Photochemistry of *N*-Acetyl-, *N*-Trifluoroacetyl-, *N*- Mesyl-, and *N*-Tosyldibenzothiophene Sulfilimines
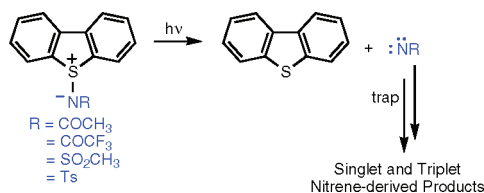
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Time-resolved infrared (TRIR) spectroscopy, product studies, and computational methods were applied to the photolysis of sulfilimines derived from dibenzothiophene that were expected to release acetylnitrene, trifluoroacetylnitrene, mesylnitrene, and tosylnitrene. All three methods provided results for acetylnitrene consistent with literature precedent and analogous experiments with the benzoylnitrene precursor, i.e., that the ground-state multiplicity is singlet. In contrast, product studies clearly indicate triplet reactivity for trifluoroacetylnitrene, though TRIR experiments were more ambiguous. Product studies suggest that these sulfilimines are superior sources for sulfonylnitrenes, which have triplet grounds states, to the corresponding azides, and computational studies shed light on the electronic structure of the nitrenes.

Introduction

The chemistry of nitrenes is, if anything, more complex than that of their isoelectronic carbene cousins.[1–6] For example, while only the closed-shell singlet is usually relevant for carbenes, the open-shell singlet can be an important state for nitrenes. Moreover, while the ground-state for simple alkylnitrenes is of triplet multiplicity (by tens of kcal/mol), relatively slow intersystem crossing rates and rapid reactions of the singlet often make detection of the triplet ground-state difficult. In cases such as methylnitrene, rearranged imines, rather than nitrenes, are detected even at cryogenic temperatures.[3]

α-Ketonitrenes, such as benzoylnitrene (**2a**), on the other hand, have singlet ground states, due to a very strong stabilizing interaction between the oxygen lone pair and the nominally empty orbital on nitrogen. This results in a narrowing of the O−C−N angle and strong bonding interactions. By contrast,

although the same interaction exists for the closed-shell singlet state, alkoxycarbonylnitrenes have triplet ground states, the singlet stabilization apparently being subtly less important.[3,7]
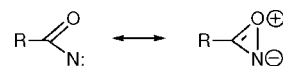
Despite their structural similarity to the carbonyl case, the available evidence is that toluenesulfonylnitrene (**2e**) has a triplet ground state, as established by the observation of a low temperature EPR signal on photolysis of tosyl azide.[3,8,9] A triplet EPR signal was also observed for mesylnitrene at very low temperature obtained in the analogous fashion.[10,11] Nonetheless, the chemistry of sulfonylnitrenes is not well established because of problems with the sulfonylazide precursor. These have often led to difficult mixtures with hard-to-characterize precipitates.[4] Other problems also exist. Despite the apparent triplet multiplic-

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ity of the sulfonylnitrene ground states, thermolysis or photolysis of sulfonyl azides generally leads to negligible amounts of triplet-nitrene-derived products.[8,12–18] Complexities deriving from the possibility of reactions of the excited states of the azide (as opposed to nitrene reactivity) and from the hazards associated with smaller azides (e.g., mesyl azide) have been noted.[13,17,19–22] Finally, SO_2 extrusion is observed under some circumstances. For these reasons, sulfonyl azides have been called only "occasionally useful" precursors to sulfonylnitrenes.[8,23] Thus, other precursors are clearly valuable in elucidating the chemistry of sulfonylnitrenes.

We recently reported the photolysis of *N*-benzoyl dibenzothiophene sulfilimine **1a**, which generates dibenzothiophene (DBT) and the nitrene **2a**.[24] Both singlet and triplet benzoylnitrene were directly observed by time-resolved infrared (TRIR) spectroscopy and confirmed byproduct studies. We have also recently reported product studies demonstrating the formation of carbenes from similarly derived S−C ylides of dimethyl malonate with thiophene derivatives.[25]

Nearly simultaneous with our publication regarding benzoylnitrene, Morita and co-workers reported photochemically induced S−N cleavage of several *N*-tosyl and *N*-acyl thianthrene sulfilimine derivatives.[26] Intra- and intermolecular trapping of presumed nitrene intermediates by thianthrene and diphenyl sulfide was noted. Tosyl amide was also formed in limited yield from the *N*-tosyl derivatives and other reactions related to stereochemical inversion of the thianthrene derivatives.[26]

Much earlier, the first chemical trapping evidence of nitrene formation from sulfilimines arose from photolysis of the *N*-tosyl sulfilimine of dimethyl sulfide and a few related derivatives,[27–29] though in these instances, the nitrene provided the chromophore, rather than the sulfide. As a matter of principle, the use of either thianthrene or dibenzothiophene should represent an improvement over dimethyl sulfide for the basic reason that the chromophore does not need to be tied to the nitrene being produced.

We report here a systematic study using a set of *N*-substituted analogues of **1a** designed to produce different carbonylnitrenes and sulfonylnitrenes from the dibenzothiophene chromophore.

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CHART 1
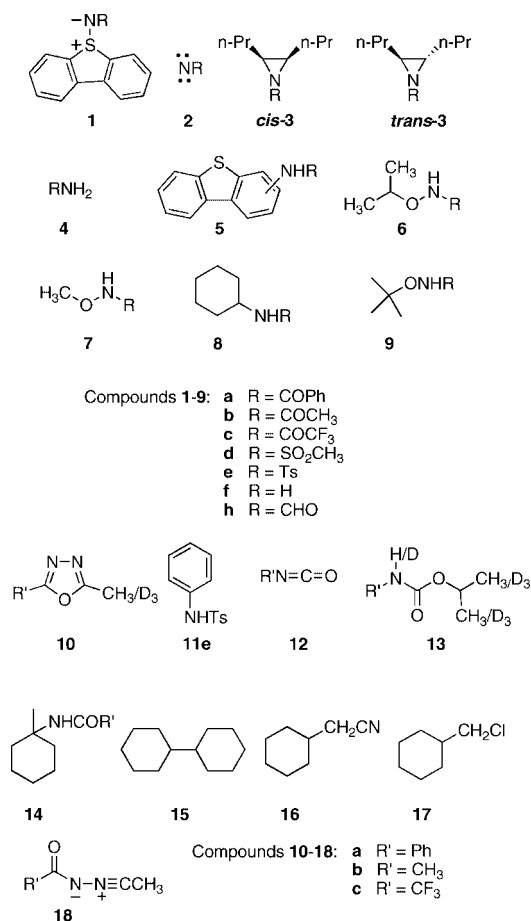
These compounds are analogs of those studied by Morita, using dibenzothiophene, rather than thianthrene, as the base sulfide. Though we do not directly compare the two systems here, the photochemistry of the thianthrene derivatives[26] is more complex.

The starting materials and potential products deriving from the photolyses are shown in Chart 1. The compounds are numbered such that sulfilimine **1a** gives rise to nitrene **2a**, which in turn gives rise to potential products **3a**, **4a**, **5a**, and so on.

Results and Discussion

Time-Resolved IR Studies. Nanosecond TRIR methods were used to try to detect the various nitrenes directly. The TRIR spectrometer used faces the limitation that its time resolution is approximately 50 ns; intermediates that are shorter lived than that cannot be observed. Photolyses of three sulfilimines were carried out (**1b**, **1c**, and **1d**). The mesyl derivative **1d** was chosen over the tosyl derivative **1e** to reduce the complexity of the spectrum.

N-Acetyl Dibenzothiophene Sulfilimine, 1b, and Acetylnitrene, 2b. Recent results with **1a**,[24] which leads to singlet and triplet benzoylnitrene, provided an anticipated framework from which to interpret results from **1b**. TRIR difference spectra obtained on 266 nm laser photolysis of **1b** in CD_3CN and in CH_2Cl_2 are shown in Figure 1. Corresponding kinetic traces obtained from 266 nm laser photolysis are shown in Figures 2 and 3.

Methyl isocyanate was observed at 2255 cm^{-1}. It was produced faster than the 50 ns resolution of the instrument (Figure 2a), consistent with an excited state of **1b** (or an
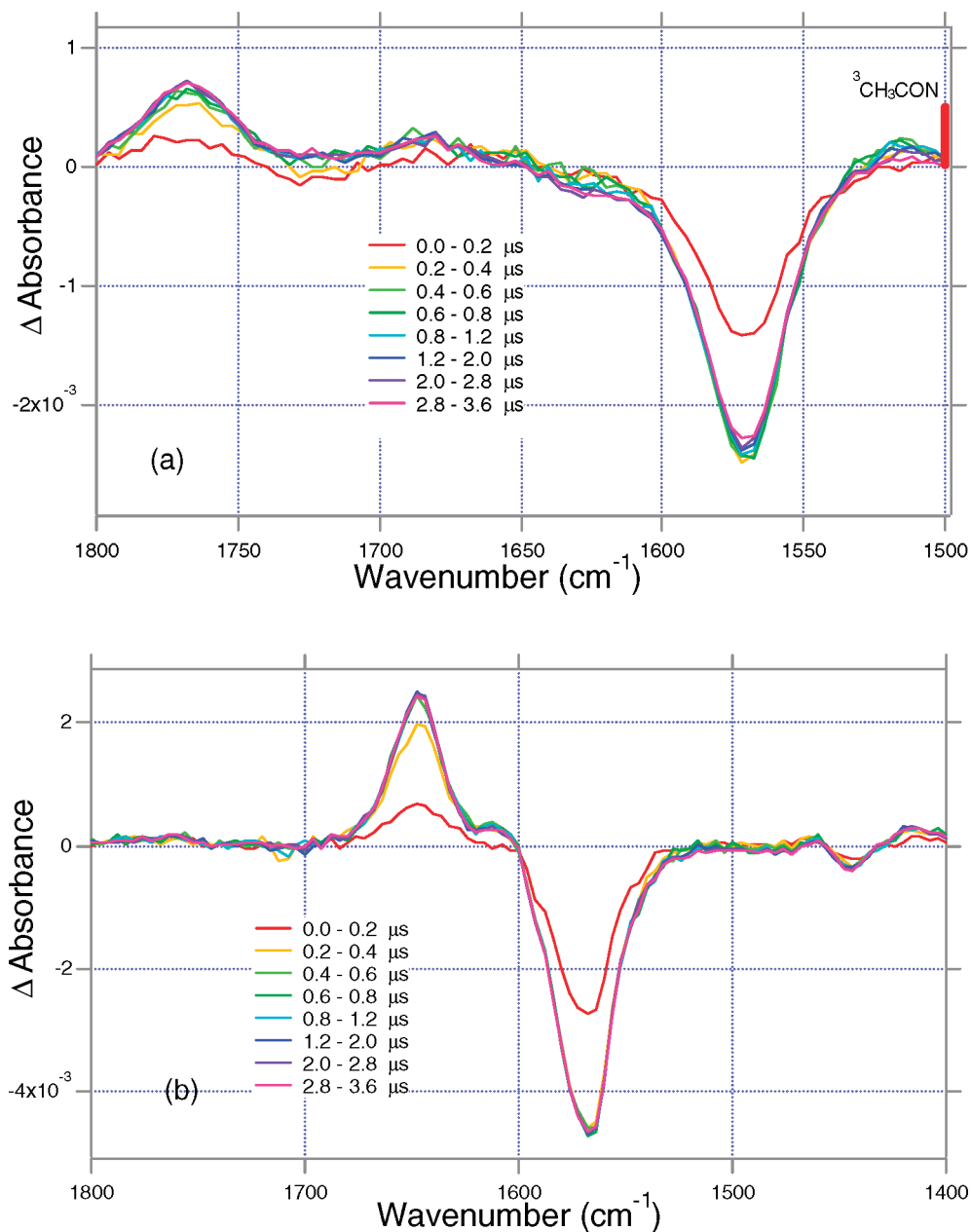
FIGURE 1. TRIR difference spectra averaged over the time scales indicated following 266 nm laser photolysis of **1b** (1 mM) in argon-saturated (a) CH_2Cl_2 and (b) CD_3CN. The red bar indicates the B3LYP/6-31G(d)-calculated IR frequency (scaled by 0.96) of triplet acetylnitrene, ^{3}**2b**.

electronically or vibrationally excited nitrene) being its source, as was found for the analogous product from **1a** (Scheme 1).[24]

In dichloromethane, a peak at 1518 cm^{-1} grows in with a ~230 ns time constant and decays over a few microseconds (Figure 2d). We attribute it to ^{3}**2b**. B3LYP/6-31G(d) calculations on acetylnitrene predict a strong IR band at 1774 cm^{-1} for the singlet nitrene and 1500 cm^{-1} for the triplet nitrene (frequencies scaled by 0.96[30]).

Singlet acetylnitrene was not observed due to an overlapping IR band near 1776 cm^{-1}. This band grows in at the same rate as the triplet nitrene, and the rate depends on the initial concentration of the precursor. Figure 2b shows that this band does not decay noticeably within several microseconds, which is not compatible with it being the singlet nitrene. Because of

these kinetic observations, the 1776 cm^{-1} band is therefore attributed to the reaction product between the singlet acetylnitrene and DBT or the starting material. Finally, another band at 1680 cm^{-1} was observed (Figure 2c), which is believed to arise from the singlet nitrene reaction with dichloromethane.

In CD_3CN, the band at 1776 cm^{-1} was weak and a new, strong band at 1648 cm^{-1} was observed. The 1648 cm^{-1} band was attributed to the formation of acetonitrile−ylide from the singlet acetylnitrene. A strong vibration for this species was calculated at 1694 cm^{-1}, in reasonable, but not outstanding, agreement with the observed value. The decreased intensity of the 1776 cm^{-1} band is attributed to the competition between acetonitrile ylide formation and reaction of the singlet nitrene with DBT. A decreased intensity of the 1776 cm^{-1} band enabled us to observe a kinetic trace at 1780 cm^{-1} (albeit not of high

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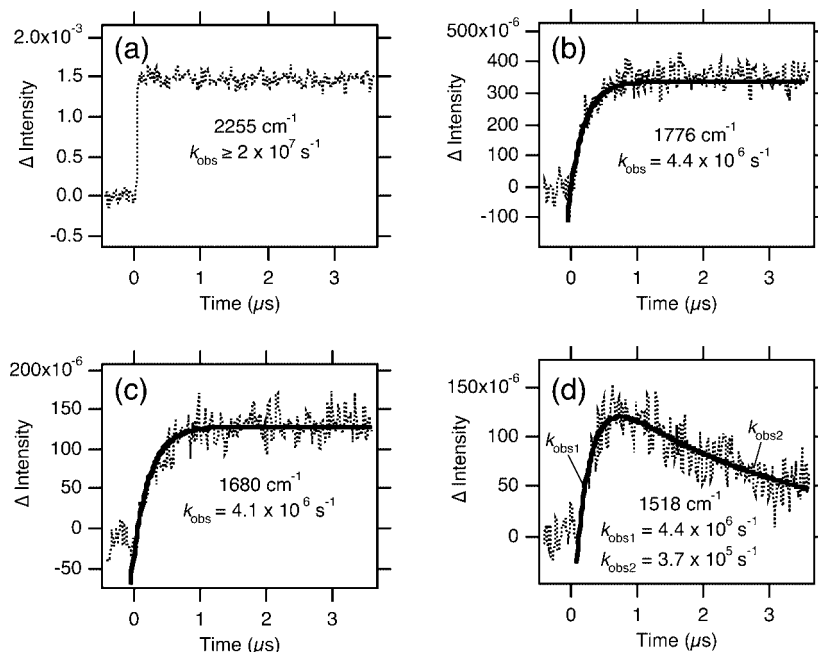
FIGURE 2. Kinetic traces obtained at (a) 2255 cm^{-1}, (b) 1776 cm^{-1}, (c) 1680 cm^{-1}, and (d) 1518 cm^{-1} after 266 nm laser photolysis of **1b** (1 mM) in argon-saturated CH$_2$Cl$_2$. The dotted-line curves are experimental data and the black solid curves are the calculated best fit to a single-exponential function.

FIGURE 3. Kinetic traces obtained at (a) 1648 cm^{-1}, (b) 1515 cm^{-1}, and (c) 1780 cm^{-1} after 266 nm laser photolysis of **1b** (1 mM) in argon-saturated CD$_3$CN. The dotted-line curves are experimental data and the black solid curves are the calculated best fit to a single-exponential function.
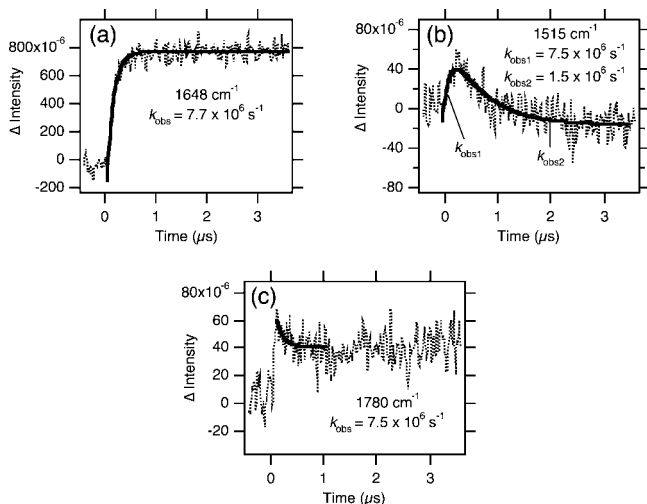
quality) that decays at the same rate as the growth of the 1515 cm^{-1} band and the ylide band. The decay trace at 1780 cm^{-1} is attributed to singlet acetylnitrene; we believe that the singlet nitrene is the most likely source for the ylide and at least most of the triplet nitrene, as shown in Scheme 1.

Based on the lack of a literature report of a triplet EPR spectrum of acetylnitrene at low temperature and recent calculations at the CBS-QB3 level,[7] we presume that the energies of the singlet and triplet states of acetylnitrene are very similar but that the singlet is slightly lower. Thus, population of the triplet acetylnitrene by the singlet is presumably an endothermic relaxation toward that thermal equilibrium. The triplet nitrene is then depleted by reactions of either the singlet or triplet

SCHEME 1. Proposed Photochemical Processes for 1b Based on IR Data
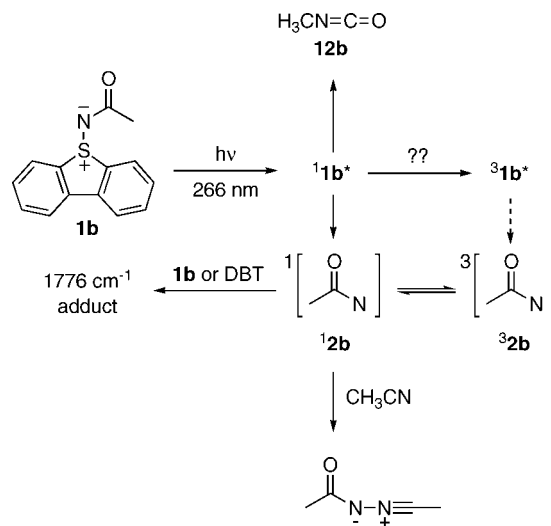
species, as long as this equilibrium is maintained. This model comports well with the appearance time constant of the 1518 cm^{-1} band observed in dichloromethane (Figure 2d, first order growth time constant ca. 230 ns) and 1515 cm^{-1} band observed in acetonitrile (Figure 3b, time constant ca. 130 ns). Since at room temperature, an energy difference of ~1.4 kcal/mol corresponds to a 10:1 population ratio, we presume this is an approximate upper limit for the energy difference between the two nitrene multiplicities. Detection of the higher energy triplet would become very difficult with lower populations. Product studies (vide infra) are also consistent with mainly singlet chemistry, as can be understood in terms of greater rate constants for reaction from the singlet nitrene than from the triplet, in addition to the greater equilibrium population of the lower energy singlet state.
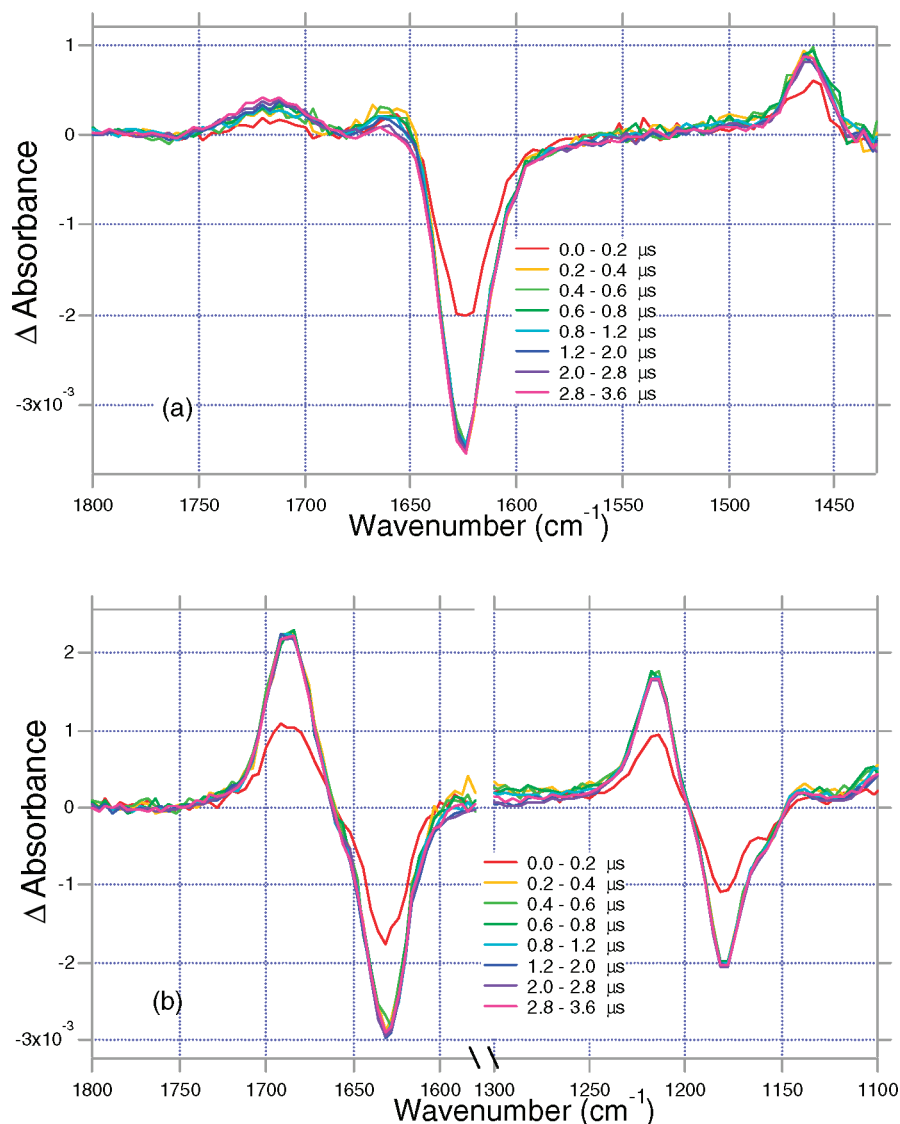
FIGURE 4. TRIR difference spectra observed over the time scales indicated following 266 nm laser photolysis of **1c** (1 mM) in argon-saturated (a) CH_2Cl_2 and (b) CH_3CN.

***N*-Trifluoroacetyl Dibenzothiophene Sulfilimine, 1c, and Trifluoroacetylnitrene, 2c.** Similar TRIR measurements were performed using **1c** as the photochemical precursor. Representative difference spectra are shown in Figure 4 in (a) Ar-saturated dichloromethane and (b) Ar-saturated acetonitrile. Kinetic traces for the positive bands in dichloromethane, observed at 1660, 1715, and 2270 cm^{-1}, are shown in Figure 5, while kinetic traces for the positive bands observed at 1688, 1218, and 2270 cm^{-1} in acetonitrile are shown as Figure 6. (The kinetic trace at 1460 cm^{-1} is essentially identical to that at 2270 cm^{-1} observed in argon-saturated dichloromethane in that the band is permanent on this time scale.)

In dichloromethane, the negative band observed at 1624 cm^{-1} is due to depletion of precursor **1c**. A positive band observed at 1660 cm^{-1} is formed at a rate faster than our instrumental time resolution (50 ns) and decays at a first-order rate of 6.5 $\times 10^4$ s^{-1}, as shown in Figure 5a. (Note the 1660 cm^{-1} band partly overlaps with the precursor depletion band observed at 1624 cm^{-1}.) Additionally, the decay rate of this band is unaffected by the presence of oxygen, suggesting that it is due to a singlet species. The decay rate of the 1660 cm^{-1}

band is linearly dependent upon the concentration of methanol, indicating a second-order reaction between the carrier and methanol, with a second-order rate constant of $k_{methanol}$ = 5.0 $\times 10^6$ M^{-1} s^{-1}. This rate constant is comparable with that of singlet benzoylnitrene reaction with methanol (6.5 $\pm$ 0.4 $\times 10^6$ M^{-1} s^{-1}).[24]

On the basis of these results, the most reasonable assignment to the 1660 cm^{-1} band is to singlet trifluoroacetynitrene (^{1}**2c**). However, we face the difficulty that the vibrational frequencies nearest 1660 cm^{-1} predicted by the B3LYP/6-31G(d) calculations (scaled by 0.96) for ^{1}**2c** are not close to this value, as shown in Table 1. The listed frequencies are the two that are closest to 1660 cm^{-1} for each multiplicity of the nitrene. Like for the singlet, there is not a triplet nitrene frequency predicted near 1660 cm^{-1}.

Another potential assignment for the 1660 cm^{-1} band is the dimerization product of two nitrenes, i.e., the azo compound. (See, for example, ref 31.) However, we eliminate that product on kinetic grounds. The appearance of the band in less than 50 ns is not reasonable for a bimolecular reaction of low concentra-
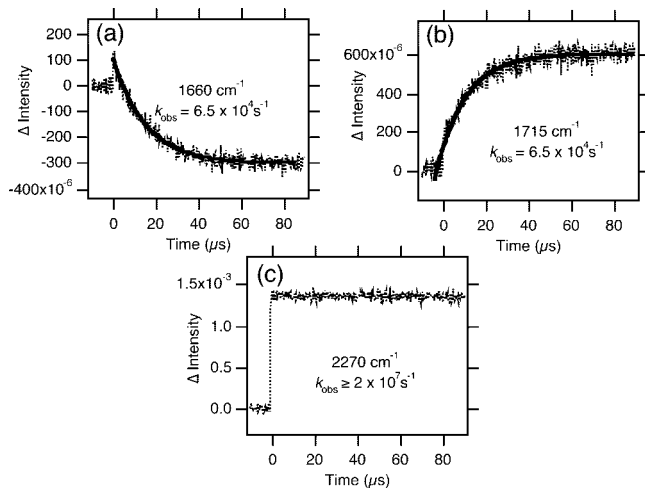
FIGURE 5. Kinetic traces observed at (a) 1660, (b) 1715, and (c) 2270 cm^{-1} following 266 nm laser photolysis of **1c** (1 mM) in argon-purged CH$_2$Cl$_2$. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.

tion species. Moreover, the decay of the band (Figure 5a) on the time scale of tens of microseconds would have produced a product band, presumably acyl radicals, that would have been easily detectable above 1800 cm^{-1}.[32,33] The reactivity of the 1660 cm^{-1} band (vide infra) also does not comport well with the azo compound as a potential assignment.

Another positive band is observed at 1715 cm^{-1}. Its growth rate ($k_{obs} = 6.5 \times 10^4$ s^{-1}, Figure 5b) matches the decay of the 1660 cm^{-1} band. This band is not observed in acetonitrile, nor is its appearance rate affected by the concentration of the precursor. It is thus assigned to a reaction product between dichloromethane and the 1660 cm^{-1} intermediate.

In dichloromethane, trifluoromethyl isocyanate **12c** is detected at 2270 and 1460 cm^{-1}, in good agreement with the 2255 cm^{-1} value observed for **12b**.[34] Again, its rate of growth is faster than instrumental resolution (Figure 5c), indicating that its precursor is not the relaxed singlet nitrene, but more likely the excited-state precursor **1c**, or potentially an excited nitrene. In acetonitrile, it is detected similarly at 2270 cm^{-1} (Figure 6e).

In acetonitrile, no band attributable to singlet nitrene was observed. However, we assign two new positive bands observed at 1688 and 1218 cm^{-1} (Figure 6) to the acetonitrile ylide **18c**, formed from singlet nitrene **1 2c** reaction with acetonitrile, in good agreement with B3LYP/6-31G(d) calculated frequencies of 1706 (scaled by 0.96)[35] and 1241 cm^{-1}. Both bands are formed more rapidly than instrumental response, and decay, presumably to oxadiazole **10c**, with a first-order rate of 6.5 × 10^2 s^{-1}.

In order to confirm this assignment and check for self-consistency, we examined the behavior of the 1660 cm^{-1} band in dichloromethane solutions with smaller added amounts of acetonitrile. Kinetic traces for solutions in dichloromethane containing 1 mM acetonitrile are shown in Figure 7 at
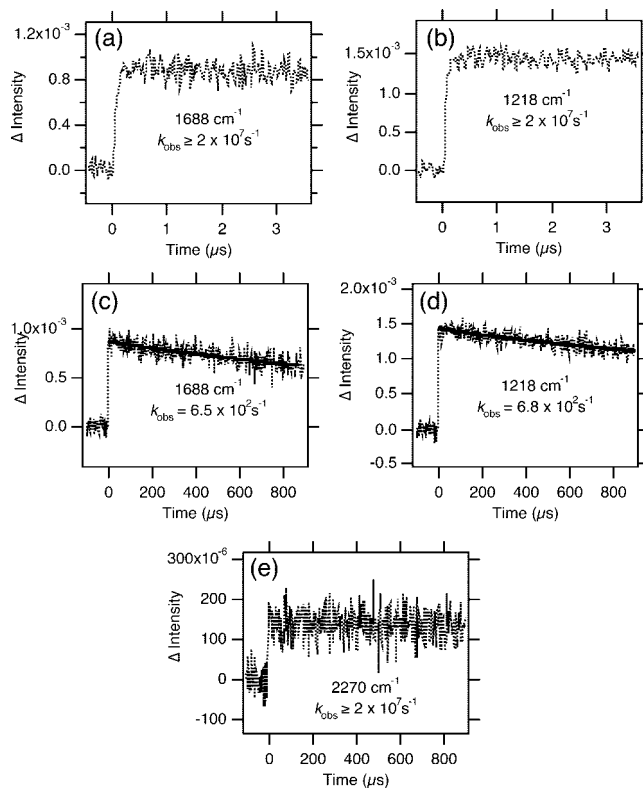
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FIGURE 6. Kinetic traces observed at (a) 1688 cm^{-1} from −0.4 to 3.6 μs, (b) 1218 cm^{-1} from −0.4 to 3.6 μs, (c) 1688 cm^{-1} from −100 to 900 μs, (d) 1218 cm^{-1} from −100 to 900 μs, and (e) 2270 cm^{-1} following 266 nm laser photolysis of **1c** (1 mM) in argon-purged CH$_3$CN. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.

TABLE 1. Frequencies Nearest 1660 cm^{-1} for ^{1}2c and ^{3}2c, As Predicted by B3LYP/6-31G(d) Calculations

	frequency, cm^{-1}	scaled frequency, cm^{-1} (0.96)	assignment
^{1}2c	1356	1301	CO stretch, combination
	1841	1768	CN stretch, combination
^{3}2c	1310	1258	CC off-line stretch
	1553	1491	CO stretch

frequencies of 1660, 1688, 1715, and 1218 cm^{-1}. The growth rates of the ylide bands at 1688 and 1218 cm^{-1} is the same as the decay of the 1660 cm^{-1} band, indicating a kinetic parent−daughter relationship between the bands. (Note that the 1218 cm^{-1} band of ylide **18** overlaps with another instantaneous growth band.) Additionally, the rate of decay of the 1660 cm^{-1} band is linearly dependent on the concentration of acetonitrile, from which a second order rate constant of 1.5 × 10^7 M^{-1} s^{-1} can be derived. This is 2 orders of magnitude larger than the rate constant reported for benzoylnitrene and acetonitrile ((3.4 ± 0.6) × 10^5 M^{-1} s^{-1}).[7] The 1715 cm^{-1} band previously attributed to reaction between singlet nitrene and dichloromethane (Figure 5b) is also observed with added acetonitrile (Figure 7c). However, its growth rate is correspondingly faster, reflective of additional singlet nitrene reactivity with acetonitrile.

We did not detect any transients easily assignable to the triplet nitrene, but product studies presented below are clearly consistent with triplet nitrene reactivity. Absent the mismatched frequency calculations, it would be straightforward to assign
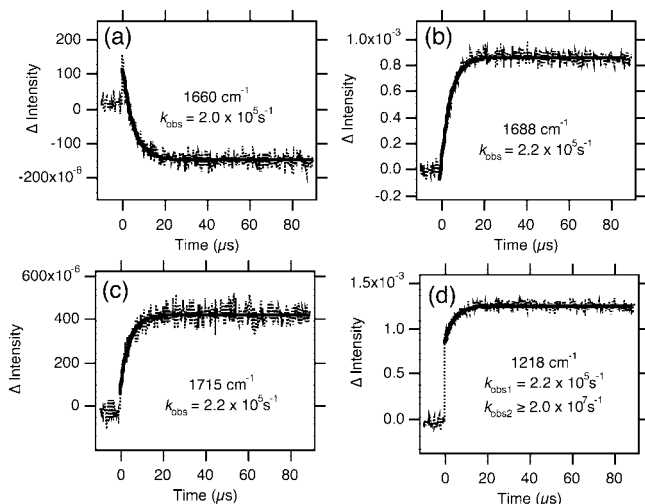
FIGURE 7. Kinetic traces observed at (a) 1660, (b) 1688, (c) 1715, and 1218 cm^{-1} following 266 nm laser photolysis of **4** (1 mM) in argon-purged CH$_2$Cl$_2$ in the presence of added CH$_3$CN (1 mM). The dotted-line curves are experimental data, and the solid lines are calculated best fits to a single-exponential function.

SCHEME 2. Potential Reaction Scheme for 1c, Based on Assignment of the 1660 cm^{-1} Band to Singlet Nitrene ^{1}2c
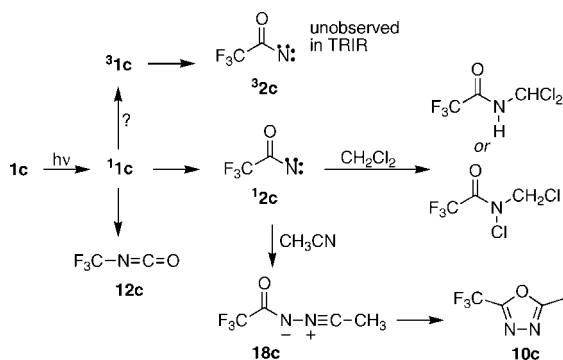
the 1660 cm^{-1} band to ^{1}**2c**, with the μs time scale decay of the singlet nitrene in dichloromethane presumably attributable to reaction with solvent. There would be only a minor if any contribution from intersystem crossing to the triplet nitrene, which is not kinetically observed. The more rapid reaction with the nucleophilic end of acetonitrile might be rationalized on the basis that the CF$_3$ group makes the nitrene more electrophilic. This possibility is represented as Scheme 2, an otherwise by now conventional diagram that does not address the interplay between the two nitrene multiplicity states. It should be noted that it does not necessarily eliminate the unobserved triplet nitrene ^{3}**2c**; there simply is not strong evidence for it from the TRIR experiments.

Given the lack of a singlet nitrene signal calculated near 1660 cm^{-1}, we must also entertain the possibility that the 1660 cm^{-1} band represents the triplet nitrene. Under this scenario, one must assume that the apparent singlet reactivity (acetonitrile, methanol) is due to rapid equilibration of the two spin states of the nitrene, which draws down the concentration of the triplet. We must also assume unusually rapid triplet nitrene formation and an unusually slow reaction between ^{3}**2c** and O$_2$. The latter might be plausible because of the electron-withdrawing nature of the CF$_3$ group, but is not attractive. Instead, we favor the interpreta-

tion based on the chemical results that ignores the vibrational calculations, i.e., that the 1660 cm^{-1} band is due to the singlet nitrene.

***N*-Mesyl Dibenzothiophene Sulfilimine, 1d, and Mesylnitrene, 2d.** The TRIR difference spectra obtained on laser photolysis of **1d** in Ar-flushed CD$_3$CN are shown in Figure 8, and corresponding kinetic traces at 1330 cm^{-1} and 1150 cm^{-1} are shown in Figure 9. Similar data were obtained in dichloromethane. B3LYP/6-31G(d) calculations on triplet mesylnitrene (^{3}**2d**) in C_s symmetry predict a strong IR band at 1241 and 1058 cm^{-1}. As is evident from the figure, these bands were not observed, though the latter might be obscured by the observed peak near 1150 cm^{-1}. On computational examination, the singlet nitrene has a stationary point with Cs symmetry, but it is a transition state connecting two identical structures of low symmetry. Optimizing the structure in C1 symmetry allows the minimum to be found (vide infra), and characteristic strong IR bands are predicted at 1134 cm^{-1} and 1023 cm^{-1}. Neither of these frequencies was observed.

As is evident from Figures 8 and 9, we observed two strong and permanent bands at 1330 and 1150 cm^{-1}. We tentatively assign these bands to sulfonylazepine **19** (Scheme 3) arising from the attack of singlet nitrene onto the DBT nucleus, based on the IR measurements of sulfonyl azepine **20** by Paquette.[36] The reported IR frequencies for *N*-mesylazepine in CHCl$_3$ are 1330 and 1155 cm^{-1}, which is in good agreement with the observed TRIR signals. (In order to be consistent with product data, we must also assume that the azepine slowly rearranges to the net C–H insertion products **5c**.) Furthermore, it is long established that **20** and related derivatives easily rearrange to the corresponding *N*-phenylmethanesulfonamides, and product studies (vide infra) show formation of such rearranged products, e.g., **5**.[17,19] Both these bands were produced at a time scale faster than the instrument resolution (50 ns). We infer that the short-lived singlet nitrene is responsible for this chemistry, assuming the assignment is correct. We did not observe the triplet nitrene by TRIR, but these negative results do not rule out its formation.

Product Studies. Photolyses of the various sulfilimines were carried out in Ar-purged solvents with initial concentrations of 1–4 mM. (A few experiments were carried out with intentionally added O$_2$.) As described below, some samples were analyzed directly by ^{1}H NMR, using deuterated solvents, while others required concentration before ^{1}H NMR or HPLC analysis. The yield of DBT was generally quite high (>90%) when the photolysis was carried out to high conversion. Yields in the tables below are reported relative to DBT formation (or DBT + **5** when relevant), however, because DBT proved much easier to precisely quantify when using the chromatographic methods. Also, we believed that DBT formation was the more direct stand-in for nitrene precursor formation[37] than loss of **1** for any case in which some **1** might be consumed by other means.

***N*-Acetyl Dibenzothiophene Sulfilimine, 1b.** Representative product studies for photolysis of **1b** are shown in Table 2. The observed products indicate a predominance of singlet chemistry. For example, stereochemistry of the alkene is preserved in the formation of aziridines from 4-octenes in acetonitrile (entries 1 and 2).[38] Potential products **4b**, **10b**, and **12b** were not detected in these experiments.

(36) Paquette, L. A.; Kuhla, D. E.; Barrett, J. H.; Haluska, R. J. *J. Org. Chem.* **1969**, *34*, 2866–2878.

(37) As seen below, the excited sulfilimine can produce the nitrene and the isocyanate competitively.
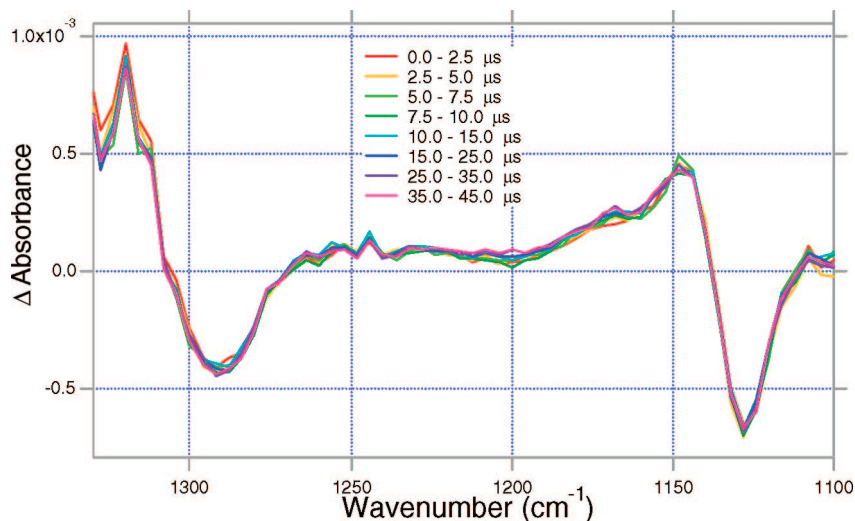
FIGURE 8. TRIR difference spectra averaged over the time scales indicated following 266 nm laser photolysis of **1d** (1 mM) in argon-saturated CD$_3$CN.
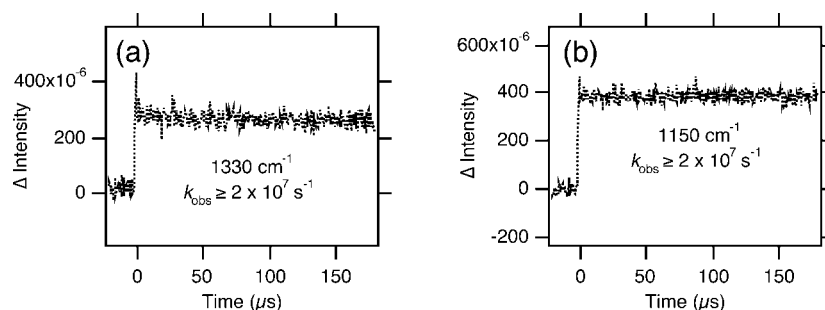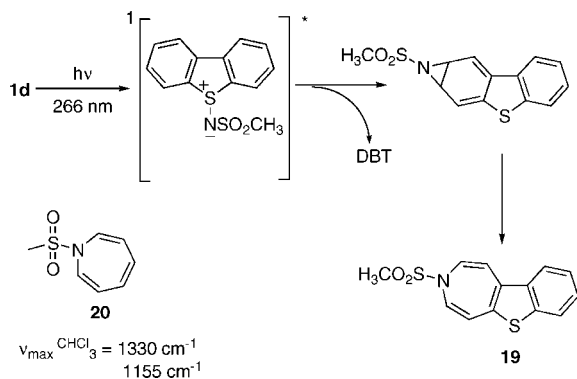

FIGURE 9. Kinetic traces obtained at (a) 1330 cm^{-1} and (b) 1150 cm^{-1} after 266 nm laser photolysis of **1d** (1 mM) in argon-saturated CD$_3$CN.

SCHEME 3

The experiments with octene required evaporation of most of the solvent (and octene) for either chromatographic or NMR analysis. For this reason, it cannot be ruled out that volatile products such as **4b**, **10b**, and **12b** were formed, but not detected. Entry 4 shows that **10b** and **12** are formed in the absence of alkene, where detection can be done without the evaporation step.

The reaction with *i*-PrOH as solvent is dominated by O–H insertion, rather than hydrogen abstraction (entry 3), also consistent with singlet nitrene chemistry. Entry 3 shows evidence

for formation of the isocyanate, as seen by formation of **13b** and reported in the TRIR section. These results are broadly consistent with those we recently reported for benzoylnitrene generated by photolysis of **1a**.[39]

In CD$_3$CN without any additional trapping agent, where evaporation before NMR analysis is not necessary, the cyclized product **10b** and methyl isocyanate **12b** are detected directly, along with an unidentified adduct. The assignment of **12b** is based on the appearance of a methyl singlet at 2.98 ppm in the ^{1}H NMR. The unidentified compound (in entries 4–6) has a methyl peak at 2.31 ppm, consistent with an acetamide derivative, presumably an adduct to DBT.

Photolysis in acetonitrile with methylcyclohexane provides the same unidentified adduct. (Detection could be done directly by NMR, as the methylcyclohexane signals did not interfere with the necessary region, and GC–MS was also used.) It also affords some C–H insertion product due to reaction with methylcyclohexane. The major isomer was the illustrated form of **14b**, i.e., the result of the insertion into the single tertiary CH position (as determined with authentic sample). None of the product due to insertion into a primary C–H bond was observed (authentic sample), but other minor GC–MS peaks were assigned to some of the 10 possible secondary C–H insertions. Authentic samples were not obtained for these. The high selectivity for tertiary insertion is consistent with very early work by Lwowski using different precursors and dimethylcy-

(38) GC–MS analysis indicated very small quantities of isomeric compounds, also of mass 281. These were interpreted as deriving from small isomeric impurities in the octene.

(39) Desikan, V.; Liu, Y.; Toscano, J. P.; Jenks, W. S. *J. Org. Chem.* **2007**, 72, 6848–6859.

TABLE 2. Product Yields from Photolysis of 1b

				product yields (%), relative to DBT								
entry	solvent	λ_{ex}, nm	Φ_{DBT}	cis-**3b**	trans-**3b**	**4b**	**6b**	**10b**	**12b**	**13b**	**14b**[c]	U[e]
1	10% cis-4-octene in CH$_3$CN[a]	320	0.49	54	0	nd[b]		nd	nd			
2	10% trans-4-octene in CH$_3$CN[a]	320	0.69	0	61	nd		nd	nd			
3	iPrOH-d_8	320	0.62			<1	72			19[f]		
4	CD$_3$CN[e]	320						24	30			22
5	10% MCH[g] in CD$_3$CN[e]	320	0.91					27	31		5	25
6	10% MCH in CD$_3$CN[e]	350 X[d]	0.62					61	6		6	22

[a] Product yields determined from ^{1}H NMR integration of the concentrated photolysate. [b] Not determined. Volatile materials that were not observed after evaporation of solvent, but may have been in the mixture originally. [c] Overall yield of **14b** and isomers of **14b**. The illustrated tertiary product **14b** identified by comparison with authentic sample using GC. Other isomers of **14** were identified on the basis of their GC−MS data. [d] Xanthone (ca. 4 mM) sensitized photolysis. [e] Uncharacterized product: percentage reported from ^{1}H NMR integration of the peak at 2.31 ppm. [f] **13b** contains the requisite 8 deuteria when prepared from iPrOH-d_8. [g] Methylcyclohexane.

TABLE 3. Product Yields on Photolysis of 1c[a]

				product yields (%) relative to DBT[a]				
entry	solvent	Φ_{DBT}	purge	cis-**3c**	trans-**3c**	trans/cis	**10c**[b]	**4c**
1	0.89 M cis-4-octene in CD$_3$CN[c]	0.08	Ar	14	34	2.4	5	4
2	0.89 M trans-4-octene in CD$_3$CN[c]	0.09	Ar	10	37	3.5	7	
3	0.89 M cis-4-octene in CD$_3$CN[c]		O$_2$	12	28	2.3	11	tr
4	0.89 M trans-4-octene in CD$_3$CN[c]		O$_2$	8	29	3.8	12	
5	0.012 M cis-4-octene in CD$_3$CN[c]		Ar	7	17	2.3	44	tr
6	0.012 M trans-4-octene in CD$_3$CN[c]		Ar	6	18	3.1	46	
7	i-PrOH-d_8		Ar					major[d]

[a] Excitation at 320 nm. Yields determined from ^{19}F NMR integration of photolysate spectra, using Freon 113 as an internal standard. Trace yields are indicated as "tr". Unquantified, but GC−MS identified yields are identified as "+". [b] Tentatively identified as **10e** based on ^{19}F NMR. The methyl group, of course, is deuterated. See text. [c] Other uncharacterized product peaks also observed. [d] Difficult to quantify precisely, ca.70%. There were many small, uncharacterized peaks.

clohexane. In that work, the retention of the methyl stereochemistry in the inserted product was used as evidence for singlet-based chemistry of the nitrene.[40] (Hadad and Platz report computed barriers of 14−19 kcal/mol, depending on method, for the insertion of ^{1}**2b** into the 2-position of propane.[7])

Xanthone-sensitized photolysis (entry 6) also leads to the formation of the tertiary C−H insertion product **14b** and a greater proportion of the cyclized product **10b** over methyl isocyanate than when direct irradiation is used. The presence of any isocyanate at all may be evidence for some direct photolysis, even under these conditions, according to the TRIR experiments. However, the predominance of the singlet reactions is also consistent with the equilibration between the singlet and triplet nitrene states, as proposed in the TRIR section.

N-Trifluoroacetyl Dibenzothiophene Sulfilimine, 1c. The results of product studies with **1c** contrast dramatically with those of **1b**. They unambiguously demonstrate the intervention of a triplet intermediate, presumably ^{3}**2c**.

The lack of a signature peak in the ^{1}H NMR of products derived from **1c** and their volatility led to the use of ^{19}F NMR as the principle analytical method for the experiments reported in Table 3. With this technique, neither concentration of the sample nor removal of octene was necessary, and the samples could be analyzed directly after photolysis.

A compound with the mass of [**2c** + acetonitrile] was observed from all experiments conducted in acetonitrile and never in the absence of acetonitrile. This was taken to be the adduct **10c**, formed from the ylide **18c**, as observed by TRIR. The assignment of the identity **10c** is based on spectroscopy and chemical analogy. The observed ^{19}F signal (δ −66.8) differs

(40) Lwowski, W. *Nitrenes*; John Wiley & Sons, Inc.: New York, 1970.
(41) Tanner, D.; Birgersson, C.; Gogoll, A.; Luthman, K. *Tetrahedron* **1994**, *50*, 9797−9824.

by 21 ppm from that of trifluoromethyl isocyanate, eliminating that as a possibility. Although we are unaware of any literature preparation or unambiguous characterization of **10c**, three other related compounds were found that had similar ^{19}F chemical shifts: Thus, by chemical analogy to the previous derivatives,

^{19}F NMR signal (δ)   -69.3 ppm   -66.4 ppm   -65.3 ppm
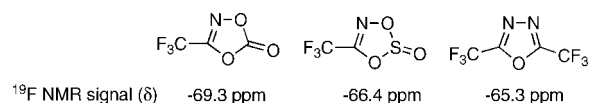
and spectroscopic analogy, we assign the observed compound and its −66.8 ppm ^{19}F NMR peak to the structure **10c**. The fact that the relative yield of **10c** increases on addition of O$_2$ implies that it is a singlet product, consistent with the proposed mechanism.

Again, the alkene to aziridine stereochemical retention test was used to probe for triplet nitrene reactivity. Based on Platz's data for benzoylnitrene,[7] at an alkene concentration of ∼1 M, a competition would be observed between addition to the alkene and trapping of the nitrene by acetonitrile. This seemed like an appropriate regime in which to begin the singlet vs triplet addition experiments. (We do not know if the ylide **18c** would react with the alkene to form the aziridine but are confident that stereochemistry would be retained if so.)

The results in Table 3, with incomplete retention of alkene stereochemistry in the aziridine products confirm the presence of ^{3}**2c** in the reaction mixture (entries 1−4). The cis-aziridine was identified by both ^{1}H and ^{19}F spectra, compared to authentic samples. The trans-aziridine was identified by spectroscopic analogy to other cis -and trans-aziridine pairs.[41]

The simplest interpretation of the different trans/cis ratios from cis- and trans-4-octenes is that both singlet and triplet nitrene reactivity is being observed. The alternate interpretation—

that only the triplet nitrene reacts with alkene, but without complete loss of stereochemistry—seems unlikely, due to the TRIR experiments that demonstrate the existence of ^{1}**2c** in the mixture.

Because the addition of a singlet nitrene to an olefin is expected by all literature precedent to have a much higher rate constant than does addition of a triplet nitrene to an olefin, the very observation of the mixed stereochemistry of the aziridines implies that the ground-state of CF$_3$CON is probably a triplet. We cannot eliminate the possibility that the branching between the two spin states of the nitrene is essentially irreversible, i.e., that, once formed, both ^{1}**2c** and ^{3}**2c** react faster in some other way than they interconvert. However, the TRIR data are interpreted as providing a thermal population of ^{3}**2c** on the submicrosecond time scale. We believe that it is reasonable for bimolecular reaction between the singlet nitrene and the alkene to be competitive with this at these high alkene concentrations.

The standard probe for simultaneous reactivity from singlet and triplet nitrenes of determining the ratio of *trans/cis*-aziridines from varying *cis*-alkene concentrations was employed.[42] Variation in the trans/cis ratio would imply that capture of the nitrene by the alkene is kinetically competitive with intersystem crossing. An invariant ratio can indicate either very rapid spin-equilibration (leading to an apparent "single intermediate") or very slow spin-equilibration, where the initial singlet/triplet branching ratio is maintained throughout the trapping reaction. In the former case of rapid spin-equilibration, the expected result would be a predominance of stereochemical retention, because the singlet trapping reaction is expected to be much faster than the triplet reaction. For loss of stereochemistry to predominate, as observed in Table 3, a triplet ground-state is required in order that its higher population outweigh the kinetic advantage otherwise held by the singlet.

We believe the lower trans/cis ratio (at lower [alkene]) for entry 6, compared to entry 2, is experimentally significant. The ratio of *trans/cis*-**3** can be determined directly by NMR integration without adding in additional errors related to calculating the yields shown in Table 3, and the trends were clear and reproducible. We may infer that less singlet nitrene is being captured by the lower octene concentration. Note also that the relative proportion of **10c** increases with lower alkene concentrations, as reaction between the singlet nitrene and acetonitrile solvent becomes a larger fraction of the total processes available to the singlet nitrene. The drop in the absolute yield of *trans*-**3c** in entry 6 (compared to entry 2) or *cis*-**3c** in entry 5, compared to entry 1, further implies that at least some of the triplet nitrene derives from the singlet nitrene, just as implied by the TRIR results.

Addition of O$_2$ (entries 3 and 4) also provides a small change in product distribution that we believe is experimentally significant. It lowers the overall yield of aziridine (accompanied by an increase in **10c**), and also marginally raises the retention of stereochemistry from the alkene to the aziridine, albeit more so when the starting material is trans. Incomplete quenching of ^{3}**1c** would provide this result, assuming that the reactions set out in Scheme 2 is elaborated as in Scheme 4. There is not enough information to determine whether O$_2$ additionally quenches the triplet nitrene or whether **18c** can lead to *cis*-aziridines.

(42) McConaghy, J. S.; Lwowski, W. *J. Am. Chem. Soc.* **1967**, *89*, 4450–4456.

SCHEME 4
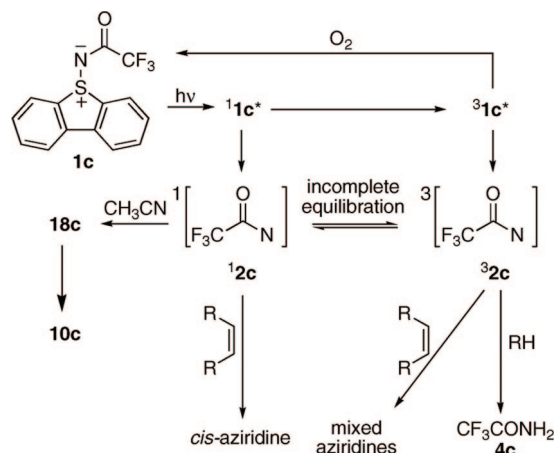
That triplet reactivity is significant is further implied by the observation of trifluoroacetamide, **4c**. Seen in small amounts in the acetonitrile/alkene experiments, it becomes the major product in *i*-PrOH. The expected singlet nitrene adduct **13c** was not identified, but we cannot rule out its formation because of analytical limitations. Many small ^{19}F signals were observed, and we cannot eliminate the possibility of some formation of the O−H insertion or any other specific products. Nonetheless, the fact that better than half the mass balance is accounted for by trifluoroacetamide again implies an ultimate predominance in triplet nitrene chemistry.

Taken together, the product studies point strongly toward a predominance of triplet nitrene chemistry in some solvents, and singlet nitrene chemistry in others. Though the computations' disagreement with the observed IR bands leads to an ambiguity, we favor an interpretation based on assigning the 1660 cm^{-1} IR peak to the singlet nitrene. This implies a certain branching ratio of ^{1}**1c*** that always provides some minimum amount of triplet nitrene by way of ^{3}**1c*** and that more triplet nitrene may be formed if the singlet nitrene is not immediately trapped by solvent. The triplet nitrene is probably lower in energy than the singlet by 3−4 kcal/mol (see below). We acknowledge the difficulty of this otherwise ordinary interpretation with not finding an appropriate frequency near 1660 cm^{-1} in the computational data.

***N*-Mesyl Dibenzothiophene Sulfilimine, 1d.** The mesyl derivative **1d** mainly yielded products attributable to the triplet nitrene on photolysis. The principle results are given in Table 4. It should be noted that one of the byproducts of sulfonyl azide chemistry can be a pseudo-Curtius rearrangement leading to compounds of the form R−N=SO$_2$. We found no positive evidence for such a rearrangement, which would inevitably involve products with R−N bonds (CH$_3$ here or C$_7$H$_7$ for **1e**, below). Moreover, entries 4 and 5 in Table 4 show that at least under the correct conditions, all of the material (carbene, isocyanate, etc.) with formula RNO$_2$S can be accounted for without invoking the Curtius-type product.

The TRIR experiments did not allow for direct observation of the nitrene in either multiplicity but did suggest products that derive from the singlet. Since we expected the triplet to be the ground state, we believed both singlet and triplet nitrene reactivity might be observed under the right conditions.

In acetonitrile/octene (entries 1−3), the trans to cis ratio of aziridines indicates equilibration of stereochemistry in large part, and thus at least mainly triplet addition. In these acetonitrile/

TABLE 4. Product Yields from Photolysis of 1d

	solvent	λ, nm	Φ_{DBT}		cis-**3d**	trans-**3d**	t/c	**4d**	**5d**	**8d**	**15**	**16**	**17**
								Product yields (%), relative to DBT[a]					
1	10% cis-4-octene in CH$_3$CN	320	0.08	Ar	28	57	2.0	15[b]					
2	10% trans-octene in CH$_3$CN	320	0.09	Ar	34	62	1.8	12[b]					
3	10% trans-octene in CH$_3$CN	320	0.04	O$_2$	27	57	2.1	9[b]					
4	i-PrOH	320		Ar				100					
5	CD$_3$OD	320		Ar				99					
6	10% cyclohexane in CH$_3$CN	320	0.06	Ar				81		<8[c]	+[e]	+	
7	50% cyclohexane in CH$_2$Cl$_2$	320		Ar				80		6[c]	+		+
8	10% cyclohexane in CH$_3$CN	350, X[d]	0.94	Ar				76		<8[c]	+	+	

[a] Product yields determined from ^{1}H NMR integration of the concentrated photolysate. [b] Combined percentages of **4d** and **5d** reported due to overlapping CH$_3$ protons in the ^{1}H NMR spectrum of the concentrated photolysate (entries 1−3 only). [c] Upper limit reported due to other overlapping peaks in the ^{1}H NMR. [d] Xanthone (ca. 4 mM) sensitized photolysis. [e] Formed in the photolysis and characterized by GC−MS, but not rigorously quantified.

TABLE 5. Product Yields from Photolysis of 1d in Varying cis-4-Octene Concentrations in Dichloromethane[a]

entry	[cis-4-octene], M	aziridine yield[b], %	trans/cis
1	0.012	74 ± 2	1.87 ± 0.05
2	0.89	97 ± 3	1.71 ± 0.05

[a] Yields determined from ^{1}H NMR integration of the concentrated photolysate. Excitation at 320 nm with Ar purge to remove O$_2$. Approximately 18% of **4c** was obtained in entry 1. [b] Relative to DBT formation.

octene mixtures, both methanesulfonamide **4d** (the double hydrogen abstraction product) and an adduct between the mesylnitrene and DBT (**5d**) were observed in modest yield. Because of overlap in the NMR spectrum of the corresponding methyl groups and the multiple peaks in the aromatic region, the two product yields could not be further distinguished. The adduct was identified as a formal C−H insertion product by the appearance of HPLC peaks that had UV spectra essentially identical to DBT. We did not determine the regiochemistry of the insertion.

Variation of the alkene concentration gave results consistent with the triplet nitrene deriving from the singlet. As shown in Table 5, raising the initial cis-alkene concentration from 12 to 890 mM not only increased the total aziridine yield but also increased the retention of stereochemistry modestly. This implies that at least some of the triplet nitrene is formed by way of a higher energy singlet nitrene, and that intersystem crossing from the singlet nitrene down to the ground state is kinetically competitive with addition by the singlet nitrene to the alkene.

On direct photolysis of **1d** in methanol (Table 4, entry 5), a nearly quantitative yield of methansulfonamide was obtained. These results are in contrast to those reported by Shingaki et al. for photolysis of methanesulfonyl azide.[43] In 1:1 cyclohexane/CH$_2$Cl$_2$, they report 18.3% of the C−H insertion product **8d** and 38.4% of H-abstraction product **4d**. In ethanol, however, they report a 48% of the O−H inserted product and 43.3% of H-abstraction product. These differences may be due either to complexities from the sulfonyl azide precursors or perhaps due to different proportions of initially formed singlet and triplet nitrene from the different precursors.

***N*-Tosyl Dibenzothiophene Sulfilimine, 1e.** Upon photolysis of *N*-tosyl dibenzothiophene sulfilimine, **1e**, in the presence of cis- or trans-4-octene, we obtained mixed-stereochemistry aziridines (entries 1−4, Table 6). A small degree of stereochemical retention is noted. This would again be consistent with

(43) Shingaki, T.; Inagaki, M.; Torimoto, N.; Takebayashi, M. *Chem. Lett.* **1972**, 1181−4.

a pathway for ground-state triplet nitrene formation that passes through the singlet.

The addition of O$_2$ decreases the overall quantum yield of product formation (Table 6), presumably because of quenching of the excited-state of the sulfilimine. Additionally, the fraction of identified products, relative to DBT formation is also lower in the presence of O$_2$. This implies an additional role for oxygen. Maloney, et al. have reported fast quenching of triplet sulfonylnitrenes by O$_2$ (ca. 10^9 M^{-1} s^{-1}) based on a transient UV assignment from photolysis of tosyl azide.[8] We suggest that both the sulfilimine excited-state and the nitrene are quenched under these conditions.

The standard experiment of examining the effect of alkene concentration on the degree of stereochemical retention in the aziridine was carried out. After some initial experiments gave unexpected results, a new set of carefully controlled measurements were done, all using cis-4-octene as the precursor. As expected, the total yield of aziridine increases with cis-octene concentration. However, a small but reproducible *loss* of retention was seen as the alkene concentration was raised (Table 7). Control photolyses of tosyl azide in the presence of cis-4-octene gave intractable mixtures.

The possibility of a singlet ground-state for tosylnitrene can be dismissed. However, a firm explanation for the data in Tables 6 and 7 is not trivial: (1) If the main precursor for triplet tosylnitrene ^{3}**2e** is ^{1}**2e** and intersystem crossing to ^{3}**2e** is slow or essentially irreversible, the increased cis-alkene concentration should lead to increased cis-aziridine due to the high reactivity of singlet nitrenes with alkenes. This is contradicted by experiment. (2) If the main precursor for ^{3}**2e** is ^{1}**2e** and intersystem crossing is extremely rapid and reversible relative to alkene addition, alkene concentration should not have much of an effect on the aziridine ratio. This is also contrary to the reported result. (3) If ^{3}**1b** (i.e., the excited-state of the sulfilimine) reacts with alkene in competition with dissociation to form ^{3}**2e**, then one has to postulate that this reaction favors the loss of stereochemistry more than does the reaction between ^{3}**2e** and the alkene. This seems unlikely, but is possible, and also requires that no more than a minimal amount of aziridine is formed by singlet channels.

Another potential explanation is shown in Scheme 5. If the triplet nitrene is born mainly through the triplet excited-state of the sulfilimine and k_S[cis-octene] > k_{ST}, then the uphill intersystem crossing step leads to some aziridine with retention. In the limit where k_{TS} becomes essentially irreversible because the singlet nitrene is rapidly quenched, the degree of retention of stereochemistry is related to $k_{TS}/k_T[octene]+k_{O_2}[O_2]+k_{TS}\}$. If this relation holds, then increasing the octene concentration

TABLE 6. Product Yields from Photolysis of 1e

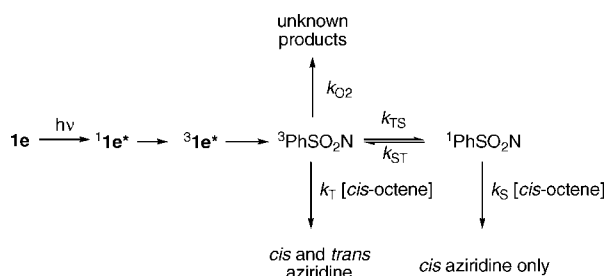| entry	solvent	λ, nm	Φ_{DBT}		3e cis	trans	trans/cis	4e[a]	8e[b]	15	16	17
1	10% *cis*-4-octene in CH$_3$CN	320	0.16	Ar	28	52	1.9					
2	10% *cis*-4-octene in CH$_3$CN	320	0.09	O$_2$	20	45	2.3					
3	10% *trans*-4-octene in CH$_3$CN	320	0.14	Ar	24	55	2.3					
4[c]	10% *trans*-4-octene in CH$_3$CN	320	0.09	O$_2$	19	40	2.2					
5	10% cyclohexane in CH$_3$CN	320	0.16	Ar				90	tr[d]	+[d]	+	
6	50% cyclohexane in CH$_2$Cl$_2$	320						95	tr	+		+
7	10% cyclohexane in CH$_3$CN	350, X^e	0.73	Ar				90	tr	+	+	

[a] Product yields determined from ^{1}H NMR integration of the concentrated photolysate. [b] Identified by GC−MS. [c] GC−MS indicates two significant peaks with *m/z* = 169. Xanthone (ca. 4 mM) sensitized photolysis. [d] tr = trace, by GC; "+" = significant but not rigorously quantified (GC).

TABLE 7. Product Yields from Photolysis of 1e in Varying Concentrations of *cis*-4-Octene in Dichloromethane[a]

entry	[*cis*-4-octene], M	total aziridines[b], %	trans/cis
1[c]	0.012	(43 ± 8)	1.55 ± 0.06
2	0.071	(70 ± 4)	1.72 ± 0.04
3	0.16	(74 ± 3)	1.81 ± 0.05
4	0.89	(83 ± 4)	1.93 ± 0.05
5	4.30	91	1.9

[a] Excitation at 320 nm, with Ar purging. [b] Relative to DBT formation, by NMR. [c] Significant amounts of **4e** were also formed when 0.012 M of *cis*-4-octene was used.

TABLE 8. Product Yields from Photolysis of 1e in Alcohols

		product yields (%), relative to DBT[a]				
entry	solvent	4e	6e	7e	9e	11e
1	77% *t*-BuOH in CH$_3$CN[a]	80			0	
2	57% *t*-BuOH in benzene	42			0	25
3	*i*-PrOH	100	0			
4	MeOH[b]	98		0		

[a] Product yields determined from ^{1}H NMR integration of the concentrated photolysate. All samples Ar purged and λ_{ex} = 320 nm. [b] GC−MS trace of the photolysate indicates a trace amount of an isomer of **7e**.

SCHEME 5

lowers the retention of stereochemistry because intersystem crossing to the singlet nitrene is competitively suppressed. For a ΔE_{ST} of about 10 kcal/mol, k_{TS} would likely be no faster than $\sim 10^6$ s^{-1}. Under the same model, addition of O$_2$ could also lower the degree of retention if triplet nitrene trapping were fast enough; this is observed when comparing entries 4 and 2 of Table 6 to entries 3 and 1, respectively.

In order to probe for singlet reactivity of tosylnitrene besides the partial retention of stereochemistry of the aziridines, we investigated both alkane solvents and alcohols. (Based on lack of radical coupling products and on retention of stereochemistry on insertion, previous workers have attributed alkane insertions observed on thermolysis or photolysis of tosyl azide to reactions of the singlet nitrene.[12,44]) Entries 5 and 6 in Table 6 indicate that only traces of *N*-cyclohexyltosamide **8e** were observed on photolysis of **1e** in cyclohexane/acetonitrile or cyclohexane/dichloromethane. Instead, the double-hydrogen abstraction product tosamide **4e** was found in high yield. (Reduction of the nitrene is normally considered a triplet nitrene reaction.) Perhaps unsurprisingly, sensitization of **1e** with xanthone (entry 7) also did not produce C−H insertion product **8e**, again leading mainly to tosamide.

Photolysis of tosyl azide in methanol has been reported to produce the formal OH insertion adduct **7e**. Both the singlet

nitrene and the singlet excited-state of the azide have been proposed as the key reactive intermediate.[21,22] We reproduced this result. However, as shown in Table 8, photolysis of **1e** in methanol results instead in nearly quantitative yield of the double-hydrogen abstraction product tosamide **4e**.

A similar result was found in *i*-PrOH. Tosyl azide has been reported to produce tosamide quantitatively on photolysis in *i*-PrOH, but the suggestion has been made that this is due to radical chain chemistry.[4]

In order to remove the ambiguity regarding radical chain mechanisms, we photolyzed **1e** in solvent mixtures containing *t*-BuOH. None of the OH insertion product (**9e**) was formed, and again a high yield of tosamide was observed with acetonitrile as the cosolvent (entry 1). With benzene as a cosolvent (entry 2), tosamide was formed with smaller yield, and the formal benzene CH insertion adduct **11e** was formed competitively. We assume that this adduct is formed by singlet nitrene addition to benzene via the azepine in much the same way that a certain amount of singlet nitrene reacts with the octenes, as described by Scheme 4.

The previously discussed results from tosyl azide photolysis in methanol have been complemented by much higher yields of insertion product (**8e**) from tosyl azide in cyclohexane[12] than we observed on photolysis of **1e** in the presence of cyclohexane. Instead, we observed mainly the reduction product (Table 6). We suggest that the sum of our evidence is in favor a much larger proportion of **1e** leading to triplet tosylnitrene without intervention of the singlet tosylnitrene than is the case for photolysis of tosylazide.

Computational Studies. Theoretical studies on formylnitrene (**2 h**) and acetylnitrene (**2b**) have been published.[7,45–47] Two major features may be extracted from these data: (1) The singlet state of these nitrenes is highly stabilized by an

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TABLE 9. Computed ΔE_{S-T} of Nitrenes 2b−e at Different Levels of Theory[a]

method[b]	CH_3CON	CF_3CON	CH_3SO_2N	$PhSO_2N$
B3LYP/6-31G(d,p)	1.9	6.3	14.1	14.5
B3LYP/6-311G+(d,p)//B3LYP/6-31G(d,p)	2.1 (4.9)[c]	6.9	15.5	
B3LYP/6-311G(3df,2p)//B3LYP/6-31G(d,p)	0.3	4.7	12.6	13.1
B3LYP/aug-cc-pV(D+d)Z//B3LYP/6-31G(d,p)	1.7	6.3	13.2	13.8
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d,p)	0.0	4.7	12.6	
B3LYP/aug-cc-pV(Q+d)Z//B3LYP/6-31G(d,p)	0.1	4.8	12.6	
MP2/6-31G(d,p)	[d]	−1.3	12.4	
MP2/6-311G(3df,2p)//B3LYP/6-31G(d,p)	−8.2	−3.9	5.1	4.1
MP2/aug-cc-pVTZ//B3LYP/6-31G(d,p)	−9.3	−4.7	4.4	
CASSCF/6-31G(d,p)[e]	2.0	6.1	6.7	
MCQDPT/6-31G(d,p)//CASSCF/6-31G(d,p)[e]	−4.8	−0.8		
CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)[f]	−0.2	3.7	12.2	
CR-CC(2,3)/aug-cc-pV(D+d)Z//B3LYP/6-31G(d,p)			15.5	
CR-CC(2,3)L/G3Large*//B3LYP/6-31G(d,p)			12.8	
CCSD(T)/6-311+G(d,p)//B3LYP/6-31G(d)	(1.9)[c]			
CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d,p)	(1.6)[c]			

[a] A positive value implies a triple ground state. All energies in kcal/mol. [b] Positive ΔE_{S-T} values indicate triplet ground states. Spherical harmonics were used on the polarization functions. All data are ΔH (298 K), with temperature corrections unscaled and taken from the Hessian calculated at the optimization method. [c] Values in parentheses are from ref 7. [d] Triplet acetylnitrene always gave an imaginary frequency corresponding to the methyl rotations and hence could not locate a minimum on the triplet nitrene surface. [e] The (6,5) active space for CH_3CON includes the carbonyl π-system, a lone pair on the oxygen and filled and empty p-orbitals on nitrogen. The (22,15) active space for mesylnitrene includes all the oxygen and nitrogen lone pairs and the S−O and S−N σ bonds. The active spaces are illustrated in the Supporting Information. [f] CR-CC(2,3) is also known as CR-CCSD(T)_L.

interaction between the in-plane lone pair on O and the empty in-plane orbital on N, resulting in the shortening in the N−O distance and narrowing of the O−C−N angle, relative to the triplet; and (2) The calculated singlet−triplet energy gap is rather method-dependent. For example, among several methods, only CBS-QB3 correctly predicts a singlet ground-state for acetylnitrene.[7]

The relative stability of the triplet state of these acylnitrenes was overestimated by several kcal/mol by B3LYP/6-31(d).[46] The consistency of this error, along with experimental results, was used to conclude that the ground-state of benzoylnitrene is a singlet with this relatively inexpensive method.

We wished to use computational methods to corroborate with the conclusions that might be drawn from the product studies reported above for tosylnitrene, mesylnitrene, and trifluoro-acetylnitrene. The implementation of B3LYP (and other computational methods) is slightly different in GAMESS than in GAUSSIAN; thus we undertook the use of GAMESS with several different methods and basis sets in order to calibrate the results obtained against those of Hadad and Platz (HP),[7] and then expanded to several other methods for the four compounds under consideration here. In addition to the density functional method, we calculate energy differences using ROHF reference functions at the MP2 and completely renormalized coupled cluster (CR-CC(2,3)[48,49] methods. Additionally, we examined selected molecules using multireference MP2 methods with MCSCF reference functions.[50,51] The results of these calculations are given in Table 9, where the values in parentheses are taken from HP.

As can be seen immediately from Table 9, there is a wide variance in the calculated ΔE_{S-T} values for any given compound.[52] However, in contrast to results for formylnitrene,[46] there is only a fairly modest dependence of ΔE_{ST}—ap-

proximately 2 kcal/mol—on the basis set (at least at the B3LYP level) for any of the present nitrenes. This is, presumably, due to fairly efficient cancelation of errors when comparing the singlet and triplet species.[53] Especially notable is that data obtained with the 6-311G(3df,2p) basis set are within about 1 kcal/mol of those from the aug-cc-pV(T+d)Z basis set, and often much closer than that. The cc basis set is computationally much more expensive, but of similar (though not identical) quality in terms of polarization and having a triple-ζ valence shell. Thus, we infer that the data for the coupled cluster calculations at the latter, larger basis set would be similar to the ones reported in Table 9.

In contrast, the correlation energy picked up by each method for the different multiplicity states varies; thus, the ΔE_{ST} values are more dependent on method than basis set. As noted previously, we expect that the density functional values are too positive by several kcal/mol.

Some specific discussion of the CASSCF calculations is required. Careful choice of active space is required to ensure that the calculations are on equal footing for singlet and triplet states of the nitrenes. For the two carbonylnitrenes, an active space of 6 electrons in 5 orbitals was sufficient. These included the carbonyl π system, a lone pair on the oxygen, and the filled and empty p-orbitals on N at the beginning of the calculation. These orbitals are approximately preserved in the triplet states (see the Supporting Information). In the singlet state, the geometric distortion leads to formation of a partial single bond between the N and O, but the general locations of the orbitals is the same. The geometries obtained by optimizing at the CASSCF are quite similar to those obtained at the B3LYP level, and vibrational analysis showed them to be minima. For mesylnitrene, after extensive experimentation, the only satisfactory active space was 22 electrons in 15 orbitals (Supporting Information). This corresponds to a full valence active space on the SO_2N fragment of the molecule. Again, the resulting

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(52) It should also be noted that these are gas-phase calculations. Polar solvents would presumably favor the singlet state by a few kcal/mol.

(53) In our experience, simplification of a molecule by reducing the first substituent methyl to a hydrogen atom, as in H_2SO for $(CH_3)_2SO$, for example, often leads to surprisingly different computational behavior of the simplified system, compared to the carbon-substituted analogues.
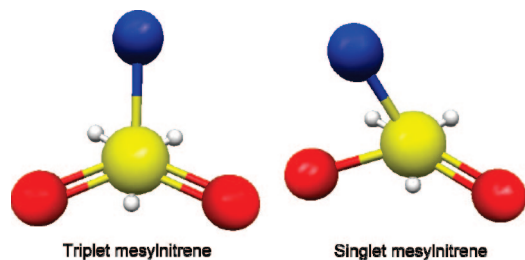
FIGURE 10. Calculated geometries for mesylnitrene, calculated at the B3LYP/6-31G(d,p) level. The view down the S—C axis obscures the carbon atom; the methyl hydrogens are visible.

geometries were very similar to those from B3LYP, and vibrational analysis proved the structures to be minima.

As noted by HP, the B3LYP density functional overestimates the relative stability of the triplet state by several kcal/mol, leading to an incorrect prediction of ground-state multiplicity for acetylnitrene. The true ΔE_{ST} for acetylnitrene, while its exact magnitude remains unknown, is surely slightly negative. (As we discuss in the TRIR section, we believe it most likely to be between 0 and -1.4 kcal/mol.) We obtain a singlet ground-state using multireference MP2 but the magnitude is larger than we expect.

Despite this uncertainty in the absolute value of ΔE_{ST}, the data in Table 9 show that the increments from one compound to the next are approximately the same, regardless of the computational method. The ΔE_{ST} values for CF_3CON are consistently 4–5 kcal/mol more positive than those for CH_3CON. Clearly the singlet state of CF_3CON is somewhat *less* stabilized by the adjacent carbonyl than is the case for CH_3CON. Taken with the experimental TRIR results for CH_3CON that show that the triplet is positioned no more than about 1 kcal/mol above the triplet, we can infer that ΔE_{ST} for CF_3CON is ca. 4 kcal/mol.[54] This is consistent with the product study data as well, which also imply a triplet ground-state for CF_3CON. The single calculation that gives these results most closely (CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)) may also very well be the best quality calculation shown in Table 9.

It also seems safe to suggest that the computations show that both mesyl and tosylnitrene (or its stand-in for Table 9, benzenesulfonylnitrene) have triplet ground states, consistent with earlier low temperature EPR studies.[3,8–11] The magnitude of the energy gap is probably close to the 12 kcal/mol figure obtained from the coupled-cluster calculations.

Furthermore, the "insulation" provided by the sulfonyl group means that the ΔE_{ST} is not so different between the mesylnitrene and tosylnitrene. It is not practical yet to carry out extraordinarily high level calculations for benzenesulfonylnitrene. However, the consistency of the data at the B3LYP and MP2 level with those of mesylnitrene give us confidence that higher level calculations would give similar results.

Figure 10 illustrates the geometric result common to both mesylnitrene and benzenesulfonylnitrene: the triplet states have symmetric geometries common to other sulfonyl derivatives, but the singlet nitrenes have distorted geometries that indicate that there is significant bonding interaction between the O and N. Key geometric parameters for all four nitrenes are given in

Table 10. Also shown are the Mulliken bond orders, taken from the B3LYP/6-31G(d,p).[55]

The geometries and bond orders reveal an interesting story. The S—O bond lengths and bond orders for $^3CH_3SO_2N$ and $^3PhSO_2N$ are in reasonable agreement with "ordinary" sulfonyl compounds; the bond orders of approximately 1.7 include the traditional σ bond and the interaction represented either as the second bond in many drawings or the "ylidic" portion of the bond if written in that style. (See, for example, ref 56.) However, the bond orders are dramatically different for the singlet sulfonylnitrenes. One S—O bond remains approximately the same as before, but the other is lengthened and weakened. The S—N bond is shortened and strengthened to be above the level of a "single" bond, and of course a much more significant O—N bond order index is achieved: 0.75 vs <0.2 for the other O—N or for the triplet states. This set of results can be rationalized by the following picture for the singlet nitrene state, based on the ylide representation of sulfur oxides:
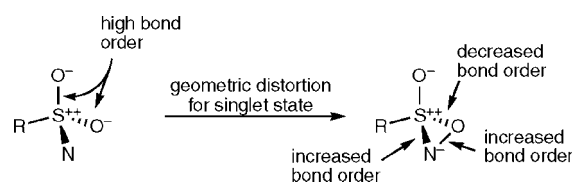
The O—N bond order indices for the singlet carbonylnitrenes are fractionally higher than those for the sulfonylnitrenes, perhaps reflective of the greater singlet-state stabilization in the carbonylnitrenes. On going from the triplet to singlet state, the carbonyl bonds lengthen and the bond order indices drop significantly, from about 1.9 to nearly 1.1. Additionally, the C—N bond order rises substantially, and of course the O—N bonding order index goes up from a small value (<0.2) to almost 0.9. The lengths change in concert with these bond order indices. Taken together, these structural parameters confirm that the structural character of the singlet carbonylnitrene resembles the substituted oxazirene more than the dipolar structure that more obviously shows the origin of the stabilizing interaction: The OCN bond angle
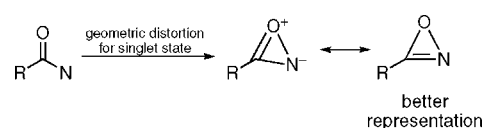
for $^1CF_3CON$ is marginally less acute than that for $^1CH_3CON$, and the O—N distance is correspondingly a bit longer. These geometric parameters correlate well with the observed trends in ΔE_{ST} data for **2b** and **2c**, though we will not make the error of ascribing cause and effect with this level of analysis.

The comparison of the carbonylnitrenes to the sulfonylnitrenes, however, does merit discussion. The question with the sulfonylnitrene is whether the adjacent sulfonyl oxygen atom could provide the level of stabilization to the closed-shell state of the nitrene as is seen from adjacent carbonyls. In retrospect, perhaps the negative result might have been predicted, based on standard S—N and S—O lengths, vs C—N and C—O bond lengths. Simply put, the expansion of the S—N and S—O lengths (relative to the C—N and C—O lengths in the carbonylnitrenes) means that the third edge of that triangle must also be longer,

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(54) The singlet–triplet energy gap is undoubtedly also somewhat dependent on the solvent.

(55) The Mulliken bond orders are better behaved with modest basis sets such as 6-31G(d,p). There are other, more sophisticated models of bond order, but these values serve as very adequate comparative and qualitative guides.

TABLE 10. Key Calculated Geometric Parameters^a

nitrene	$r_{C=O}$ or r_{S-O}, Å	r_{C-N} or r_{S-N}, Å	r_{O-N}, Å	$r_{S-O'}$, Å	∠OCN or ∠OSN (deg)
$^1CH_3CON$	1.31 (1.12)	1.26 (1.66)	1.77 (0.87)		86.9
$^3CH_3CON$	1.23 (1.88)	1.40 (1.12)	2.25 (0.18)		117.7
$^1CF_3CON$	1.30 (1.15)	1.26 (1.64)	1.81 (0.87)		89.8
$^3CF_3CON$	1.22 (1.87)	1.39 (1.12)	2.27 (0.17)		121.4
$^1CH_3SO_2N$	1.56 (1.06)	1.58 (1.29)	1.77 (0.75)	1.45 (1.78)	68.9
$^3CH_3SO_2N$	1.47 (1.70)	1.72 (0.89)	2.56 (0.12)	1.47 (1.70)	106.7
$^1PhSO_2N$	1.56 (1.05)	1.58 (1.27)	1.76 (0.76)	1.46 (1.76)	68.3
$^3PhSO_2N$	1.47 (1.68)	1.71 (0.92)	2.55 (0.12)	1.47 (1.68)	106.4

^{a} All data obtained from B3LYP/6-31G(d,p) optimizations, including bond order indicies (BOI). Mulliken bond orders are given in parentheses.

assuming a common angle. However, the O−N distances in the singlet sulfonylnitrenes and carbonylnitrenes are comparable. The O−S−N angle in **2c** and **2d** is more acute than in the carbonylnitrenes by almost 20 degrees. One presumes, then, that there is a higher price to pay for the short O−N distance due to an increased angle strain.

But if we are to even qualitatively rely on strain as an argument, we must at address how much strain is introduced by the O−X−N contraction. We cannot know that with certainty from the current data. However, the geometric changes from triplet to singlet states can be used as a guide: the carbonylnitrene OCN bond angle contracts by a 31−32° on going from triplet to singlet, whereas the sulfonyl nitrenes have a corresponding 38−39° contraction. A more complete energy surface calculation would be required to establish the causality of this association. However, the fact that the difference between the two types of functionality is in the bond angle, rather than the N−O distance is clearly established.

Summary

The data presented here indicate that the dibenzothiophene sulfilimine platform is a useful one for observation of nitrenes with electron-withdrawing substituents. Direct observation by TRIR spectroscopy of two nitrenes (benzoylnitrene and acetylnitrene) now complement the product studies. While not quantitative, the mass balances reported here are at least in line with and much better than many reports of product studies using azide precursors. In the following paragraphs, we attempt to correlate information derived from each of our techniques—spectroscopic, product studies, and computational—to provide insight to the dynamics of nitrene formation from sulfilimines **1b−e** and comment, as appropriate, on the chemistry of the nitrenes themselves.

***N*-Acetyl Dibenzothiophene Sulfilimine.** Previous work on this nitrene is consistent with a singlet ground state. Certainly, nothing in our product studies contradicts this; we see no evidence of triplet reactivity. The computations we have carried out are in line with those of HP, in that they are very method-dependent and predict ΔE_{ST} to be only a few kcal/mol, regardless of sign. Of the four compounds we examined, only this one gave only singlet nitrene products, and its calculated ΔE_{ST} is also the most negative among them. Importantly, the triplet-sensitized products are also singlet-derived, which implies that intersystem crossing from the triplet nitrene to the singlet nitrene is downhill (and faster than reaction by the triplet). The evidence from the TRIR data suggests that the triplet state of the nitrene is populated slowly (on the sub-μs time scale), which we take to be thermal population from the singlet nitrene. We thus conclude also that the ground-state of acetylnitrene is a

singlet, and that it is the only of the four nitrenes reported here for which that is true. From the intensity and growth rate of the TRIR signal attributed to the triplet nitrene, we estimate that the triplet state is no more than about 1 kcal/mol above the singlet ground state.

***N*-Trifluoroacetyl Dibenzothiophene Sulfilimine.** Calculations on trifluoroacetylnitrene imply a more positive ΔE_{ST} than for acetylnitrene by about 5 kcal/mol; we thus take it to be about 4 kcal/mol. The product studies indicate a predominance of triplet-derived products (reduction product, loss of stereochemistry in formation of aziridines, etc.). Despite the ambiguity in the direct detection of the intermediates, we can tentatively infer a triplet ground-state for the nitrene from these results. We have no reason to believe that the usual pattern of faster rate constants for singlet reactions over triplet reactions would be broken and thus assume that the triplet products indicate that the nitrene spends significant time in the triplet state. While that could be assigned also to initial formation of the nitrene in the triplet state, followed by slow intersystem crossing to the ground singlet, that hypothesis seems to be contradicted by the data in Table 3. Those data indicate that the singlet nitrene is (at least a partial) precursor to the triplet nitrene, and not the reverse.

***N*-Mesyl Dibenzothiophene Sulfilimine and Mesylnitrene.** It is unfortunate that we were unable to detect either nitrene on photolysis of this sulfilimine in the TRIR data because this degrades the certainty with which the chemistry can be assigned to that intermediate. However, based on the precedent of the acetyl and benzoyl analogs, along with the product studies, we are willing to conclude that the nitrene is formed. Computational results indicate a triplet ground-state by perhaps as much as 10 kcal/mol. However, the product studies clearly indicate a certain amount of "singlet product" in the form of some retention of stereochemistry in the aziridines. To rationalize these product distributions, it is necessary to rely on the precedent of slow singlet-to-triplet intersystem crossing of related nitrenes,[3,24] and the assumption that reaction of the singlet nitrene is kinetically competitive with downhill intersystem crossing.

***N*-Tosyl Dibenzothiophene Sulfilimine and Tosylnitrene.** The computational results for tosylnitrene and mesyl nitrene are so similar that they indicate that there is little electronic communication between the phenyl (or methyl) and the nitrene center. We again conclude that a triplet ground-state is correct for this nitrene, consistent with the previous reports of EPR data from photolysis of tosyl azide at low temperature. Again, however, the product data show some singlet chemistry. In this instance, we see an unusual dependence of the aziridine stereochemistry on the concentration of the alkene, in which raising the concentration of the alkene leads to a decrease in retention. In Scheme 4, we presented a speculative explanation

for this phenomenon, in which we suggest that most of the nitrene is formed initially in the triplet state. With sufficiently slow triplet reactivity with the alkene and modest ΔE_{ST} (≤ 10 kcal/mol), one could imagine thermal population of the singlet nitrene on the μs time scale, which would accommodate the data easily. However, it does require that little if any singlet nitrene is formed on direct photolysis, a result that is not common to the other analogs in this series. That said, the alcohol trapping results (Table 7), which show no typical singlet O–H insertion product, regardless of conditions, is also unique to this compound.

Experimental Section

Time-Resolved IR Methods. The TRIR experiments have been conducted following the method of Hamaguchi and co-workers, as previously described.[57-59] In short, the broadband output of a MoSi$_2$ IR source is crossed with excitation pulses from either a Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ) operating at 200 Hz or a 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, amplified, digitized with an oscilloscope, and collected for processing. The experiment is conducted in dispersive mode with a commercial spectrometer.

Computational Methods. Vibrational frequencies for the TRIR experiments were calculated at B3LYP/6–31G(d), using the GAUSSIAN 98[60] suite of programs. All other computations were carried out using the GAMESS[61] suite. The output of the GAMESS calculations was visualized using MacMolPlt.[62] Initial geometries for the GAMESS runs were obtained from semiempirical or HF runs done with Spartan.[63] Triplet calculations were based on ROHF wave functions. The coefficients and exponents for the G3Large basis set were obtained from http://chemistry.anl.gov/compmat/g3theory.htm. All stationary points, except as noted, are confirmed as energy minima on the potential energy surface by vibrational frequency analysis. The notation G3Large* refers to the use of the G3Large basis set on key atoms S, O, and N and the use of 6–31G(d) on carbon and hydrogen.

Steady-State Photolysis Methods. Solvents were spectral grade and were used without further purification. The quantum yield measurements were carried using a 75 W Xe arc lamp fitted to a monochromator set to the specified wavelength with ±12 nm linear

dispersion. Azoxybenzene was used as the actinometer.[64] Samples were placed in a 1 cm square quartz cell mounted on a holder such that all the light exiting the monochromator hits the sample directly. Except as noted, initial concentrations were 1–4 mM and the solutions were bubbled with Ar for at least 10 min to remove O$_2$ prior to photolysis. The progress of reactions was monitored by HPLC, using a diode array UV/vis detector with a C18 reversed-phase column for separation. All reported yield data represent at least duplicate experiments, and most were carried out in triplicate or greater. Experiments done with octene were either done at an approximate 10% (±approximately 0.5%, by volume) or at precisely measured concentrations of alkenes as stated in the text.

Quantum yields for appearance of dibenzothiophene were determined using HPLC detection with reactions carried out only to low conversion. Product yields were determined from reactions run to nearly complete conversion of starting materials. Identification and quantification were done by a combination of ^{1}H NMR, ^{19}F-NMR and GC-MS (EI, DB-5 column) on concentrated reaction mixtures. All compounds, save for *trans*-3, were compared to authentic samples. Previous literature[41] with both cis and trans isomers of analogues provided clear precedent for assignment of the aziridine stereochemistry by ^{1}H NMR.

Materials. Products **7e**,[65] **8e**,[66] **8d**,[66] **10b**,[67] and **11**[66] were prepared using literature methods. The compounds *cis*-3 were prepared from 4-octene by analogy for a preparation based on 3-hexene.[41] Compound **6b** was prepared using a method given for the benzoyl analogue.[68] Its water solubility and relatively high volatility made purification beyond about 75% difficult, but the NMR data were clear, and the photolyzates were clearly identified as identical by spiking the samples with the synthetic mixture. Similarly, urethane **13**, prepared by treatment of isopropoxycarbonyl imidazole[69] with excess methylamine in water, could not be completely purified, but was spectroscopically and chromatographically identified. NMR data for previously unreported aziridines and **6b** are given in the Supporting Information.

***N*-Acetyl Dibenzothiophene Sulfilimine, 1b.** To a solution of trifluoroacetic anhydride, (0.14 mL, 1 mmol) in dichloromethane (40 mL) at −78 °C, was slowly added dibenzothiophene *S*-oxide (0.1 g, 0.5 mmol) in dichloromethane (3 mL). After cooling and stirring at −78 °C for 1 h, powdered acetamide (80 mg, 1.3 mmol) was added as the solid. After 2 h, the reaction was warmed to −20 °C and then quenched with ice−water. The reaction mixture was extracted with saturated sodium bicarbonate, and the organic layer was dried and concentrated to give the crude product. The title compound was obtained in 30% yield after silica chromatography with a gradient of ethyl acetate in dichloromethane: ^{1}H NMR (CDCl$_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 6.9 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (CDCl3) δ 24.2, 123.7, 129.0, 130.6, 133.3, 138.5, 138.4, 182.2; HRMS calcd for C$_{14}$H$_{11}$NOS 241.0561, found 241.0562.

***N*-Trifluoroacetyl Dibenzothiophene Sulfilimine, 1c.** The compound was prepared as was **1b**, save for use of trifluoroacetamide in place of acetamide: 65% yield; ^{1}H NMR (CDCl$_3$) δ 8.18 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ, 117.1 (q, J = 286.2 Hz), 122.9, 129.28, 130.7, 133.6, 135.9, 138.7, 169.0 (q, J = 35.3 Hz); HRMS calcd for C$_{14}$H$_8$F$_3$NOS 295.0279, found 295.0283.

***N*-Mesyl Dibenzothiophene Sulfilimine, 1d.** The procedure described for **1e** was used, save with chloramine M in place of chloramine T. The crude product was purified using column

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chromatography on silica with 15% ethyl acetate in dichloromethane. The yield of the pure compound was 54%: ^{1}H NMR (CDCl$_3$) δ 3.08 (s, 3H), 7.6 (t, J = 7.5 Hz, 2H), 7.711 (t, J = 7.5 Hz, 2H), 7.93 (d, J = 7.2 Hz, 2H), 8.03 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 43.5, 122.9, 127.7, 130.5, 133.4, 137.6, 138.3; HRMS calcd for C$_{13}$H$_{11}$NO$_2$S 277.0231, found 277.0222.

_N_-Tosyl Dibenzothiophene Sulfilimine, 1e. Chloramine T (1.53 g, 6.57 mmol) and DBT (1.00 g, 5.43 mmol) were added to 15 mL of methanol. To this solution was added, dropwise, 1 mL of glacial acetic acid. The resulting solution was heated to 50 °C with stirring. After about 14 h, the reaction mixture was poured into 10% aqueous NaOH on ice. This solution was filtered and recrystallized from methanol and water to give the title compound in 33% yield: ^{1}H NMR (CDCl$_3$) δ 2.44 (s, 3H), 7.83 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 9 Hz, 2H), 7.65 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 6.3 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.25−2.28 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 21.8,122.7, 126.9, 127.8, 128.5, 129.6, 130.3, 133.2, 137.7, 137.5; HRMS calcd for C$_{19}$H$_{15}$NO$_2$S$_2$ 353.0544, found 353.0546.

Supporting Information Available: Spectroscopic characterization of compounds and computational data, including coordinates and absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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