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PAPER

Nanosecond time-resolved IR study of thiobenzoylnitrene†

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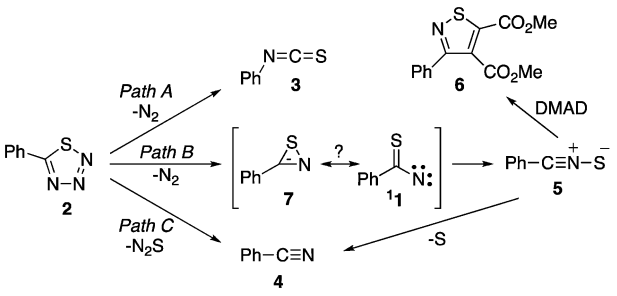
Nanosecond time-resolved infrared (TRIR) spectroscopy has been used to observe singlet thiobenzoylnitrene at 1740 cm^{-1} upon photolysis of 5-phenyl-1,2,3,4-thiatriazole in acetonitrile and dichloromethane. Consistent with the experimental observations, thiobenzoylnitrene is predicted by B3LYP/6-31G* calculations to have a singlet ground state with an intense IR band at 1752 cm^{-1}. Phenyl isothiocyanate is also produced. Kinetic measurements indicate that it is not formed from singlet thiobenzoylnitrene, but rather directly from the thiatriazole. Unlike benzoylnitrene, singlet thiobenzoylnitrene does not react with acetonitrile or dichloromethane on the nanosecond timescale. However, it does react with dimethyl sulfoxide (DMSO) to produce a sulfoximine detected at 1180 cm^{-1} ($k_{DMSO} = 3 \times 10^5\ M^{-1}\ s^{-1}$). Benzonitrile (observed at 2230 cm^{-1}) is produced from both singlet thiobenzoylnitrene (presumably through a short-lived, unobservable benzonitrile sulfide intermediate) and directly from the thiatriazole. B3LYP/6-31G* calculations also show that the structure of singlet thiobenzoylnitrene is analogous to that of related acylnitrenes, with a significant bonding interaction between the nitrogen and sulfur. Triplet thiobenzoylnitrene, on the other hand, is predicted computationally to have a biradical structure.

Introduction

The sulfur analogue of benzoylnitrene, thiobenzoylnitrene (**1**), has been proposed as an intermediate in the photolysis and thermolysis of 5-phenyl-1,2,3,4-thiatriazole (**2**), which produces phenyl isothiocyanate (**3**), benzonitrile (**4**), sulfur, and nitrogen (Scheme 1).[1–6] Holm and co-workers have studied the photochemistry of thiatriazole **2** extensively.[7–9] Triplet sensitization and oxygen quenching experiments indicate that all products are derived only from the singlet manifold. Experiments at 85 K reveal the formation of isothiocyanate **3** without the detection of any intermediate species by UV-Vis or EPR spectroscopy. In addition, since the yield (*ca.* 7%) of isothiocyanate **3** was independent of the solvent employed and was also constant over a wide temperature range (193–300 K), it was concluded that thiobenzoylnitrene is not involved in its formation. Rather, Holm *et al.* suggested that isothiocyanate **3** is formed directly from the singlet excited state of thiatriazole **2** (Scheme 1, Path A).[7]



Scheme 1 Photochemistry of 5-phenyl-1,2,3,4-thiatriazole (**2**).

Holm and co-workers also proposed that nitrile **4**, which is found in *ca.* 70% yield, arises from benzonitrile sulfide (**5**).[7–9] Nitrile sulfides are transient species known for their synthetic utility in 1,3-dipolar cycloadditions,[10] and have been the subject of numerous mechanistic and spectroscopic investigations.[11] These spectroscopic investigations have included flash-vacuum pyrolysis (FVP) and neutralization-reionization mass spectrometry in the gas phase,[12,13] and UV-Vis and IR spectroscopy in low temperature matrices following either photolysis or FVP.[7,8,13–16]

Following photolysis of thiatriazole **2**, Holm and co-workers found evidence for benzonitrile sulfide (**5**) by low-temperature UV-Vis spectroscopy in ether-isopentane-ethanol (EPA) and polyvinyl chloride (PVC) matrices (Scheme 1, Path B).[7,8] Additional evidence for the involvement of nitrile sulfide **5** is provided by room temperature trapping experiments in neat dimethyl acetylenedicarboxylate (DMAD), where the cycloadduct **6** was observed in 9% yield.[7] On the other hand, nitrile sulfide **5** was not detected by UV-Vis spectroscopy following photolysis of thiatriazole **2** in an argon matrix at 10 K; nitrile **4** was observed directly.[8] Similarly, Wentrup *et al.* found no evidence for nitrile sulfide **5** by IR

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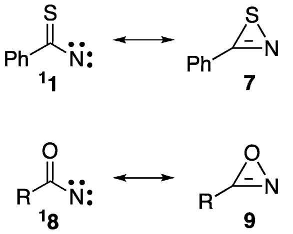


Fig. 1 Representative structures of singlet thiobenzoylnitrene ^{1}**1**, acylnitrenes ^{1}**8**, and related cyclic structures.

spectroscopy following Ar matrix photolysis of **2**, but rather observed the direct formation of nitrile **4** (2228 cm^{-1}) along with dinitrogen sulfide (N_2S) at 2030 cm^{-1} (Scheme 1, Path C).[17] N_2S is unstable and disappeared on warming to 160 K, presumably forming N_2 and S_2.[11,17] Additionally, isothiocyanate **3** was observed at 2190 and 2120 cm^{-1} in these experiments. Through the use of alternative heterocyclic precursors, however, the low temperature matrix IR spectrum of benzonitrile sulfide **5** has been reported at 2185 cm^{-1}.[13,14]

Although thiobenzoylnitrene was considered, Holm *et al.* suggest that phenylthiazirine (**7**) is formed as an unstable intermediate precursor to nitrile sulfide **5** (Scheme 1, Path B).[8] As discussed in more detail below, the relationship between singlet thiobenzoylnitrene and phenthiazirine is analogous to that between singlet acylnitrenes ^{1}**8** and cyclic oxazirines **9** (Fig. 1). Previous computational studies have demonstrated that the singlet states of acylnitrenes are stabilized relative to the corresponding triplet by a significant bonding interaction between the nitrogen and oxygen.[18–22] This interaction is reflected in the calculated geometry, which is intermediate between those of a nitrene and an oxazirine.

To examine the potential involvement of thiobenzoylnitrene, we are pleased to report herein nanosecond time-resolved infrared (TRIR) studies of the photochemistry of thiatriazole **2**. These studies, which parallel our previous TRIR investigations of acylnitrenes generated from azide and sulfilimine-based precursors,[19,22,23] clarify the photochemistry of **2** and, to our knowledge, represent the first direct detection of a thioacylnitrene.

Results and discussion

Time-resolved IR observation of thiobenzoylnitrene and isothiocyanate

Typical TRIR data observed following 266 nm laser photolysis of thiatriazole **2** in argon-saturated acetonitrile-d_3 for the spectral region 1800–1200 cm^{-1} and in argon-saturated dichloromethane for the spectral region 2270–2000 cm^{-1} are shown in Fig. 2 and 4, respectively. Similar spectra are observed in each of these regions for each solvent, although data collection above 2200 cm^{-1} in acetonitrile-d_3 or below 1500 cm^{-1} in dichloromethane is not possible due to strong solvent IR absorbance. Kinetic traces for the prominent positive IR bands observed in acetonitrile-d_3 and dichloromethane are given in Fig. 3 and 5, respectively.

The negative signals observed at 1410 and 1244 cm^{-1} are due to depletion of thiatriazole **2**. Positive bands observed at 2174, 2100, and 1500 cm^{-1} are assigned to isothiocyanate **3**, in good agreement with the Wentrup's previous low-temperature Ar matrix study,[17] and also with the IR spectrum of an authentic sample of phenyl isothiocyanate (Fig. 4). Isothiocyanate **3** is formed at a rate which is faster than our instrumental time resolution (50 ns), and is stable for at least 100 μs.

The 1740 cm^{-1} band is produced at a rate beyond our instrumental time resolution and decays with lifetime of *ca.* 2 μs in both acetonitrile-d_3 and dichloromethane. Oxygen has no effect on the decay of this species. To aid in the assignment of this peak, we performed a B3LYP/6-31G* geometry optimization and vibrational frequency analysis on both singlet and triplet thiobenzoylnitrene (^{1}**1** and ^{3}**1**, respectively). Such calculations have been found previously to predict IR frequencies of acylnitrenes fairly accurately.[19,22,23]

Singlet nitrene ^{1}**1** is found by these calculations to be more stable than ^{3}**1** with $\Delta E_{ST} = -16.2$ kcal mol^{-1}. B3LYP/6-31G* calculations have been found to overestimate the stability of triplet acylnitrenes relative to singlet acylnitrenes by a few kcal mol^{-1}.[21,22] Thus, the true value of ΔE_{ST} is expected to be even more negative and thiobenzoylnitrene should certainly have a singlet ground spin state. An intense IR band for singlet thiobenzoylnitrene ^{1}**1** is calculated at 1752 cm^{-1} (using a scaling factor of 0.96)[24] and at

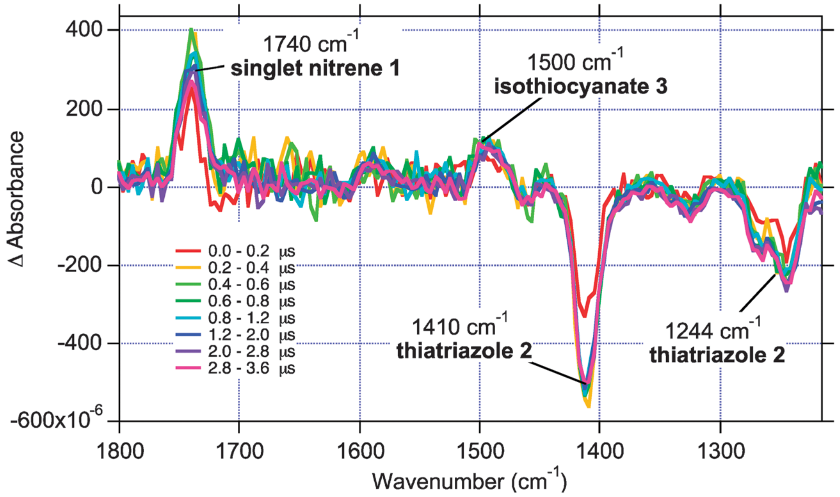


Fig. 2 TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis of thiatriazole **2** (2 mM) in argon-saturated acetonitrile-d_3.

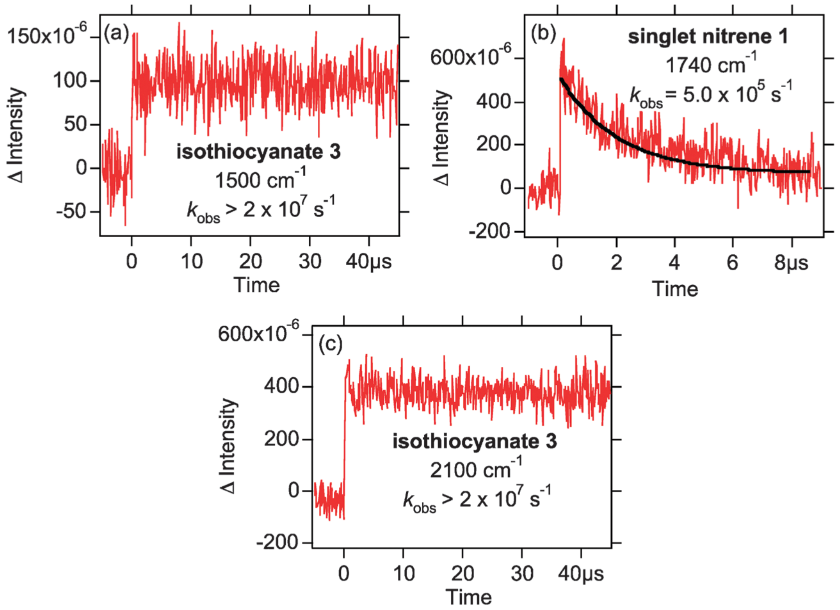


Fig. 3 Kinetic traces observed at (a) 1500, (b) 1740, and (c) 2100 cm^{-1} following 266 nm laser photolysis of thiatriazole **2** (2 mM) in argon-saturated acetonitrile-d_3. The red curves are experimental data; the black curve is the best fit to a single-exponential function. The error in derived rates is estimated to be ±10%.

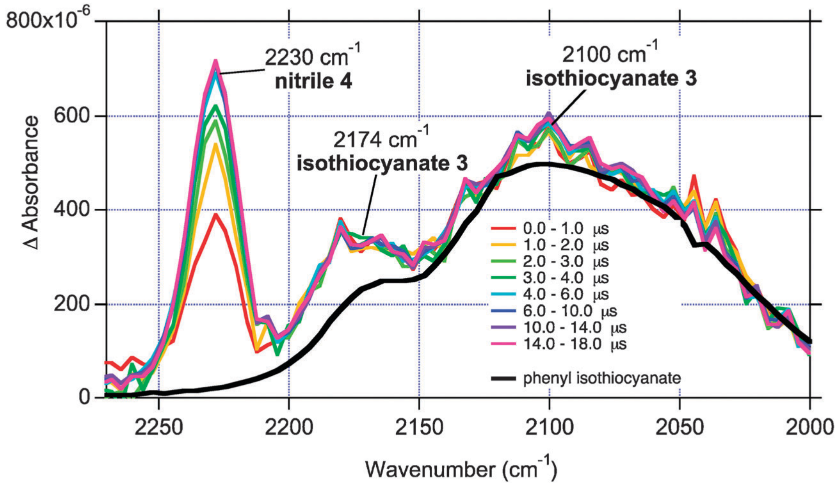


Fig. 4 TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis of thiatriazole **2** (2 mM) in argon-saturated dichloromethane. Overlaid on the TRIR spectra is the normalized IR spectrum of phenyl isothiocyanate taken of an authentic sample under the same experimental conditions (black trace).

1380 cm^{-1} for triplet thiobenzoylnitrene ^{3}**1** (Supporting Information). On the basis of these computational results and the observed lack of reactivity with oxygen, we assign the IR band at 1740 cm^{-1} to singlet nitrene ^{1}**1**.

Since phenyl isothiocyanate (1500, 2100, and 2174 cm^{-1}) is observed within the 50 ns instrument response, it is clearly not produced from singlet nitrene ^{1}**1**, which decays with a lifetime of *ca.* 2 μs. This result is analogous to our previous TRIR studies of acylnitrenes, which also confirmed that isocyanates are not formed from relaxed singlet acylnitrenes following photolysis of benzoyl azide[19] and sulfilimine-based precursors.[22,23] More recently, ultrafast TRIR studies have confirmed directly that the singlet excited state of acyl azides undergoes Curtius rearrangement to form isocyanate.[25]

Structure of thiobenzoylnitrene

The B3LYP/6-31G* calculated structures of both singlet and triplet thiobenzoylnitrene are shown in Fig. 6. The singlet C–S bond length (1.780 Å) is longer than that in the triplet state (1.753 Å) and is close to typical C–S single bond (1.79–1.82 Å).[26] In addition, the singlet C–N bond length (1.246 Å) is shorter than that in the triplet (1.288 Å) and resembles a typical C–N double bond (1.25–1.26 Å in strained cyclic compounds).[27–29] The singlet NCS bond angle (79°) is much smaller than that calculated for ^{3}**1** (111°). Thus, the calculated structure of ^{1}**1** is analogous to that of singlet acylnitrenes (Fig. 1),[18–22] with the C–S–N fragment having significant three-membered ring character. Although the S–N

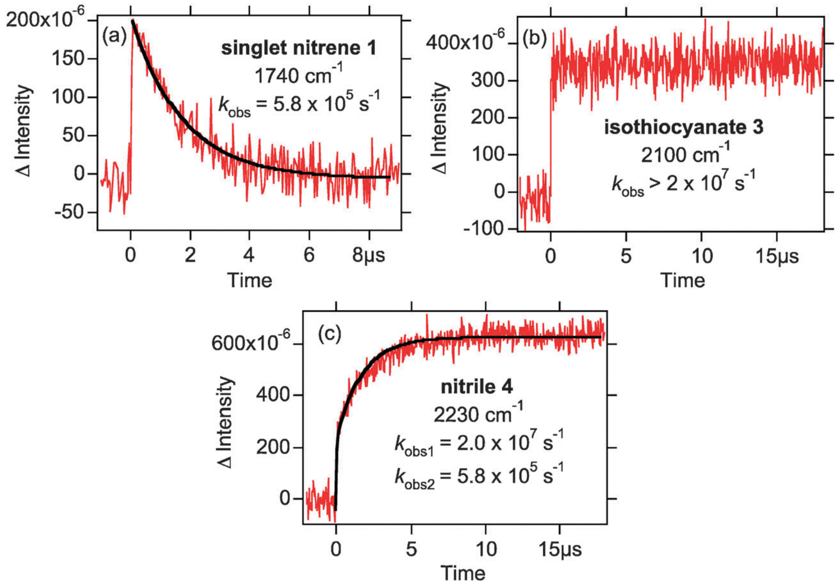
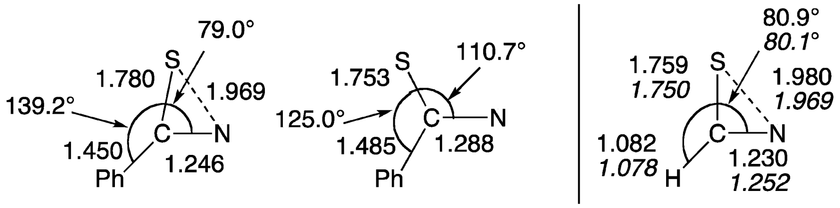


Fig. 5 Kinetic traces observed at (a) 1740, (b) 2100, and (c) 2230 cm^{-1} following 266 nm laser photolysis of thiatriazole **2** (2 mM) in argon-saturated dichloromethane. The red curves are experimental data; the black curves are best fits to a single- (a) or double- (c) exponential function. The error in derived rates is estimated to be ±10%.



singlet thiobenzoylnitrene ^{1}1 **triplet thiobenzoylnitrene ^{3}1** **singlet "thiazirine" ^{1}10**

Fig. 6 B3LYP/6-31G* calculated bond lengths (Å) and bond angles in the singlet and triplet states of thiobenzoylnitrene **1**, and for comparison with ^{1}**1**, the recently reported B3LYP/6-31G* (normal font) and MP2 (italics) calculated bond lengths and angles for the parent thiazirine ^{1}**10**.[30]

bond is elongated (1.97 Å), a significant bonding interaction exists between the nitrogen and sulfur in ^{1}**1**.

In the triplet state, the calculated C–S bond length (1.753 Å) is substantially longer than a typical C–S double bond (1.55 Å).[31] The calculated C–N bond length (1.288 Å), on the other hand, is shorter in comparison with the C–N bond in other triplet nitrenes (1.381 Å for benzoylnitrene,[18] 1.34 Å for phenylnitrene,[32] and 1.42 Å for methylnitrene.[33]). These structural data suggest a biradical structure for ^{3}**1** as shown by the simplified Lewis dot structures in Fig. 7. One electron resides in an allylic π orbital that is polarized towards the sulfur and the other electron is localized in an in-plane σ orbital centered on nitrogen. A biradical structure is also supported by the B3LYP/6-31G* calculated spin densities, which indicate approximately equal spin on the sulfur and nitrogen atoms of ^{3}**1** (Supporting Information). B3LYP/6-31G* calculations also suggest similar biradical structures for the triplet states of thioacetylnitrene and thioformylnitrene (Supporting Information). Interestingly, analogous computational studies of acylnitrenes have predicted triplet nitrene structures with spin density located almost exclusively on the nitrogen,[18–22] which we have also confirmed for triplet acetylnitrene and formylnitrene (Supporting Information).

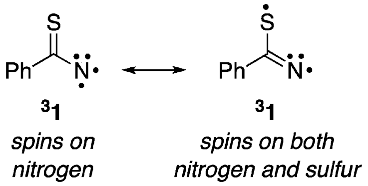
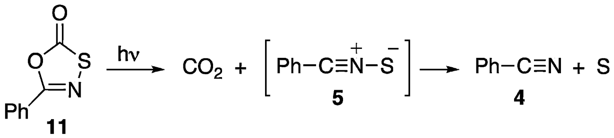


Fig. 7 Representative Lewis dot structures of triplet thiobenzoylnitrene ^{3}**1**.

Since phenyl thiazirine **7** was proposed as a precursor of benzonitrile sulfide **5** (Scheme 1),[7] we attempted to calculate its B3LYP/6-31G* structure and IR frequencies. However, with phenyl thiazirine **7** as the starting geometry, B3LYP/6-31G* optimization led to the singlet nitrene structure (^{1}**1**) shown in Fig. 6. (Similarly, we find that B3LYP/6-31G* computational studies with phenyl oxazirene **9** (R = Ph) as the starting structure lead to singlet benzoylnitrene as the optimized geometry.) The structure of the related cyclic parent thiazirine ^{1}**10** (Fig. 6) was recently examined by B3LYP/6-31G* and MP2 methods.[30] An inspection of the reported bond lengths and angles indicates that its structure is very similar to that found for singlet thiobenzoylnitrene ^{1}**1**. As has been pointed out previously,[18–22] singlet acylnitrenes ^{1}**8** and cyclic



Scheme 2 Photochemistry of 5-phenyl-1,3,4-oxathiazol-2-one (**11**).

oxazirines **9** are different representations of the same intermediate. Likewise, these computational results reveal that the same is true for singlet thioacylnitrenes and thiazirines.

Formation of benzonitrile

In addition to singlet thiobenzoylnitrene and isothiocyanate, we also detect an IR band at 2230 cm^{-1} in dichloromethane. On the basis of previous studies,[7–9] this band is assigned to benzonitrile **4**, in good agreement with the literature reported frequency of 2235 cm^{-1} (in THF).[34] Nitrile **4** is formed with biexponential kinetics, consisting of a fast, unresolvable component and a slower component (Fig. 5c). The double exponential fit for these data was generated by fixing the fast component at our instrument response rate (2×10^7 s^{-1}) and allowing the slower component as well as the ratio of fast : slow components to vary. This fit provides a fast : slow ratio of approximately 1 : 4 with a slower exponential growth of 5.8×10^5 s^{-1}, which matches very well with the decay rate of singlet thiobenzoylnitrene **^{1}1** (Fig. 5a).

Thus, as shown in Scheme 1, these data indicate that nitrile **4** is formed *via* two pathways, one of which is production from **^{1}1** (Scheme 1, Path B). On the basis of previous work,[17] we propose that the fast component of nitrile production arises directly from thiatriazole **2** along with N_2S (Scheme 1, Path C). We do not observe any TRIR evidence for N_2S, which has been detected at 2030 cm^{-1} by low temperature matrix IR spectroscopy.[17] This signal may be buried under the broad isothiocyanate signal (Fig. 4), or may be too short-lived ($\tau < 50$ ns) for detection under our current experimental conditions.

Although benzonitrile sulfide **5** has been proposed as an intermediate in the photochemistry of thiatriazole **2**,[7–9] we observe no evidence for its formation at 2185 cm^{-1},[13,14] suggesting that its lifetime is too short for observations under our experimental conditions (Scheme 1, Path B). (The production of sulfur was confirmed by trapping with triphenylphosphine to form triphenylphosphine sulfide,[35,36] which was detected by HPLC.) Additionally, our attempts to observe sulfide **5** from the alternative precursor, phenyl-1,3,4-oxathiazol-2-one (**11**), were also unsuccessful. Since the formation of **5** has also been reported following the photolysis of oxathiazolone **11**,[7–9] and it has been observed at 2185 cm^{-1} by low temperature matrix IR spectroscopy following FVP of **11**,[13] we examined the photochemistry of **11** in dichloromethane by TRIR spectroscopy. We see immediate ($k_{obs} \geq 2 \times 10^7$ s^{-1}) formation of carbon dioxide at 2335 cm^{-1} and nitrile **4** at 2230 cm^{-1} with no evidence for sulfide **5**, again suggesting a lifetime shorter than 50 ns (Scheme 2). Thus, our experiments indicate that the photochemistry of thiatriazole **2** shown in Scheme 1 involves nitrene **^{1}1** as well as a short-lived nitrile sulfide **5**.

Reactivity of thiobenzoylnitrene

Singlet thiobenzoylnitrene **^{1}1** appears to be less reactive than singlet benzoylnitrene. Previous TRIR studies have demonstrated that singlet benzoylnitrene reacts with acetonitrile to form an ylide intermediate and with dichloromethane presumably to form an insertion product.[19,23] Reactions of singlet nitrene **^{1}1** with solvents such as acetonitrile, dichloromethane, isopropanol, and anisole have not previously been observed.[7] Likewise, we observed no evidence for adducts of singlet nitrene **^{1}1** with acetonitrile or dichloromethane; **^{1}1** appears to decay exclusively to benzonitrile **4** in these solvents (Scheme 1).

Since dimethyl sulfoxide (DMSO) is known to react very efficiently with singlet nitrenes to form sulfoximines,[37–40] we examined its reactivity with thiobenzoylnitrene. In the presence of significant concentrations of DMSO (over 1 M) we observe trapping of nitrene **^{1}1** and a new TRIR signal is detected at 1180 cm^{-1} (Fig. 8). The rate of growth of this signal correlates well with the rate of nitrene decay at 1740 cm^{-1} (Fig. 9). On the basis of the expected nitrene-DMSO reactivity and B3LYP/6-31G* calculations (Supporting Information), which predict strong IR bands at 1159, 1169, 1199, and 1251 cm^{-1} (using a scaling factor of 0.96),[24] we assign this band to sulfoximine **12** (Scheme 3).

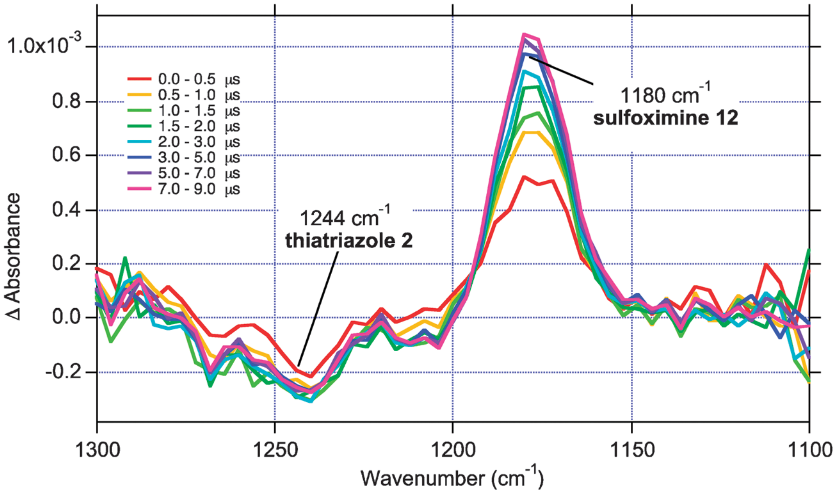


Fig. 8 TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis of thiatriazole **2** (2 mM) in argon-saturated acetonitrile.

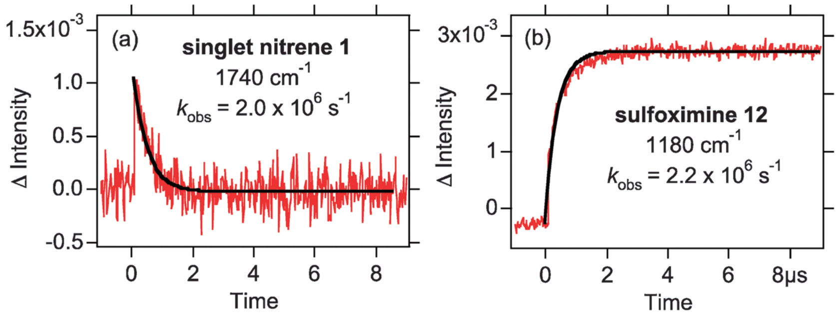
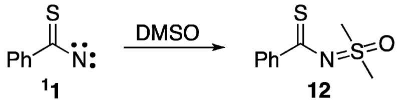


Fig. 9 Kinetic traces observed at (a) 1740 and (b) 1180 cm^{-1} following 266 nm laser photolysis of thiatriazole **2** (2 mM) in the presence of DMSO (5.3 M) in argon-saturated acetonitrile. The red curves are experimental data; the black curves are best fits to a single-exponential function. The error in derived rates is estimated to be ±10%.



Scheme 3 Reactivity of singlet thiobenzoylnitrene with DMSO.

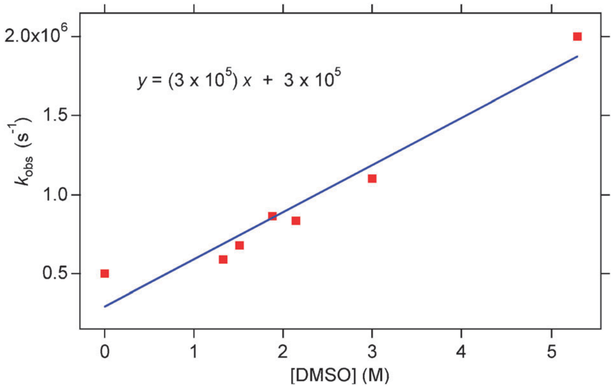


Fig. 10 Plot of the observed rate of nitrene decay (k_{obs}) monitored at 1740 cm^{-1} *versus* the concentration of DMSO in acetonitrile (R^2 = 0.97).

(The predicted band at 1251 cm^{-1} is likely obscured by overlap with the 1244 cm^{-1} thiatriazole precursor depletion band.)

By monitoring the observed decay rates of ^{1}**1** (k_{obs}) as a function of DMSO concentration, the second-order rate constant for the reaction of ^{1}**1** with DMSO (k_{DMSO}) can be estimated from the pseudo-first-order equation, $k_{obs} = k_0 + k_{DMSO}$ [DMSO], where k_0 is the rate of nitrene decay in the absence of DMSO. This analysis (Fig. 10) yields $k_{DMSO} = 3 \times 10^5$ M^{-1} s^{-1}, which is over three orders of magnitude smaller than that for the reaction of singlet arylnitrenes with DMSO,[39,40] indicating that singlet nitrene ^{1}**1** is quite unreactive, even with DMSO.

Conclusions

The first direct evidence for the involvement of singlet thiobenzoylnitrene in the photochemistry of 5-phenyl-1,2,3,4-thiatriazole has been obtained by nanosecond TRIR spectroscopy. To our knowledge, this represents the first spectroscopic observation of a thioacylnitrene intermediate. Kinetic measurements indicate that singlet thiobenzoylnitrene does not form the observed isothiocyanate product, but rather produces benzonitrile presumably through a short-lived, unobservable benzonitrile sulfide intermediate. Benzonitrile is also produced directly from the thiatriazole. The structure of singlet thiobenzoylnitrene is analogous to that of related acylnitrenes, with a significant bonding interaction between the nitrogen and sulfur. In contrast to singlet benzoylnitrene, singlet thiobenzoylnitrene is unreactive with acetonitrile or dichloromethane. It does, however, react with DMSO to produce a sulfoximine. Although not detected experimentally, triplet thiobenzoylnitrene is predicted computationally to have a biradical structure.

Experimental

General methods

Unless otherwise noted, materials were obtained from Aldrich Chemical Company, Fisher Scientific, or Cambridge Isotope Laboratories and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz FT-NMR operating at 400 MHz and 125 MHz, respectively. All resonances are reported in parts per million, and are referenced to solvent (DMSO-d_6 ^{1}H NMR δ 2.5, ^{13}C NMR δ 39.5). Resonances are reported in δ units downfield from tetramethylsilane. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. High-resolution mass spectra were obtained on a VG70SE double focusing magnetic sector mass spectrometer operating in fast atom bombardment ionization mode. Reported masses were referenced to a doubly potassiated PEGMME mass calibrant. Ultraviolet-visible (UV-Vis) absorption spectra were obtained using a Hewlett Packard 8453 diode array spectrometer. Infrared (IR) absorption spectra were obtained using a Bruker IFS 55 Fourier transform infrared spectrometer. All DFT calculations were performed using Spartan '04 for Macintosh or Spartan '08 for Windows using the B3LYP/6-31G* method and basis set. Geometries were fully optimized and all stationary points were confirmed to be energy minima by vibrational frequency analysis.

5-Phenyl-1,2,3,4-thiatriazole (2). Thiatriazole **2** was synthesized following the literature reported procedure.[41] mp 95–97 °C, Lit.[41] 94–96 °C; ^{1}H NMR ($CDCl_3$) δ 7.5–8.1 (5 H); FAB-MS (3-NBA): m/z calc 164.02824 [MH$^+$], found 164.02827; IR (neat) 1405 and 1240 cm^{-1} ($\nu_{C=S}$).

Phenyl-1,3,4-oxathiazol-2-one (11). Oxathiazolone **11** was synthesized following the literature reported procedure.[42]

^{1}H NMR ($CDCl_3$): δ 7.97 (2H, d); 7.57 (1H, t); 7.49 (2H, t); mp 68–72 °C, Lit.[42] 69–71 °C.

Time-resolved IR methods

Nanosecond TRIR experiments were conducted (with 16 cm^{-1} spectral resolution) following the method of Hamaguchi and co-workers[43,44] as has been described previously.[45] Briefly, the broadband output of a $MoSi_2$ IR source (JASCO) is crossed with excitation pulses from a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 2 mJ) operating at 15 Hz. Changes in IR intensity are monitored using an AC-coupled mercury/cadmium/tellurium (MCT) photovoltaic IR detector (Kolmar Technologies, KMPV11-J1/AC), amplified, digitized with a Tektronix TDS520A oscilloscope, and collected for data processing. The experiment is conducted in dispersive mode with a JASCO TRIR 1000 spectrometer.

Acknowledgements

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