitoring the decay rate of the transient absorption at 1728 cm^{-1} (Figure 3B), the lifetime of **4** in acetonitrile at ambient temperature was found to be 3.2 ± 0.6 μs. This finding is in excellent agreement with Schrock and Schuster's observation of an azirine lifetime of 2.8 ± 0.2 μs in benzene using the LFP method and monitoring the growth of triplet nitrene UV−vis absorption.[16]

To investigate the reaction of azirine **4** with diethylamine (DEA), the lifetime of **4** was examined using TRIR spectroscopy in solvent mixtures of 1:3 and 1:1 DEA/acetonitrile (Figure 4). Inspection of the data in Figure 4 reveals that the observed rate constant for the disappearance of azirine **4** doubles from 3.1 × 10^5 to 6 × 10^5 s^{-1} in the presence of 25% DEA and that this rate constant increases to 1 × 10^6 s^{-1} as the concentration of DEA increases to 50 vol %. Thus, DEA reacts with **4** with an absolute bimolecular rate constant of approximately ~1.4 × 10^5 M^{-1} s^{-1}, a value much smaller than that of a diffusion-controlled process. The slow rate of reaction of DEA with **4** is consistent with the reported low yield of DEA photoadduct observed upon photolysis of 1-naphthyl azide **1**.[8]

2-Naphthylnitrene. The cyclization of 2-naphthylnitrene **6s** toward the α-carbon forms azirine **7**. According to the results shown in Scheme 2, this reaction is predicted to be exothermic by 4.4 kcal/mol, with a barrier of 3.0 kcal/mol. This barrier is ca. 2.5 kcal/mol lower than that for the cyclization of the isomeric 1-naphthylnitrene **3s**. If one applies the 3 kcal/mol correction at the CASPT2 level,[27] the cyclization of **6s** is predicted to proceed with essentially no barrier.

CASSCF/CASPT2 calculations predict that singlet 2-naphthylnitrene **6s** absorbs UV and visible light at 516, 421, 412, 338, and 296 nm (Table S3). All of these transitions involve $\pi-\pi^*$ excitations. Triplet nitrene **6t** has a weak absorption at 580/540 nm, a stronger one at 430 nm, and a very intense absorption at 355 nm.[17]

Unlike 1-naphthyl azide, LFP (266 nm) of 2-naphthyl azide **2** in an organic glass at 77 K failed to produce a detectable transient absorption above 320 nm. Even the presumably persistent spectrum of triplet 2-naphthylnitrene **6t** was not observed. Although this result is consistent with Schrock and Schuster's[16] report that laser flash photolysis of 2-naphthyl azide **2** does not produce triplet 2-naphthylnitrene within hundreds

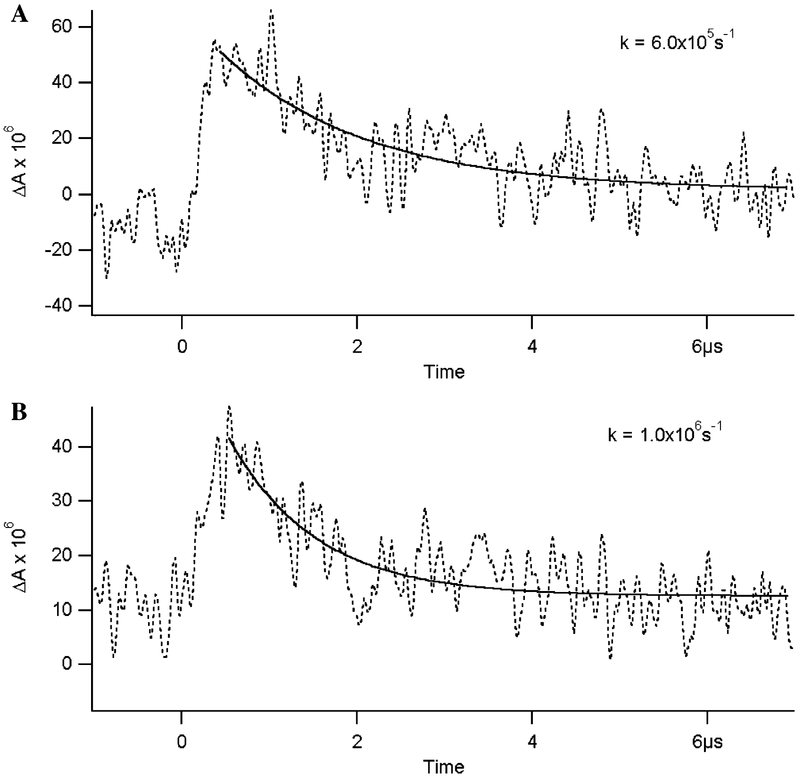


Figure 4. Kinetic traces for the disappearance of naphthazirine **4** monitored at 1728 cm^{-1} produced by LFP of 1-naphthyl azide **1** at ambient temperature in (A) 1:3 diethylamine/acetonitrile and (B) 1:1 diethylamine/acetonitrile.

of nanoseconds of the laser pulse, it appears at first sight to contradict the finding of Maltsev et al.[17] that photolysis of 2-naphthyl azide in Argon at 10 K produces **6t** as a primary photoproduct. However, it may well be that **6t** is formed as a secondary photoproduct in Argon at 10 K on 313 nm irradiation of 2-naphthyl azide, e.g., from **7**.

One way to reconcile these observations is to posit that $k_c > k_{isc}$ at 77 K, but that $k_{isc} > k_c$ at 20 K for singlet 2-naphthylnitrene. If we assume that $k_{isc} = 1.1 \times 10^7\ s^{-1}$ (the value observed for singlet 1-naphthylnitrene) and is temperature independent, and that $A = 10^{13}\ s^{-1}$ for cyclization of singlet nitrene **6s**, we can conclude that the barrier to cyclization, E_a, can be bracketed as follows: $0.6 < E_a < 2.1$ kcal/mol. This result is consistent with theoretical predictions,[17] if the errors in CASPT2 calculations of the naphthylnitrene cyclizations are smaller than those of the singlet phenylnitrene cyclization.[27]

Our results are consistent with Schrock and Schuster's failure to obtain the steady-state spectrum of **6t** by exciting 2-naphthyl azide at 77 K without sensitization.[16] It seems likely that singlet 2-naphthylnitrene **6s** converts to azirine **7** at a rate much faster than its rate of intersystem crossing, even at 77 K, because the former process is predicted to be almost barrierless.[17]

Azirine **7** has a characteristic IR absorption involving C═N stretching observed at 1739 cm^{-1} in an argon matrix.[17] Figure 5A illustrates the transient IR spectrum produced by LFP of 2-naphthyl azide **2** in acetonitrile at ambient temperature. This spectrum, with an absorption maximum at ~1724 cm^{-1}, is attributed to **7** on the basis of its similarity to the matrix IR spectrum.[15,17]

The lifetime of **7** in acetonitrile at ambient temperature was determined to be 150 ± 10 μs by monitoring the rate of disappearance of the transient absorption at 1724 cm^{-1} (Figure 5B). Thus, azirine **7** has a lifetime ~50 times longer than that of the azirine **4** produced by LFP of 1-naphthyl azide. This finding is in excellent agreement with Schrock and Schuster's observation of a markedly slow rate of growth of 2,2′-azonaphthalene.[16] The long lifetime of **7** is consistent with theoretical calculations as well, because this azirine is predicted to be 3−4 kcal/mol more stable than singlet 2-naphthylnitrene **6s**, whereas the cyclization of singlet 1-naphthylnitrene **3s** to azirine **4** is essentially thermoneutral.[17] Presumably, **7** can serve as a reservoir of the singlet nitrene **6s**, which then undergoes intersystem-crossing to its ground triplet state **6t,** followed by dimerization to generate the azo product. The slower rate of reversion of azirine **7** back to singlet 2-naphthylnitrene **6s** is due to the larger difference in energy between **7** and **6s** compared to that between **4** and **3s** in the 1-naphthylnitrene system.

Inspection of the potential energy surfaces in Schemes 1 and 2 reveals that the CASPT2 energy of azirine **7** is 0.46 kcal/mol above that of **4**, and that singlet 2-naphthylnitrene **6s** is 4.48 kcal/mol less stable than singlet 1-naphthylnitrene **3s**.[17] Thus, it would seem that the relative instability of **6s**, which is presumably due to a lower resonance energy, is the decisive factor for the long lifetime of azirine **7**.

To investigate the reaction of naphthazirine **7** with diethylamine (DEA), the rate constants of the decay of **7** were determined in the presence of 25% and 50% DEA in acetonitrile at ambient temperature (Figure 6). Inspection of the data in Figure 6 reveals that the pseudo-first-order observed rate constant of disappearance of naphthazirine **7** accelerates from 6.7×10^3 to $5.6 \times 10^5\ s^{-1}$ in the presence of 25% DEA and to $1.2 \times 10^6\ s^{-1}$ in the presence of 50% DEA. Thus, DEA is apparently trapping **7** with a bimolecular rate constant (k_{DEA}) of $\sim 2.5 \times 10^5\ M^{-1}\ s^{-1}$. This rate constant is slightly faster but still similar to that of azirine **4** ($1.4 \times 10^5\ M^{-1}\ s^{-1}$), which is generated by LFP of 1-naphthyl azide **1**.

The observed reaction of azirine **7** with DEA is not particularly fast, but trapping by DEA is still a major process because **7** has a long lifetime (150 μs) in the absence of amine

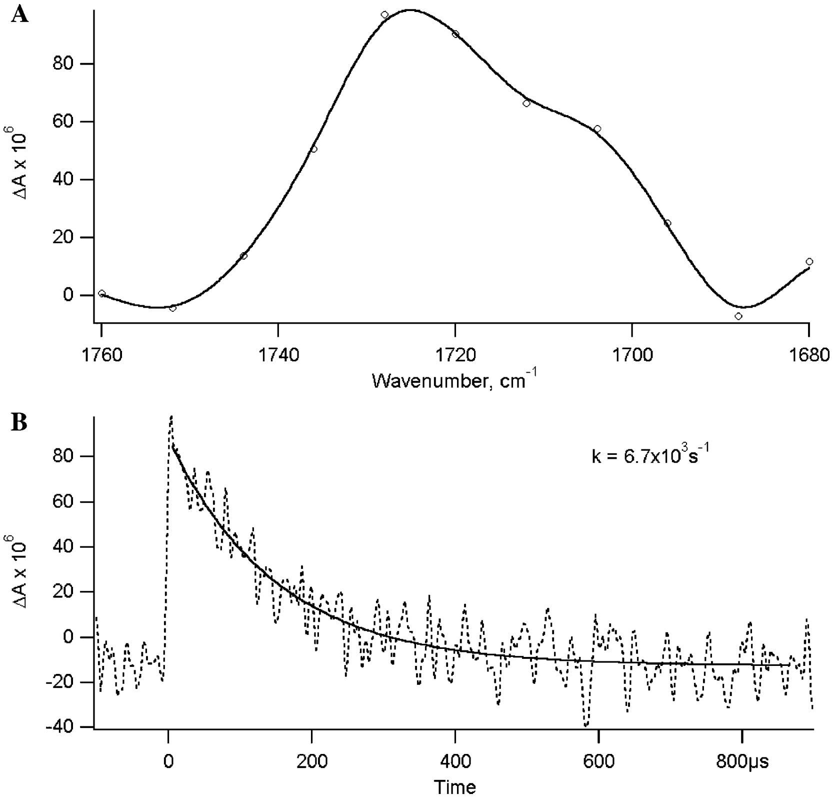


Figure 5. (A) Transient IR spectra detected over a window of 1 μs following LFP (266 nm) of 2-naphthyl azide **2** in acetonitrile at ambient temperature immediately after the laser pulse. (B) Kinetic traces for the disappearance of naphthazirine **7** monitored at 1724 cm^{-1}.

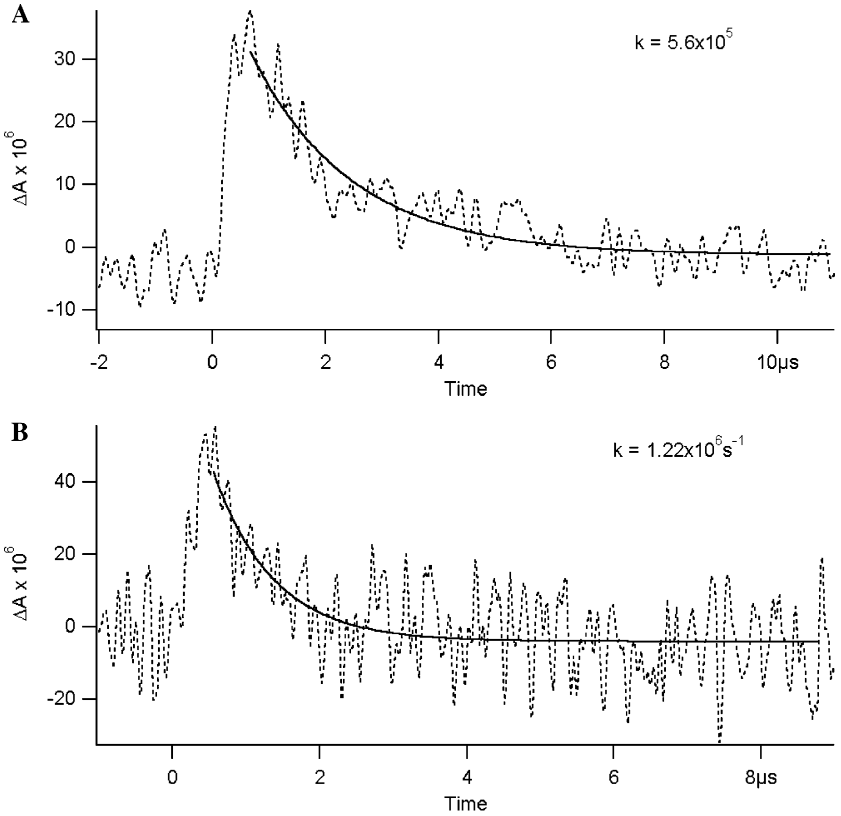


Figure 6. Kinetic traces for the disappearance of naphthazirine **7** monitored at 1724 cm^{-1} produced by LFP of 2-naphthyl azide **2** at ambient temperature in (A) 1:3 diethylamine/acetonitrile and (B) 1:1 diethylamine/acetonitrile.

trap. This is consistent with the reported high yields of adducts formed upon photolysis of 2-naphthyl azide **2** with the presence of secondary amine.[8,9,11] A DEA adduct is inefficiently formed upon photolysis of 1-naphthyl azide **1** at ambient temperature because of the shorter lifetime of its naphthazirine derivative (**4**), which converts to triplet 1-naphthylnitrene **3t** in two steps, and consequently renders this azirine unavailable to nucleophiles.

IV. Conclusions

Singlet 1-naphthylnitrene **3s** was directly detected upon LFP of 1-naphthyl azide **1** at 77 K. Absorption maxima of **3s** were observed at 397, 383, and 362 nm, and the rate of intersystem crossing of **3s** to **3t** was determined to be $(1.1 \pm 0.1) \times 10^7$ s^{-1} in a rigid-glass at 77 K. Azirine **4**, the most favorable intermediate in the cyclization of **3s**, was directly observed using time-resolved infrared (TRIR) spectroscopy, in excellent agreement with the matrix IR spectra ($\nu_{C=N} = 1728$ cm^{-1}).[15,17] In addition, the solution phase lifetime of **4** (3.2 μs) is in excellent agreement with Schrock and Schuster's estimation deduced from the growth rate of triplet 1-naphthylnitrene **3t**.[16] In the presence of diethylamine (DEA), azirine **4** reacts with this amine trap with a rate constant of 1.4×10^5 M^{-1} s^{-1}. In the absence of nucleophilic trap, **4** serves as a reservoir of singlet nitrene **3s** which subsequently relaxes to its triplet ground state, **3t**, followed by the formation of triplet nitrene derived products.

Our results are perfectly consistent with the product-based studies of Suschitzky et al.[8−12] Photolysis of 1-naphthyl azide produces singlet 1-naphthylnitrene which interconverts with a nearly isoenergetic azirine. The short-lived azirine is not efficiently trapped at ambient temperature. It reverts to singlet nitrene which relaxes to the lower energy triplet. The azirine derived from 2-naphthyl azide photolysis is ∼4 kcal/mol lower in energy than singlet 2-naphthylnitrene, is much longer-lived and is more readily trapped than its isomeric azirine.

The photochemistry of 2-naphthyl azide **2** follows a similar pattern. Azirine **7** was directly observed by TRIR spectroscopy with an IR absorption at ∼1724 cm^{-1}, and has a lifetime of 150 ± 10 μs at ambient temperature. Azirine **7** can be intercepted with DEA with a rate constant of 2.5×10^5 M^{-1} s^{-1}. However, because the barrier to cyclization of **6s** to form **7** is much smaller than that of its 1-naphthylnitrene isomer, singlet 2-naphthylnitrene **6s** could not be observed upon LFP of **2** in an organic glass at 77 K.

Why is the reversion of azirine **4** to singlet 1-naphthylnitrene **3s** more facile than the corresponding process involving azirine **7** and 2-naphthylnitrene **6s**? The calculations of Maltsev et al.[17] provide the answer. CASPT2 calculations indicate that azirine **4** is 0.46 kcal/mol more stable than **7**, but that singlet 1-naphthylnitrene **3s** is 4.48 kcal/mol more stable than singlet 2-naphthylnitrene **6s**. The instability of 2-naphthylnitrene relative to the 1-naphthyl isomer, presumably due to its less extensive delocalization, retards the reversion of azirine **7** to the nitrene singlet, and accounts for its extended lifetime relative to **4**.

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Supporting Information Available: Tables of vertical excitation energies of **3s**, **3t**, **6s**, and **6t**. This material is available free of charge via the Internet at http://pubs.acs.org.

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