Study of Singlet and Triplet 2,6-Difluorophenylnitrene by Time-Resolved Infrared Spectroscopy

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Received: October 17, 2004; In Final Form: January 24, 2005

The solution-phase photochemistry of 2,6-difluorophenyl azide was studied by time-resolved infrared (TRIR) spectroscopy. A vibrational band of singlet 2,6-difluorophenyl nitrene (^1N) was observed at 1404 cm^{-1} between 243 and 283 K. At ambient temperature, it was not possible to detect this intermediate. At 298 K, only the decay products of the singlet nitrene, the isomerized products ketenimine (K) and triplet-2,6-difluorophenyl nitrene (^3N), were observed at 1576 and 1444 cm^{-1}, respectively. The assignments are consistent with density functional theory calculations and previous studies of this system by laser flash photolysis techniques with UV−visible detection.

I. Introduction

Photolysis of aryl azides in solution at ambient temperature releases singlet arylnitrenes (^1N), which can either rearrange to ultimately form ketenimines (K) or relax to form triplet arylnitrenes (^3N) as shown in Scheme 1 for 2,6-difluorophenyl azide (A).[1] The singlet nitrene is the key intermediate whose partitioning determines whether stable products are ultimately formed from the ketenimine or the lower energy triplet nitrene intermediate. The partitioning is temperature-dependent. Higher temperatures favor the formation of ketenimine (in an activated process) while lower temperatures favor intersystem crossing (ISC), which is a barrierless process.[1]

The lifetime of singlet phenylnitrene at ambient temperatures is about 1 ns.[2] Ortho fluorine substituents lengthen the lifetime of singlet arylnitrenes in solution.[3] Singlet and triplet arylnitrenes have been well characterized previously by nanosecond time-resolved UV−vis spectroscopy but not as yet by time-resolved vibrational spectroscopy.[1] Most singlet aryl nitrenes will have lifetimes too short to monitor by nanosecond time-resolved vibrational spectroscopy.[1] As singlet 2,6-difluorophenylnitrene is the longest lived singlet aryl nitrene known in solution,[3] it appears to be the most attractive singlet arylnitrene for study by this technique, thereby motivating this study of the photochemistry of 2,6-difluorophenyl azide by time-resolved infrared (TRIR) spectroscopy.

II. Materials

2,6-Difluorophenyl azide was synthesized as described in the literature.[3] Solvents were obtained from Cambridge Isotope Laboratories and Aldrich Chemicals and were purified by distillation before use.

Protocols for TRIR Spectroscopy. The Ohio State University TRIR spectrometer has been described in the literature.[4] Briefly, all TRIR experiments were performed with a Jasco TRIR-1000 dispersive type IR spectrometer, which has 16 cm^{-1} resolution. A reservoir of 7−10 mL of sample solution [3−7 mM 2,6-difluorophenyl azide in CD_3CN or cyclohexane-d_{12}, with or without diethylamine or dimethyl sulfoxide (DMSO)], was held in a constant-temperature bath of either ethanol and ice (273 K), dry ice and acetonitrile (243 K), or water (283 K) and monitored constantly to maintain the desired temperature ±5 K. A typical concentration was between 3 and 7 mM in terms of azide precursor concentration. The sample solution was circulated between two barium fluoride plates with a path length of 0.5 mm. The sample was excited with a 266 nm laser pulse from a Nd:YAG laser (50 Hz repetition rate, 0.5 mJ/pulse power), and the IR spectrum was obtained from the broadband output of a $MoSi_2$ IR source.

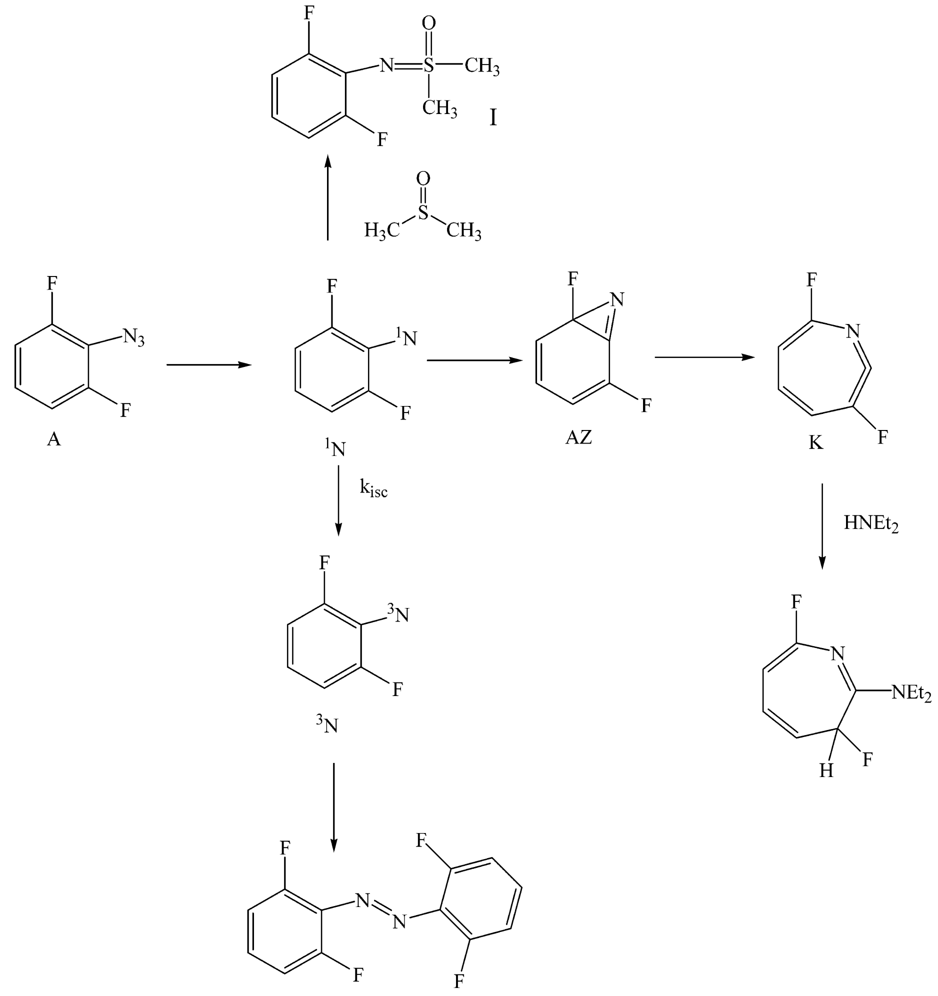
Protocols for Time-Resolved UV Spectroscopy. A Nd:YAG laser (Continuum PY62C-10, 17 ns, 10 mJ, 266 nm) and a Lambda Physics LPX (XeCl, 30 ns, 50 mJ, 308 nm) were used as the excitation light sources. Laser flash photolysis (LFP) experiments with 2,6-difluorophenyl azide were performed with either a 266 nm pump or a 308 nm pump. The ketenimine intermediate (K) was probed at 380 nm, and the decay of the singlet nitrene ^1N was monitored at 340 nm in acetonitrile. The Ohio State University nanosecond LFP spectrometer has been described elsewhere.[5] Briefly, all samples were dissolved in spectroscopic-grade solvent with an absorption of ∼1 at either 266 or 308 nm and placed in a 3 mL quartz cuvette. For the transient UV experiments reported, all samples had an absorption of approximately 1 at the excitation wavelength. Samples were not purged with argon before use. Quenchers (diethylamine, dimethyl sulfoxide) were present in solution at the desired concentrations.

Computational Methods. Density functional theory (DFT) has been applied in this study.[6] The geometries were completely optimized at the B3LYP/6-31G* level. Analytical vibrational frequencies were calculated at the same level for each stationary point to verify a minimum energy structure. As noted below, vibrational frequencies were scaled by 0.9613.[7] To study the influence of solvent, polarizable continuum model (PCM)[8] calculations were performed with acetonitrile as the solvent.

CASSCF methods[9] provide accurate results for singlet open-shell nitrenes.[1,3] However, although both Gaussian 98[10] and Gaussian 03[11] can compute vibrational frequencies at the CASSCF level, the IR intensities are not provided; therefore, the utility of this method for predicting IR spectra is limited. Due to this limitation, we resorted to using open-shell DFT calculations as pioneered by Cramer et al.[12] for treating the open-shell singlet nitrene. In these calculations, the $\langle S^2 \rangle$ value for

10.1021/jp045254b CCC: $30.25

SCHEME 1



the triplet nitrene was 2.05, and for the open-shell singlet, the $\langle S^2 \rangle$ value was 0.91 (see Supporting Information). Therefore, the open-shell singlet nitrene appears to be almost an equal mix of singlet and triplet wave functions. The unscaled vibrational frequencies obtained by DFT and CASSCF have been compared, and DFT is found to generate frequencies comparable to those predicted by CASSCF. Thus, DFT calculated vibrational (IR) frequencies and intensities are used for the open-shell singlet nitrene.

Karney and Borden[13] have demonstrated that CASSCF methods accurately predict the barriers to singlet aryl nitrene rearrangements. Theory also accurately predicts the singlet−triplet energy separation of phenylnitrene.[15−17]

All DFT and CASSCF calculations were performed at the Ohio Supercomputer Center by use of the Gaussian suite of programs.[10,11]

III. Results

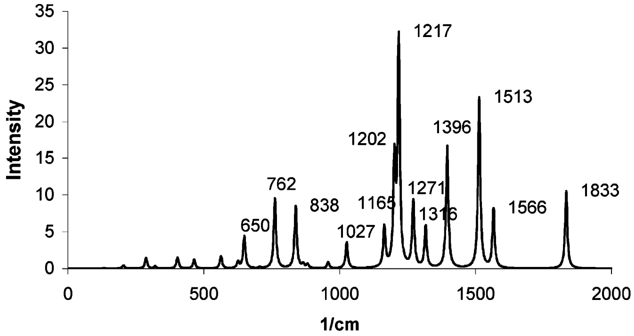
III.1. Computational Chemistry. Density functional theory (DFT) methods were used to predict the vibrational spectra of ketenimine (K) and singlet (^{1}N) and triplet 2,6-difluorophenyl nitrene (^{3}N). The vibrational spectrum of the singlet nitrene (^{1}N) was also predicted by CASSCF theory and was in excellent agreement with DFT calculations (see Supporting Information). The spectra predicted by theory are shown in Figure 1.

III.2. TRIR Spectroscopy. The lifetime of singlet 2,6-difluorophenyl nitrene (^{1}N) in hexane[3] is 240 ± 20 ns but is shorter in the more polar solvent acetonitrile at ambient temperature (140 ns) as determined by nanosecond UV LFP experiments.[18] These lifetimes are at the limit of detection of the TRIR spectrometer. Thus, initial experiments were performed at subambient temperatures.

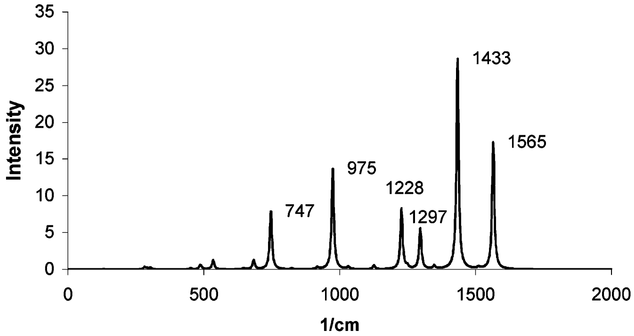
LFP (266 nm) of 2,6-difluorophenyl azide in cyclohexane-d_{12} at 283 K produces the TRIR spectrum of Figure 2. The bleaching observed at 1490 cm^{-1} is attributed to the consumption of the azide precursor. A transient species with a vibrational band at 1404 cm^{-1} is present with a lifetime of 1.2 ± 0.5 μs. This absorption is formed faster than the time resolution of the spectrometer. As the 1404 cm^{-1} band decays in cyclohexane-d_{12}, a band at 1444 cm^{-1} grows in intensity with the identical, observed rate constant, within experimental error ($3 \pm 0.3 \times 10^6$ s^{-1}, Figure 3).

At 273 K, a strong absorption band at 1444 cm^{-1} is also observed upon LFP of azide in CD_3CN, along with the bleaching of the azide precursor at 1490 cm^{-1} (Figure 4). A weak band at 1576 cm^{-1} is detected as well under these conditions. The vibrational band observed at 1444 cm^{-1} is formed faster than the time resolution of the spectrometer and decays with $k_{obs} = 2.7 \times 10^5$ s^{-1} ($\tau = 370$ μs, 7 mM azide). The lifetime of the carrier of the weak signal at 1576 cm^{-1} could not be measured at this temperature due to its low signal intensity.

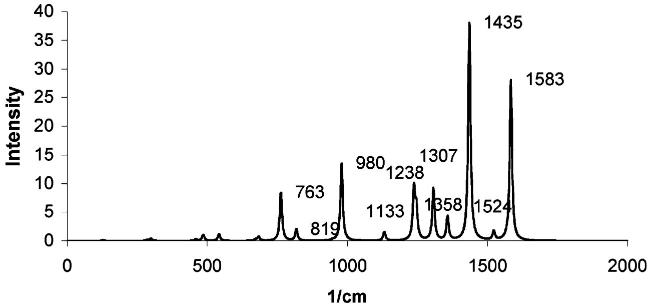
It is economical to propose that the carrier of the 1404 cm^{-1} vibration is the first formed intermediate and that it decays to form the carriers of both the 1444 and 1576 cm^{-1} vibrations. On the basis of prior LFP studies of this system with UV−vis detection[3] and taking note of the vibrational spectra predicted



(a) ketenimine (K)



(b) triplet 2,6-difluorophenyl nitrene (^{3}N)



(c) singlet 2,6-difluorophenyl nitrene (^{1}N)

Figure 1. IR spectra of (a) ketenimine (K), (b) triplet nitrene (^{3}N), and (c) singlet nitrene (^{1}N), calculated at the B3LYP/6-31G* level of theory by use of the PCM model for acetonitrile. An open-shell (UB3LYP) description was used for the singlet and triplet nitrenes.

Figure 2. Transient IR spectra produced upon excitation (266 nm) of 2,6-difluorophenyl azide (7 mM) in cyclohexane-d_{12} at 283 K. Bleaching at 1490 cm^{-1} is attributed to depletion of the starting material. The signal at 1444 cm^{-1} is attributed to the triplet nitrene (^{3}N). The signal at 1396 cm^{-1} is attributed to the singlet nitrene (^{1}N). The spectrum was recorded 0.7 μs (—) and 1.2 μs (- - -) after the laser pulse.

by theory, we assign the 1404 cm^{-1} band to singlet 2,6-difluorophenylnitrene (^{1}N) and the 1444 cm^{-1} band to the lower energy triplet state (^{3}N). DFT calculations indicate that the IR band observed at 1404 cm^{-1} is due to the symmetrical carbon−carbon double bond stretches of the singlet nitrene (^{1}N). The IR band observed at 1444 cm^{-1} arises from aromatic ring carbon−carbon double bond stretches of the triplet nitrene (^{3}N) according to theory. The signal at 1576 cm^{-1} is assigned to carbon−carbon double bond stretches of the ketenimine (K).

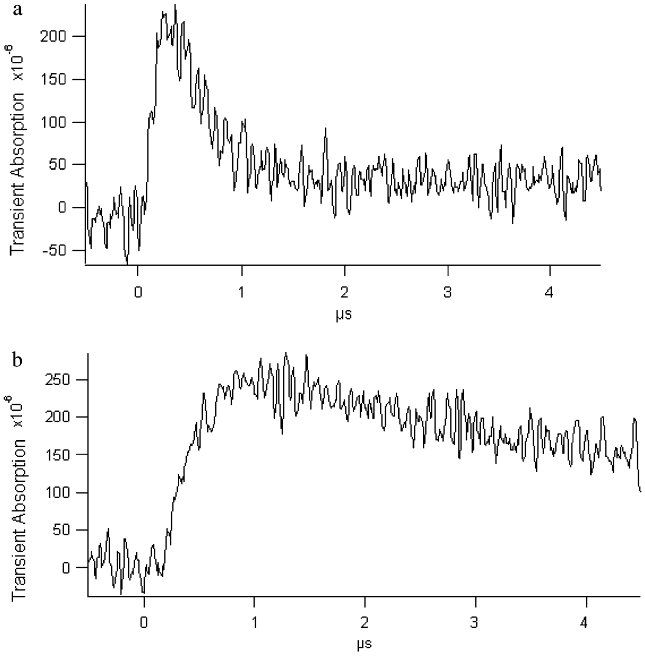


Figure 3. (a) Decay of the transient absorption of the singlet nitrene (^{1}N) at 1400 cm^{-1} in cyclohexane-d_{12} at 273 K (7 mM azide concentration). (b) Growth of transient absorption of triplet nitrene (^{3}N, 1444 cm^{-1}) in cyclohexane-d_{12} at 283 K (7 mM azide concentration).

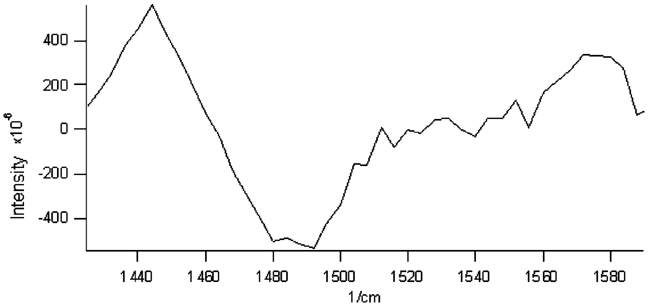


Figure 4. Transient IR spectrum produced upon excitation (266 nm) of 2,6-difluorophenyl azide (7 mM) in CD$_3$CN at 273 K. The new signal at 1444 cm^{-1} is attributed to the triplet nitrene (^{3}N). The spectrum was recorded 0.7 μs after the laser pulse.

Similar results were obtained in CD$_3$CN at 243 K (Figure 5). The singlet nitrene lifetime and the growth of the triplet nitrene are too short to measure under these conditions. The lifetime of the triplet nitrene is 1.1 μs under these experimental conditions (7 mM azide). Similar results were obtained in CD$_3$CN at 273 K (Supporting Information, Figure S1).

The singlet nitrene is not observed at 1404 cm^{-1} upon LFP of 2,6-difluorophenyl azide at 298 K in CD$_3$CN (Figure 6). This is consistent with the anticipated shorter lifetime ($\tau \approx 100$ ns) of ^{1}N under these conditions.[3] The triplet nitrene absorption is observed; however, it is shifted to 1418 cm^{-1} under these conditions. The triplet lifetime is 3.7 μs (3 mM azide) and shortens with increasing concentration of azide precursor (Supporting Information, Figure S2, $k_{az} = 6.9 \times 10^6$ M^{-1} s^{-1}).

A transient absorption at 1576 cm^{-1} is present in CD$_3$CN at 298 K and is observed at lower temperatures but is of relatively low intensity (Figures 4 and 6). The carrier of the 1576 cm^{-1}

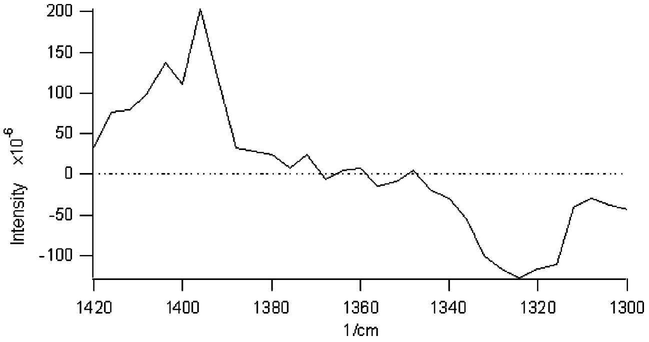


Figure 5. Transient IR spectrum produced upon excitation (266 nm) of 2,6-difluorophenyl azide (7 mM) in CD_3CN at 243 K. The bleaching at 1326 cm^{-1} is attributed to depletion of the starting material, and the new signal at 1404 cm^{-1} is attributed to the singlet nitrene (^1N). The spectrum was recorded 0.5 μs after the laser pulse.

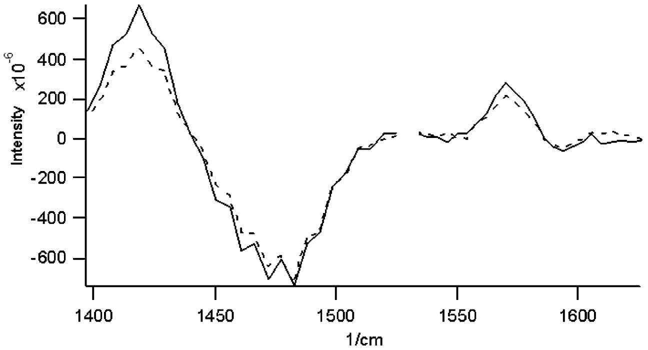


Figure 6. Transient IR spectra produced upon excitation (266 nm) of 2,6-difluorophenyl azide (7 mM) in CD_3CN at 298 K. Bleaching at 1490 cm^{-1} is attributed to depletion of the starting material, and the new signal at 1576 cm^{-1} is attributed to the ketenimine (K). The peak at 1444 cm^{-1} is attributed to the triplet nitrene (^3N). The spectra were recorded 1.0 μs (—) and 3.1 μs (---) after the laser pulse.

transient absorption has a significantly longer lifetime (30 μs) than the triplet nitrene (1444 cm^{-1}, Figure 6). As shown in Figure 7, the intensity of the transient absorption at 1576 cm^{-1}, relative to that at 1444 cm^{-1}, is greater at 283 K than at 243 K. The lifetime of this species is too long to be that of benzazirine AZ. Experimental and computational studies indicate that this species will open to form a ketenimine on the pico/nanosecond time scale as the CASPT2 barrier of isomerization of AZ to K is only 5.7 kcal/mol.[3] The calculated spectrum of AZ is given in the Supporting Information (Figure S11). We predict that AZ absorbs most strongly at 1695 cm^{-1}, in fair agreement with the observation of this species in a cryogenic argon matrix (1679.3, 1609.8, and 1519.7 cm^{-1}, with relative intensities of 0.28, 0.10, and 0.25, respectively).

Morawietz and Sander[19] predicted vibrational bands of AZ at 1637 (0.64 relative intensity), 1574 (0.85), and 1483 cm^{-1} (0.29) using the RMP2/6-31G(d) level of theory. In this work very weak vibrational bands were observed between 1600 and 1700 cm^{-1}, further evidence against assigning the carrier of the transient IR spectra observed between 1400−1600 cm^{-1} to azirine AZ.

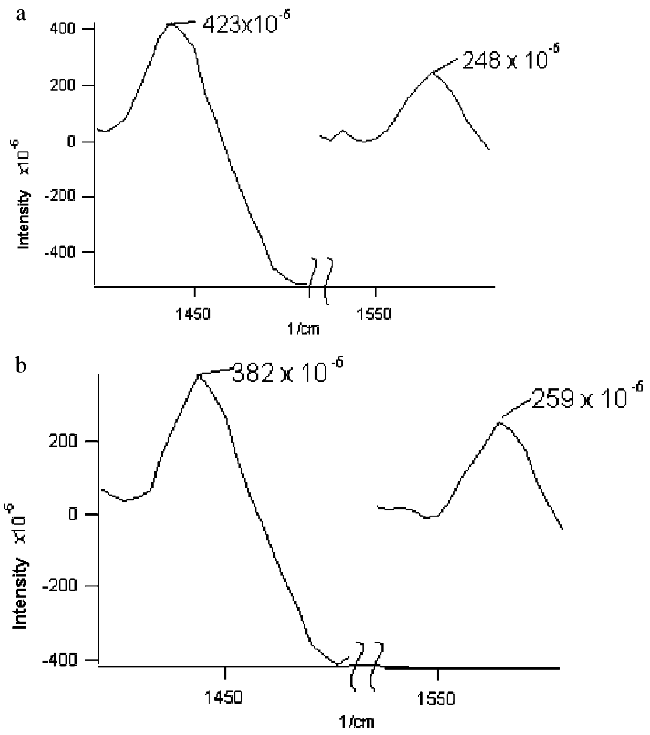


Figure 7. TRIR spectra produced upon LFP of 2,6-difluorophenyl azide (3 mM) in CD_3CN at (a) 253 K and (b) 283 K. Each spectrum was collected 1.8 μs after the laser pulse.

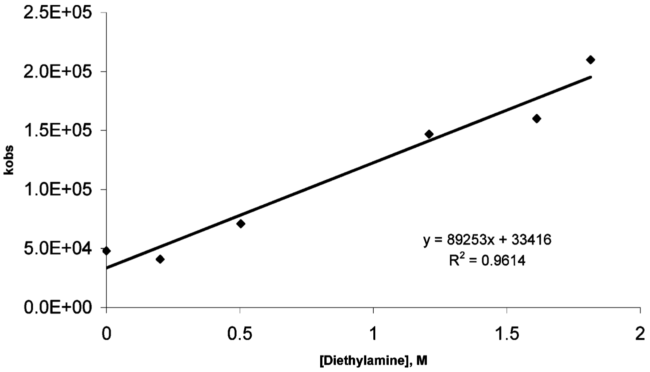


Figure 8. Plot of the observed rate constant of decay of the 1576 cm^{-1} absorption versus [diethylamine] in CD_3CN at ambient temperature.

The lifetime of the transient species absorbing at 1576 cm^{-1} is shortened by the presence of diethylamine in CD_3CN at 298 K. A plot of k_{obs} versus the concentration of diethylamine is linear (Figure 8) with $k_{HNEt2} = 9.0 \times 10^4$ M^{-1} s^{-1}. The yield of the species absorbing at 1576 cm^{-1}, formed immediately after the laser pulse, is also reduced by the presence of diethylamine. A Stern−Volmer plot is of poor quality due to the low signal intensity of the ketenimine vibrational band. Diethylamine quenching of the yield of triplet nitrene and ketenimine is not suprising because singlet polyfluorinated arylnitrenes are known to react with amines to form hydrazines.[3,20]

To verify that diethylamine quenches singlet nitrene ^1N and the yield of ketenimine K as dictated by the TRIR results, the related experiments were performed by LFP (308 nm) with UV−vis detection. Singlet nitrene ^1N was detected at 340 nm in acetonitrile following laser flash photolysis. The singlet nitrene decays exponentially and the pseudo-first-order rate constant for the singlet nitrene decay increases linearly with diethylamine concentration (Figure 9). The slope of this plot is 4.2×10^7 $M^{-1}s^{-1}$, the absolute second-order rate constant of the reaction of ^1N with diethylamine. The intercept of this plot indicates that the lifetime of ^1N is 72 ns in acetonitrile under these conditions, which is too short for detection by TRIR spectroscopy. The lifetime of the singlet nitrene is probably limited by the “dryness” of the solvent.[18]

As expected, the yield of ketenimine (K, 380 nm) observed upon 308 nm LFP is reduced by the presence of diethylamine (Supporting Information, Figure S3). The results confirm that

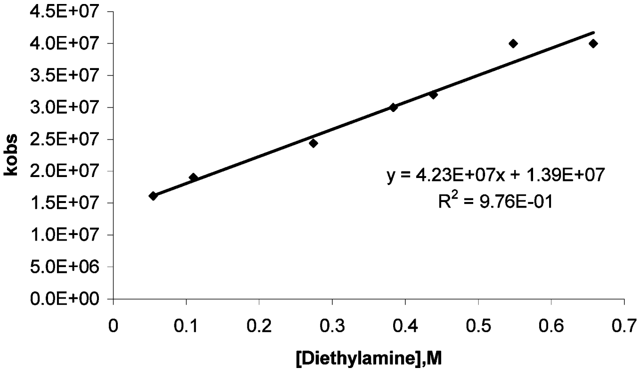


Figure 9. Pseudo-first-order rate constant of ^{1}N decay monitored at 340 nm as a function of diethylamine concentration at ambient temperature.

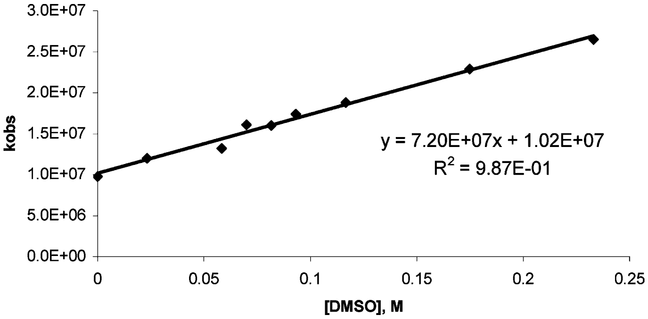


Figure 10. Plot of k_{obs} of ^{1}N decay monitored at 340 nm versus [DMSO] in acetonitrile at ambient temperature.

diethylamine suppresses ketenimine formation and supports our assignment of the 1576 cm^{-1} band to ketenimine K.

According to Scheme 1, diethylamine should quench the yield of triplet nitrene (by scavenging the singlet nitrene precursor) but should not shorten its lifetime. Thus, the effect of diethylamine on the initial yield of triplet nitrene following LFP and on the lifetime of the triplet nitrene was also studied. Diethylamine was found to quench the yield of triplet nitrene (^{3}N) transient absorption but did not shorten the lifetime of this species (Supporting Information, Figures S4 and S5).

The yield of the 1576 cm^{-1} absorbing transient, measured immediately after the laser pulse, is also reduced in the presence of dimethyl sulfoxide (DMSO) (another singlet nitrene scavenger[15]), but Stern−Volmer analysis was again unreliable due to the poor signal-to-noise ratio of the ketenimine vibrational band. Once again, related experiments were easily performed by LFP (308 nm) with UV−vis detection. The presence of DMSO quenched the yield of ketenimine measured at 380 nm (Supporting Information, Figure S6).

DMSO also increases the pseudo-first-order rate constant of singlet nitrene decay (k_{obs}) measured at 340 nm in acetonitrile. A plot of k_{obs} versus [DMSO] is linear (Figure 10). The absolute rate constant of reaction of singlet nitrene with DMSO is 7.2×10^7 M^{-1} s^{-1}, almost twice the size of the corresponding diethylamine rate constant. The singlet nitrene lifetime was found to be 100 ns in this experiment. DMSO also lowers the yield of triplet nitrene (1444 cm^{-1}) produced by LFP in CD_3CN at 298 K (Supporting Information, Figure S7) but does not appear to affect the lifetime of the triplet nitrene ^{3}N.

LFP of 2,6-difluorophenyl azide in the presence of DMSO leads to the presence of new (1300, 1560 cm^{-1}) and persistent ($\tau \gg 100\ \mu$s) vibrational bands (Supporting Information, Figure S8). The carrier of these bands was assigned to sulfoximine (I, Scheme 1), the expected[20] adduct of the singlet nitrene (^{1}N) and DMSO. The positions of the vibrational bands are in good agreement with the predictions of DFT calculations (Supporting Information, Figure S10) after scaling by a factor of 0.9613[7] (1317 and 1578 cm^{-1}).

The carrier of the transient absorption at 1576 cm^{-1} is attributed to ketenimine (K) despite the fact that scanning of the 1800−1900 cm^{-1} region shows no evidence of transient absorption after LFP. We note that the intensity of the C=C=N band predicted by DFT is unusually low relative to ketenimines generated from nonfluorinated aryl azides, many of which which have been studied in low-temperature matrixes.[21] Our results are consistent, however, with studies of fluorinated aryl azides in inert matrices, for which IR spectroscopic studies of the photochemistry of polyfluorinated aryl azides have conspicuously failed to detect the ketenimine vibration after photolysis of the azide precursor.[19,22]

IV. Discussion

Laser flash photolysis of 2,6-difluorophenyl azide produces the analogous singlet nitrene (^{1}N).[3] The singlet nitrene is the first reactive intermediate detectable in solution by nanosecond time-resolved UV−vis spectroscopy and decays at ambient temperature both by relaxation to the lower energy triplet (^{3}N) and by rearrangement to ultimately form ketenimine (K) according to Scheme 1.[1] As the temperature is cooled below ambient, the lifetime (τ) lengthens as k_R, the rate constant for rearrangement, decreases: $1/\tau = k_R + k_{isc}$, where τ is the singlet lifetime and k_R and k_{isc} are defined in Scheme 1. The rate constant of nitrene intersystem crossing (k_{isc}) is independent of temperature.[1] Thus, as the temperature decreases, the ratio of triplet nitrene (^{3}N) to ketenimine (K) formed by the decay of the singlet nitrene increases. Both ^{3}N and K have lifetimes on the microsecond time scale.[3]

The TRIR data are consistent with previously reported LFP experiments with UV−vis detection.[3] The singlet nitrene, which has a lifetime of ∼100 ns at ambient temperature, can only be observed by TRIR spectroscopy at reduced temperatures. At ambient temperature, two transient IR bands are observed at 1444 and 1576 cm^{-1}. The carriers of both bands have microsecond lifetimes. At subambient temperatures, the ratio of transient absorbance at 1444 cm^{-1} to that at 1576 cm^{-1} increases (Figure 7). On the basis of this observation, it is straightforward to assign the carrier of the 1444 cm^{-1} transient absorption to triplet nitrene ^{3}N and that of the 1576 cm^{-1} band to ketenimine (K). These assignments are in satisfactory agreement with DFT calculations (Figure 1).

Our previously reported calculations[3] suggest that the isomerizations of singlet 2,6-difluorophenylnitrene (^{1}N) to azirine AZ and ketenimine (K) will be irreversible in the presence of diethylamine. The barrier for reversion of ketenimine to azirine is calculated by CASPT2 to be 9.4 kcal/mol, and the barrier for reversion of azirine to singlet nitrene is predicted by the same method to be 12.4 kcal/mol. Thus, reversion will be slow relative to trapping of the intermediates in the presence of 1 M diethylamine, and the formation of azirine and ketenimine can be considered to be irreversible under these conditions. The calculations used in this study predict that the triplet nitrene is 9 kcal/mol lower in energy than the singlet nitrene in acetonitrile and thus will also be formed irreversibly.

Several experiments were performed to test these assignments. Ketenimines react with diethylamine to form azepine adducts,[23] but triplet nitrenes do not. Indeed, the carrier of the 1576 cm^{-1} transient absorption reacts with diethylamine with an absolute second-order rate constant of $k = 9.0 \times 10^5$ M^{-1} s^{-1}. This compares to a value of $k = 6.5 \times 10^6$ M^{-1} s^{-1} for reaction of nonfluorinated ketenimine with diethylamine.[24] The reaction of fluorinated ketenimine (K) with diethylamine is slower than we expected. Halogen substituents at the para position of an aryl azide accelerate the reaction of the analogous ketenimine with diethylamine.[19] Ortho fluoro substituents on the aryl azide apparently have the opposite effect.

The carrier of transient absorption at 1444 cm^{-1} does not react with diethylamine at a measurable rate, as expected for a triplet nitrene.

Singlet 2,6-difluorophenylnitrene is much longer-lived than the parent singlet phenylnitrene and is more easily intercepted. Polyfluorinated arylnitrene singlets are intercepted by amines and by dimethyl sulfoxide.[20] Thus, the presence of these nucleophiles in a TRIR experiment should reduce the yield of both triplet nitrene ^{3}N and that of ketenimine K. Indeed, DMSO reduces the initial yield of transient absorption of ketenimine at 1576 cm^{-1} and triplet nitrene at 1444 cm^{-1} (Supporting Information, Figures S6 and S7, respectively).

Our previous study[20] demonstrated by chemical analysis of reaction mixtures that singlet pentafluorophenyl nitrene reacts with DMSO about 10 times more rapidly than with diethylamine. Thus, the difference in the rate of 1.7 observed with these two reagents and 2,6-difluorophenyl nitrene seems reasonable.

V. Conclusions

Time-resolved infrared (TRIR) spectroscopy has been used for the first time to study the solution-phase photochemistry of an aryl azide and to detect the reactive intermediates generated. Laser flash photolysis (LFP, 266 nm) of 2,6-difluorophenyl azide releases open-shell singlet 2,6-difluorophenylnitrene (^{1}N, 1404 cm^{-1}), which is detected in cyclohexane-d_{12} at 283 K and in CD_3CN at 253 and 273 K. At ambient temperature, it is possible to detect the products of singlet nitrene decay, which are the isomeric ketenimine (K) at 1576 cm^{-1} and the lower energy triplet nitrene at 1444 cm^{-1}. Diethylamine and dimethyl sulfoxide can scavenge the singlet nitrene ($k = 4.2 \times 10^7$ M^{-1} s^{-1} and 7.2×10^7 M^{-1} s^{-1}, respectively) and reduce the yield of triplet nitrene and ketenimine. TRIR spectroscopy was used to measure the absolute rate constant for the reaction of ketenimine with diethylamine (9.0×10^4 M^{-1} s^{-1}) and of triplet nitrene with azide precursor (6.9×10^6 M^{-1} s^{-1}). The spectroscopic assignments were consistent with DFT calculations.

Acknowledgment. Support of this work by the National Science Foundation and the Ohio Supercomputer Center (OSC) is gratefully acknowledged.

Supporting Information Available: Figures showing triplet lifetime in CD_3CN at 273 K, triplet lifetime as a function of azide precursor concentration, diethylamine suppression of ketenimine formation, effect of diethylamine on the initial yield and on the lifetime of triplet nitrene following LFP, DMSO quenching of the yield of ketenimine and of triplet nitrene, LFP of 2,6-difluorophenyl azide in the presence of DMSO, theoretical predictions of vibrational bands by DFT calculations, and calculated spectrum of AZ (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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