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RESEARCH ARTICLE

Photochemistry of *N*-aryl and *N*-alkyl dibenzothiophene sulfoximines

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Abstract

N-phenyl dibenzothiophene sulfoximine has been demonstrated to produce phenyl nitrene and dibenzothiophene *S*-oxide upon irradiation with UV-A light, and dibenzothiophene *S*-oxide upon further irradiation releases triplet atomic oxygen. Thus, *N*-phenyl dibenzothiophene sulfoximine exhibits a rare dual-release capability in its photochemistry. In this work, *N*-substituted dibenzothiophene sulfoximine derivatives are irradiated with UV-A light to compare their photochemistry and quantum yield of dibenzothiophene *S*-oxide production with that of *N*-phenyl dibenzothiophene sulfoximine. Both *N*-aryl and *N*-alkyl derivatives of dibenzothiophene sulfoximine are examined to observe their effects on the quantum yield of the photolysis reaction. Adding electron withdrawing *N*-aryl substituents is shown to increase the quantum yield of dibenzothiophene *S*-oxide production, while adding electron donating *N*-aryl substituents is shown to decrease the quantum yield. The quantum yield was slightly lowered or not increased by most *N*-alkyl substituents. Furthermore, the quantum yield was not augmented by branching and steric hindrance effects associated with the *N*-alkyl substituents. These results suggest that electronic modulation of the sulfoximine bonds affects the observed photolysis reaction.

KEYWORDS

atomic oxygen, dual-release, nitrene, photocleavage, photodenitration

INTRODUCTION

Dibenzothiophene (DBT) and some of its alkylated derivatives are commonly found in coal[1] and petroleum[2,3] and subsequently removed as a sulfur-containing impurity before use. Dibenzothiophene *S*-oxide (DBTO), the *S*-oxide of DBT, has been shown to form dibenzothiophene and triplet atomic oxygen [O(^{3}P)] upon irradiation with ultraviolet (UV) light.[4–7] The O(^{3}P) produced by DBTO and some of its derivatives has demonstrated selective reactivity, which includes oxidizing thiols to sulfenic acids and disulfides[8–10] and oxidizing alkenes to aldehydes.[11–13]

Nitrenes are reactive species formed as an intermediate in many different reactions and, notably, are used in organic synthesis for the production of aziridines from alkenes.[14–16] Nitrenes can be produced by the photolysis

Abbreviations: BDE, bond dissociation energy; BOB, dissociation energy; DAD, diode array detector; DBT, dibenzothiophene; DBTO, dibenzothiophene *S*-oxide; DMAP, dimethylaminopyridine; DMSO, dimethylsulfoxide; HPLC, High-pressure liquid chromatography; LCMS, liquid chromatography mass spectrometry; MS, mass spectrometry; NMR, nuclear magnetic resonance; O(^{3}P), ground state atomic oxygen; UV, ultraviolet; UV-A, ultraviolet A; UV-Vis, ultraviolet and visible.

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of various organic precursors. The photolysis of azides, both alkyl[17–19] and aryl,[20–23] forms nitrenes through the loss of N_2. Various sulfilimines of DBT[24–26] and thianthrene[27] have also been shown to form nitrenes through the scission of the S–N bond during photolysis. Photolysis of *N*-benzoyl dibenzothiophene sulfilimine by Desikan et al.[24] supported the reactivity of its corresponding nitrene being through the singlet channel. Morita et al.[26] demonstrated that the nitrenes formed by photolysis of *N*-tosyl and *N*-acyl dibenzothiophene sulfoximines reacted with diphenyl sulfide to form the corresponding *N*-substituted sulfilimine, as well as reacting with alkenes to form aziridines and with phosphorus compounds to form iminophosphoranes.

An additional method of forming nitrenes is the photolysis of *N*-phenyl DBT sulfoximine (**1Ph**), which was first explored by Isor et al.[28] Since the bond dissociation energy (BDE) of the S–N bond of DBT was predicted computationally to be significantly weaker than the S–O bond, the S–N bond was expected to break prior to the S–O bond and thus produce the nitrene before producing O(^{3}P). This hypothesis was confirmed when after irradiation with UV-A light, the S–N bond of **1Ph** was shown to break before the S–O bond, giving DBTO as a product instead of forming *N*-phenyl DBT sulfilimine. The quantum yield of formation of DBTO from **1Ph** was found to be 0.0141 ± 0.0017. Mechanistic experiments supported a singlet phenyl nitrene being formed during this reaction, followed by intersystem crossing to produce the triplet nitrene, which dimerizes to form azobenzene. After additional irradiation, the S–O bond of DBTO then cleaves to produce O(^{3}P) and the sulfide of DBTO. This two-part reaction (Figure 1) was highlighted for its rare dual-release of two different intermediates from one chromophore and has been referred to as the Bolm-McCulla reaction.[29]

Tandem reactions with the ability to release two different reactive intermediates from the same center are quite rare.[29] The Bolm-McCulla reaction, with its ability to sequentially and independently release nitrene and O(^{3}P), represents a unique opportunity for further investigation. Since only the photolysis of the *N*-phenyl DBT sulfoximine has thus far been studied, this work seeks to examine the photochemistry of different *N*-substituted derivatives of dibenzothiophene sulfoximine **1** to study the effects of various *N*-substituents upon the effectiveness of the scission of the S–N bond. Both *N*-aryl and *N*-alkyl derivatives were synthesized to observe the effect of different *N*-substituted derivatives upon DBTO formation. In this work, *N*-aryl derivatives were substituted with an electron-withdrawing (cyano- and trifluoromethyl-), weakly electron-withdrawing (chloro-), and electron-donating groups (methoxy- and methyl-) in the para position to see if that would affect the electronics of the photoreaction and thereby affect the quantum yield of DBTO formation, and potentially the order of release. In addition, the length of the n-alkyl chain of *N*-alkyl derivatives was varied ($n = 2, 3, 4, 5$) to determine if that also would affect the photolysis of the sulfoximine. Lastly, branched and sterically hindered *N*-alkyl derivatives (isopropyl- and *tert*-butyl-) were incorporated into the study to ascertain their potential influence on the photorelease.

MATERIALS AND METHODS

All reagents and solvents used in this work were purchased from Sigma-Aldrich, Acros, Ambeed, AK Scientific, Chem-Impex, Research Products International, Combi-Blocks, Tokyo Chemical Industry Co., or Fisher Scientific and used without further purification unless indicated otherwise. HPLC grade acetonitrile was used for photochemical studies. A Bruker NMR 400 MHz Avance III was used to obtain NMR spectra, and the associated analysis was performed with the TopSpin 4.2.0 software package. A Shimadzu UV-1800 UV Spectrophotometer and an Agilent Technologies Cary Series UV–Vis Spectrophotometer were used to acquire UV–Visible absorption data. High-performance flash chromatography for purification was performed on a CombiFlash NextGen 100 (Teledyne ISCO). An Agilent 1200 series (Quad pump, DAD with autosampler) with a Higgins Analytical 5 μm

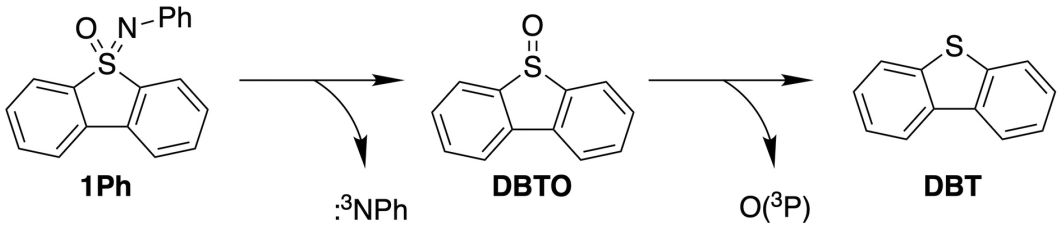


FIGURE 1 Photolysis of *N*-Phenyl dibenzothiophene sulfoximine (Bolm-McCulla).

CLIPEUS C-18 (or 150 ×4.6 mm) or a Machery-Nagel EC Nucleosil 100-5 CN (250 ×4.6 mm) column was used for HPLC analysis. Photoreactions were performed in a Photon Technologies International monochromator with a Xenon Short Arc Lamp (75 W). An Orbitrap LC–MS was used to obtain HRMS data via direct injection, and associated analysis was performed using Thermo Scientific Xcalibur software. Statistical analyses were performed with Microsoft Excel.

Quantum yield determination

Each *N*-substituted DBT sulfoximine was first dissolved in acetonitrile at a concentration of 3.2 mM, and the optical density of the resulting solution was greater than 3.0 at 325 nm for all solutions. Then, 3.5 mL of the solution was added to a quartz cuvette and sparged with argon for 15 min. The solution was photolyzed in a monochromator centered at 325 ± 3 nm for 3 h. The experiment was performed at low conversion (producing less than 7% of the corresponding sulfoxide DBTO in comparison to the parent sulfoximine) and the concentration of reactants and products was determined by HPLC. A minimum of three trials were performed per sulfoximine, and the error was calculated at a 95% confidence interval. Rearrangement of azoxybenzene in ethanol under alkaline conditions was used as a chemical actinometer to determine flux.[30] For flux determination, a solution of 400 mM potassium hydroxide and 10 mM azoxybenzene in ethanol was made, and 4 mL of the resulting solution was added to a quartz cuvette and its absorbance was measured in a UV–Vis spectrometer throughout the irradiation. The solution was irradiated in the same monochromator used for the photolysis reactions, and its absorbance was recorded every 5 min for 30 min.

General procedure for the synthesis of N-aryl dibenzothiophene sulfoximines[31]

The unsubstituted dibenzothiophene sulfoximine (**1**) was synthesized according to a previously reported method.[28,32] Sulfoximine **1** (0.95 mmol, 1 equiv.), copper (I) iodide (0.1 equiv.), and dimethylaminopyridine (DMAP) (1.1 equiv.) were stirred in 15 mL methanol for 10 min. Then, the corresponding arylboronic acid (1.5 equiv.) was added and the resulting solution was stirred overnight open to air at room temperature. The resulting solid was filtered from the solution and washed with methanol with no further purification. Details and spectra for all synthesized compounds are reported in the Supporting information.

General procedure for the synthesis of the primary N-alkyl dibenzothiophene sulfoximines[33]

Sulfoximine **1** (0.93 mmol, 1 equiv.) and potassium hydroxide (1.9 equiv.) were stirred in 5 mL dimethyl sulfoxide (DMSO) for 15 min. Then, the corresponding alkyl iodide (1.5 equiv.) was added, and the resulting solution was stirred overnight at room temperature. Deionized water (5 mL) was added, and the resulting solution was extracted twice with 10 mL dichloromethane. The organic portions were combined, dried with magnesium sulfate, and concentrated via reduced pressure. The compound was purified by flash silica chromatography. Details and spectra for all synthesized compounds are reported in the Supporting information.

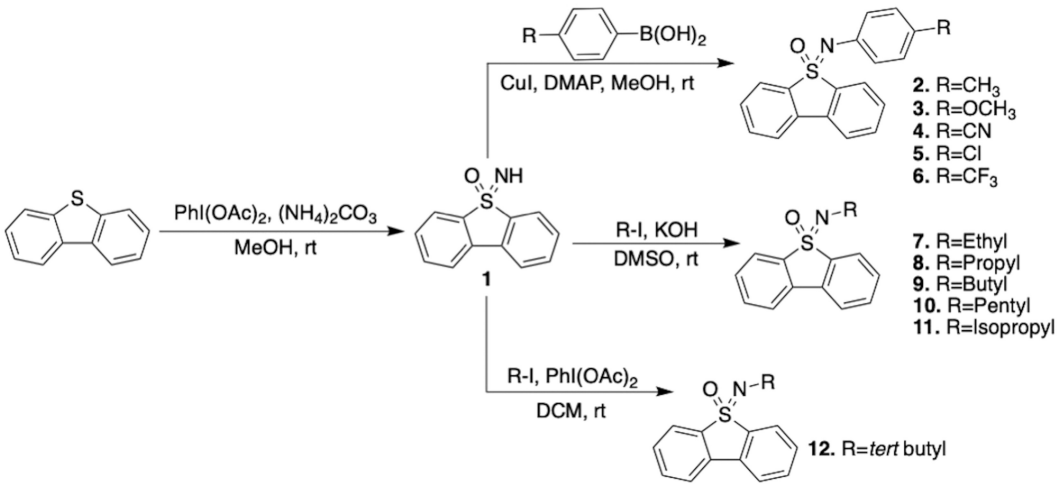
RESULTS & DISCUSSION

Synthesis of N-substituted dibenzothiophene sulfoximines

To synthesize different *N*-substituted DBT sulfoximines, the unsubstituted DBT sulfoximine (**1**) was first synthesized from dibenzothiophene by stirring (diacetoxy) iodobenzene and ammonium carbonate with dibenzothiophene in methanol at room temperature overnight. Sulfoximine **1** was then derivatized with several *N*-aryl and *N*-alkyl substituents, as shown in Scheme 1, the conditions used for the *N*-substitution differed depending on the alkyl or aryl halide added. *N*-aryl DBT sulfoximines **2–6** were obtained in 67%–77% yield. *N*-alkyl DBT sulfoximines **7–12** were obtained in 46%–56% yield.

Absorption spectra of N-substituted dibenzothiophene sulfoximines

The UV–visible absorption spectra of sulfoximines **2–12** were measured at a concentration of 0.032 mM in acetonitrile. In general, the spectra of *N*-aryl sulfoximines **2–6** (Figure 2) displayed a slightly higher molar absorptivity at their respective maxima around 230 nm compared to the spectra of *N*-alkyl Sulfoximines **7–12**, which are shown in Figure 3. Sulfoximines **5–6** exhibit the greatest molar absorptivity until 315 nm where their molar absorptivity is surpassed by **4.** Above 350 nm, *N*-aryl sulfoximines have some minor absorption while all the *N*-alkyl sulfoximines have reached their baseline. The absorption bands' maxima of **2-12** ranged from 210 to 274 nm (Table 1).



SCHEME 1 Synthesis of *N*-Substituted dibenzothiophene sulfoximines.

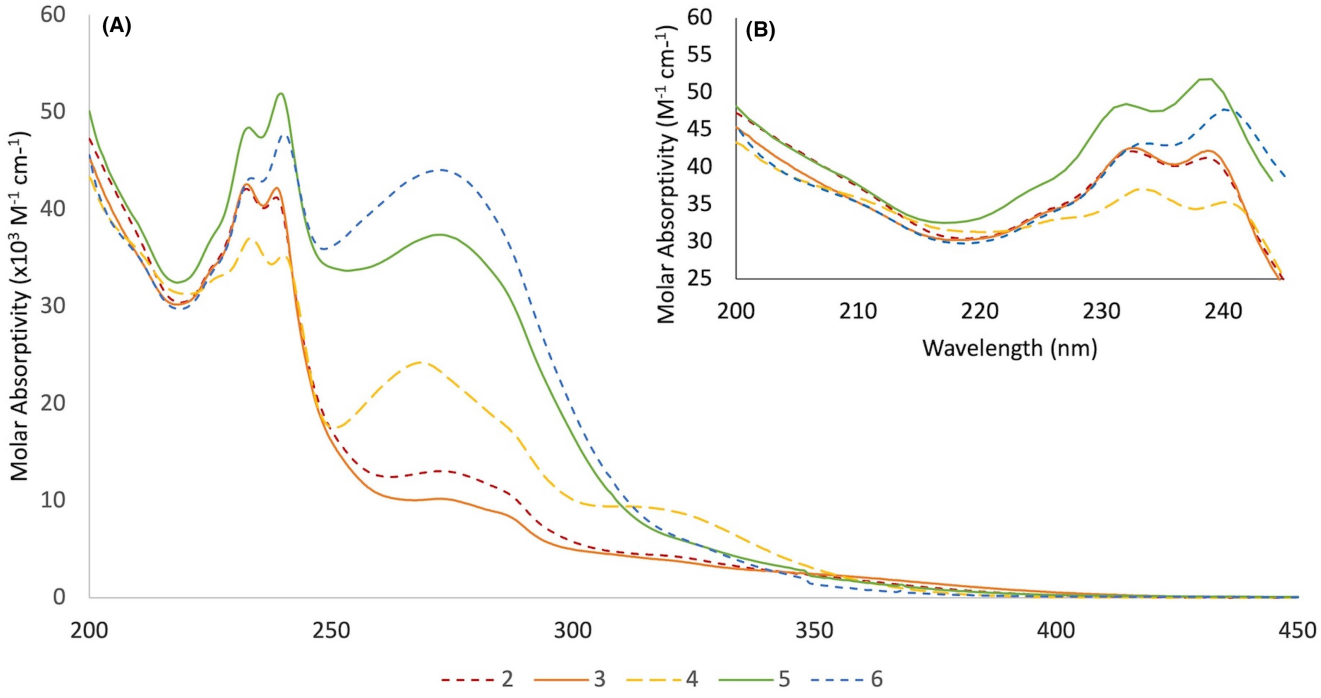


FIGURE 2 UV–Visible absorption spectra of *N*-aryl substituted dibenzothiophene sulfoximines **2–6** in acetonitrile. (A) Full spectra 200-450 nm. (B) Expansion of spectra 200-250 nm.

Photolysis of N-substituted dibenzothiophene sulfoximines

To examine the effects of *N*-substitution on the photochemistry of DBT sulfoximines, **2–12** were irradiated at 325 nm and the reaction was monitored by HPLC. Given the previous results, the S–N bond of the sulfoximine is expected to break in preference to the S–O bond unless the substitution has a large impact on the bond dissociation and excited state energies.[28] Thus, dibenzothiophene S-oxide (DBTO) was expected to be the predominant photoproduct upon irradiation with UV light for each sulfoximine, rather than the corresponding *N*-substituted sulfilimine. After irradiation at 325 ± 3 nm for 3 h and injection of the resulting solution on HPLC, DBTO was the major peak observed other than the starting sulfoximine as expected. No dibenzothiophene sulfilimines were detected after photolysis, showing that sulfoximines **2–12** did not differ in release order from **1Ph** by releasing the $O(^3P)$ before the nitrene. For *N*-alkyl compounds **7–12**, a small amount of DBTO was often observed when injecting samples prior to irradiation (t = 0 s) on HPLC (0.5%–1.5%), and this amount of DBTO present before photolysis was subtracted from the DBTO present after photolysis when calculating quantum yields. The

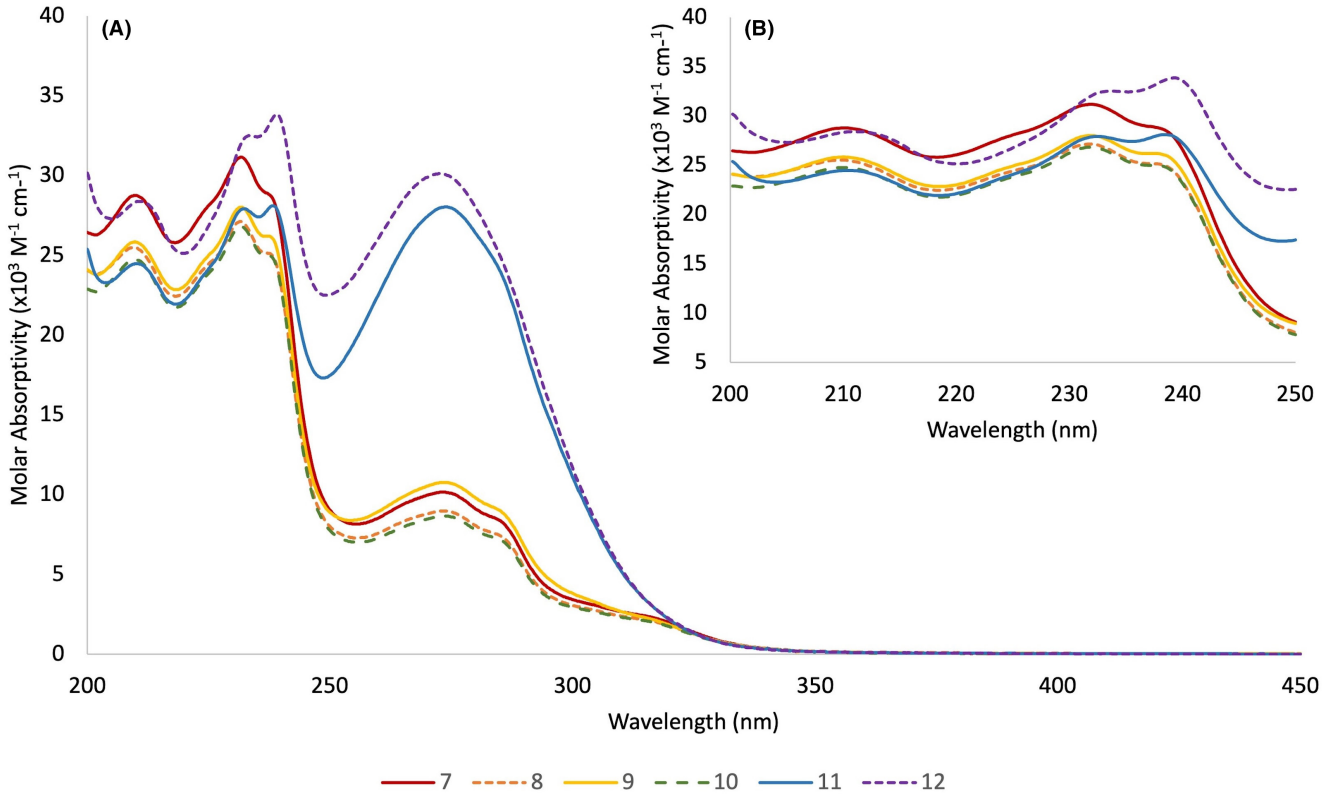


FIGURE 3 UV–Visible absorption spectra of *N*-alkyl substituted dibenzothiophene sulfoximines **7–12** in acetonitrile. (A) Full spectra 200-450 nm. (B) Expansion of spectra 200-250 nm.

TABLE 1 Absorption maxima of *N*-substituted dibenzothiophene sulfoximines.

DBT sulfoximine	Absorption maxima (λ, *nm*)
1Ph(28)	274, 319
2	233, 238, 273
3	233, 239, 272
4	233, 240, 269
5	233, 240, 273
6	233, 240, 273
7	210, 232, 273
8	210, 232, 273
9	210, 232, 274
10	210, 232, 273
11	210, 232, 274
12	211, 233, 268

TABLE 2 Quantum yield of DBTO formation with 95% confidence interval for *N*-substituted dibenzothiophene sulfoximines.

DBT sulfoximine	Quantum yield (Φ)
1Ph(28)	0.0141 ± 0.0017
2	0.0109 ± 0.0007
3	0.0089 ± 0.0006
4	0.031 ± 0.002
5	0.0125 ± 0.0013
6	0.022 ± 0.002
7	0.0107 ± 0.0007
8	0.0119 ± 0.0007
9	0.019 ± 0.008
10	0.014 ± 0.004
11	0.0079 ± 0.0001
12	0.014 ± 0.005

source of DBTO was investigated. No DBTO was detected in the solid samples by ^{1}H-NMR. Sulfoximines **7–12** were temporarily heated in a 60°C water bath via rotary evaporation after purification, 3.2 mM solutions of an *N*-aryl (**2**) and *N*-alkyl sulfoximine (**6**) were heated in a 60°C water bath for 3 h to see if DBTO was formed thermally from the sulfoximine. There was no observable increase in DBTO concentration shown by HPLC.

Quantum yields of N-aryl dibenzothiophene sulfoximines S–N dissociation

The effect of different para-substituted electron withdrawing and electron donating groups on the *N*-substituted phenyl ring upon the quantum yield of DBTO formation was examined. Previously, the effects of different substituents placed on the aryl rings of dibenzothiophene *S*-oxide have been studied computationally by Zhang et al.[34] In that study, electron donating groups were calculated to increase the bond dissociation enthalpy of the S–O bond, and electron-withdrawing substituents were calculated to decrease the BDE. If adding electron donating or electron withdrawing groups to DBTO strengthens or weakens the S–O bond, respectively, it is reasonable to expect that adding an electron donating or electron withdrawing group to the *N*-phenyl ring of *N*-phenyl DBT sulfoximine would affect the strength of the S–N bond. As shown in Table 2, the quantum yields for the formation of DBTO for **2** (4-methyl) and **3** (4-methoxy) were 0.0108 and 0.0089, respectively. These experimentally determined quantum yields of DBTO formation for **2** and **3** were over 20% and 35% less, respectively, than the quantum yield of **1Ph** (0.0141 ± 0.0017). For the electron withdrawing cyano and trifluoromethyl groups (**4** and **6**), the quantum yields of DBTO formation were 0.0306 and 0.0226, respectively. The electron withdrawing groups had a significantly larger quantum yield of DBTO formation when compared to the parent phenyl sulfoximine, **1Ph**. The weakly electron-withdrawing substituent (4-chloro) was predicted to have a greater quantum yield than **1Ph** based on the σ value for chloro substituents; however, the quantum yield of DBTO formation was slightly lower at 0.0116. For all the sulfoximines, quantum yields of all of the different synthetic batches were averaged, and the 95% confidence intervals of the batches were combined using the Type B on Bias method (BOB) method described by Levenson et al.[35,36]

The relationship between the substituent constant and quantum yield is portrayed in a Hammett-like plot (Figure 4), showing a linear relationship between the substituent constant and quantum yield.[37,38] The reaction constant (ρ) was calculated to be +0.56 (Figure 4). This indicates some degree of negative charge building on the nitrogen in the transition state or a weakening of the S–N bond by electron withdrawing groups. The S–N bond should be polarized with an excess of the negative charge residing on the nitrogen. The electron withdrawing cyano group of **4** and trifluoromethyl group of **6** would be able to stabilize the negative charge on the nitrogen while electron donating groups of **2** and **3** would destabilize this charge. The lower quantum yield of **5** suggests the lone pair on chlorine influences the photoreaction through resonance. Overall, groups that electronically interact with the S–N bond appear to affect the rate of S–N photocleavage.

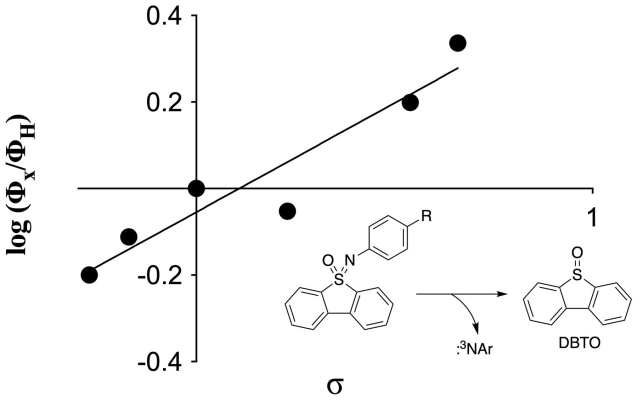


FIGURE 4 Hammett-like plot for the photolysis of *N*-aryl DBT sulfoximines.

Quantum yields of N-alkyl dibenzothiophene sulfoximines

The effect of *N*-alkyl groups, alkane chain length, steric hindrance, and branching on the quantum yield of *N*-alkyl DBT sulfoximines **7–12** was explored. For all the sulfoximines, quantum yields of all of the different synthetic batches were averaged, and the 95% confidence intervals of the batches were combined using the Type B on Bias method (BOB) method described by Levenson et al.[35,36] The *N*-alkyl groups were expected to have a similar or lower quantum yield compared to **1Ph** since they cannot contribute to the stabilization of negative charge buildup on the nitrogen. The weak electron-donating effect of an alkyl group also increased the likelihood that the quantum yield of **7–12** would be lower than that of **1Ph**. Sulfoximines 7, 8, and 10 supported this prediction by exhibiting quantum yields of 0.0107, 0.0119, and 0.0079, respectively, which were moderately lower than **1Ph**. For sulfoximine **10** and **12,** they both had a quantum yield of 0.014 which was similar to that of **1Ph**. Almost all of the sulfoximines provided similar quantum yields from different synthetic batches of the material; however, not all photolysis of sulfoximine **9** gave similar quantum yields. All the batches were examined for contamination by HPLC, LCMS, or NMR that was not present in all of the batches (i.e., small amounts of DBTO were present in $t = 0$ solutions from both batches injected on HPLC). Since other experimental variables were the same for experiments run using either batch (length of UV irradiation, acetonitrile used in solution preparation, monochromator used,

experimental protocol, etc.), this discrepancy in quantum yields between batches is believed to be caused by some undetected impurity. Thus, the measured quantum yield had a very large error (0.018 ± 0.008). The large error associated with this measurement prevents comparison to the other sulfoximines; however, it is difficult to imagine a rationale for why the butyl analog would have a higher quantum yield than the corresponding propyl and pentyl forms.

Given that groups which electronically interact with the S–N bond affect the quantum yield of DBTO formation, further investigation into the substitution of different groups on the *N*-phenyl ring of **1Ph** is warranted. In addition, *N*-substitution of the sulfoximine with non-aryl electron-withdrawing groups, as well as substitution of the aryl rings of the dibenzothiophene component of dibenzothiophene sulfoximine, presents another possibility towards increasing the quantum yield. On the other hand, substituents may also be used to decrease the quantum yield of DBTO formation to reverse the order of release so that the S–O bond breaks first. The photochemistry of such a reaction has never been explored, and achieving these conditions would represent a unique opportunity to explore the reactivity of the generated oxidant.

CONCLUSIONS

The photochemistry of some *N*-substituted dibenzothiophene sulfoximines was investigated to compare substituent effects with the previously explored *N*-phenyl dibenzothiophene sulfoximine. With all the *N*-substituted dibenzothiophene sulfoximines examined, dibenzothiophene *S*-oxide was the predominant product, as with *N*-phenyl dibenzothiophene sulfoximine. When investigating the quantum yields of dibenzothiophene *S*-oxide formation for *N*-aryl derivatives, para substitution of an electron-withdrawing cyano and trifluoromethyl groups were found to increase the quantum yield compared to **1Ph**, while para substitution of an electron-donating methoxy and methyl group were found to decrease the quantum yield of nitrene release. *N*-Substitution with an n-alkyl substituent appeared to slightly lower or had no effect on the quantum yield, except potentially in the case of the *N*-butyl derivative (**7**).

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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