2-(β-Naphthyl)benzoxazole (3g), mp 112 °C (lit.[16] mp 113–115 °C).

2-(9-Anthryl)benzoxazole (3h): dark yellow crystals after recrystallization from 2-propanol; mp 169–172 °C. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.42; H, 4.41; N, 4.75. Found: C, 85.38; H, 4.38; N, 4.64.

***trans*-2-Styrylbenzoxazole (4)**, mp 84 °C (lit.[14] mp 81 °C).

***cis*-2-Styrylbenzoxazole (4).** Into a solution of 20 g of *trans*-2-strylylbenzoxazole in 2 L of methanol was immersed a 125-W medium-pressure Hg lamp, and the solution was illuminated through Pyrex until the photostationary state was reached (control by UV spectra of aliquots). After evaporation of the solvent, the trans–cis mixture was fractionated by distillation. The first fraction [bp 140 °C (1 mm)] was the cis form: yield about 30% (6g); light yellow, almost colorless crystals; mp 35 °C; mol wt calcd 221, found 231. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.45; H, 4.98; N, 6.33; O, 7.14. Found: C, 81.79; H, 4.93; N, 6.23; O, 6.95.

2-(2-Furanyl)benzoxazole (3k), mp 89–90 °C (lit. mp 82–84 °C[14] 86–86.5 °C[15]).

2-(2-Thiophenyl)benzoxazole (3l), mp 107 °C (lit.[17] mp 104.5 °C).

2-Ferrocenylbenzoxazole (3m): orange crystals after recrystallization from ethanol and vacuum sublimation; mp 150 °C. Anal. Calcd for $C_{17}H_{13}FeNO$: C, 67.33; H, 4.29; N, 4.62. Found: C, 67.34; H, 4.41; N, 4.67.

2-*tert*-Butylbenzoxazole (3n) was prepared by the procedure of Skraup[18] from *o*-aminophenol and pivalic acid (2,2-dimethylpropanoic acid): colorless liquid; bp 222–226 °C (lit.[18] bp 226 °C).

2-*o*-Tolylbenzoxazole (24), mp 69 °C (lit.[22] mp 69 °C).

1,3-Diphenyl-2,4-bis(2-benzoxazolyl)cyclobutane (5). A 10-g sample of *trans*-2-styrylbenzoxazole (4) was horizontally and evenly distributed in Pyrex tubing of 100-mm i.d., and 500-mm length and in a horizontally located Rayonet-Reactor under slow rotation (4 turns/min) and illuminated with 300-nm light for 6 days. The unreacted styrylbenzoxazole was removed with 100 mL of ethanol and the residue recrystallized from acetone: yield 2.2 g (22%); colorless crystals; mp 248 °C; mol wt ($CHCl_3$) calcd 442, found 454; mass spectrum, main mass *m/e* 221 (styrylbenzoxazole), parent peak (*m/e* 442) only traces, no signal at *m/e* 180 (stilbene), no signal at *m/e* 262 (1,2-dibenzoxazolylethylene). Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.45; H, 4.98; N, 6.33; O, 7.24. Found: C, 81.52; H, 4.88; N, 6.28; O, 7.12.

The main mass (styrylbenzoxazole) indicates that **5** has the structure of a truxillic acid because it is highly improbable that a compound with a truxinic acid structure would cleave only into styrylbenzoxazole and not into stilbene plus 1,2-dibenzoxazolylethylene.

Furthermore, if **5** is hydrolyzed for 2 h with boiling diluted H_2SO_4 (10%), epitruxillic acid (mp 285 °C) is formed. Since either the α- or the ε-truxillic acid derivative is the most probable configuration of the photodimer derived from **4** in its trans form and since α-truxillic acid but not ε-truxillic acid yields epi-truxillic acid in boiling H_2SO_4[19] we conclude that **5** has the structure of an α-truxillic acid derivative.

2,2′-Bibenzoxazole (7), mp 262 °C (lit.[20] mp 256 °C).

Acknowledgment. We thank Miss A. Renneberg for technical assistance.

Registry No. 1a, 3230-45-3; **1b**, 1761-56-4; **1c**, 17065-03-1; **1d**, 6136-58-9; **1e**, 3117-67-7; **1f**, 5932-25-2; **1g**, 78685-68-4; **1h**, 6076-01-3; **1i**, 54638-91-4; **1k**, 6078-02-0; **1l**, 1435-04-7; **1m**, 12126-35-1; **1n**, 70299-35-3; **3a**, 833-50-1; **3b**, 835-64-3; **3c**, 3315-19-3; **3d**, 13459-17-1; **3e**, 838-34-6; **3f**, 3164-18-9; **3g**, 14625-56-0; **3h**, 78685-69-5; **3k**, 881-60-7; **3l**, 23999-63-5; **3m**, 34801-92-8; **3n**, 54696-03-6; *cis*-**4**, 78685-70-8; *trans*-**4**, 59066-62-5; **5**, 78685-71-9; **6**, 26903-08-2; **7**, 7210-07-3; **10**, 78685-72-0; **11**, 20768-44-9; **12**, 75729-97-4; **13**, 33771-63-0; **14**, 78685-73-1; **15**, 78685-74-2; **16**, 33771-65-2; **17a**, 78685-75-3; **17b**, 78685-76-4; **18b**, 78685-77-5; **19**, 78685-78-6; **20**, 78685-79-7; **21**, 78685-80-0; **22**, 78685-81-1; **23**, 78685-82-2; **24**, 32959-60-7; **25**, 78685-83-3; **27**, 78685-84-4; **28**, 78685-85-5.

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Photoreactivity of 2- and 3-Substituted Benzo[*b*]thiophene 1-Oxides in Solution

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The photochemical behavior of various benzo[*b*]thiophene sulfoxides (3-methyl, 3-phenyl, 2-methyl, 2-phenyl, 2,3-dimethyl, 2-chloro, 2-bromo, 3-chloro, 3-bromo) has been studied in benzene as solvent. The bromo and chloro derivatives gave no identifiable products. The 3-methyl and 3-phenyl compounds gave three head to head anti photodimers which differ only by the stereochemistry of the S–O bond. The kinetics of the photodimerization of 3-MeBTO was studied as a function of the concentration of substrate, triplet quencher, and triplet sensitizer. A monomeric excited triplet is the proposed precursor of the hth dimer. The 2-methyl derivative led to a photoreduction giving the corresponding sulfide probably through an excited triplet. The 2-phenyl derivative gave a mixture of the photodimer hth and the corresponding sulfide. The behavior of the sulfoxides in these series is different from that of the corresponding sulfones which lead to a mixture of hth and htt dimers for the 2-substituted compounds and to the hth dimer for the 3-substituted ones.

The photochemical behavior of sulfoxides can be classified in different categories according to the type of chemical reaction observed: epimerization of the sulfoxide group;[1-3] ring contraction with loss of oxygen as in case of 2,2-dimethylthiachroman 1-oxide[4] and of analogous cyclic sulfoxides;[5] loss of a β-hydrogen atom leading to a ring

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Table I. Photodimerization and Photoreduction of Benzothiophene Oxides and Derivatives in Solution

monomer	solvent	wavelength, nm	% dimerization (hth anti)	reduction product (% yield)
3-MeBTO (1)	C_6H_6	313	50 (**1a–c**)	
	C_6H_6 + PhC(O)Ph	366	80 (**1a–c**)	
3-PhBTO (2)	C_6H_6 + PhC(O)Ph	366	40 (**2a–c**)	
2-MeBTO (3)	C_6H_6 + PhC(O)Ph	366		**3d** (10)
	C_6H_6	313		
2-PhBTO (4)	C_6H_6 + PhC(O)Ph	366	60 (**4a** or **4c**)	**4d** (5)
2,3-Me_2BTO (5)	C_6H_6 + PhC(O)Ph	366		**5d** (35)
	C_6H_6	313		
2-Cl,2-BrBTO (6) and 3-Cl,3-BrBTO (6)	C_6H_6 + PhC(O)Ph	366		

Table II. ^{1}H NMR Assignment of Dimer Structures

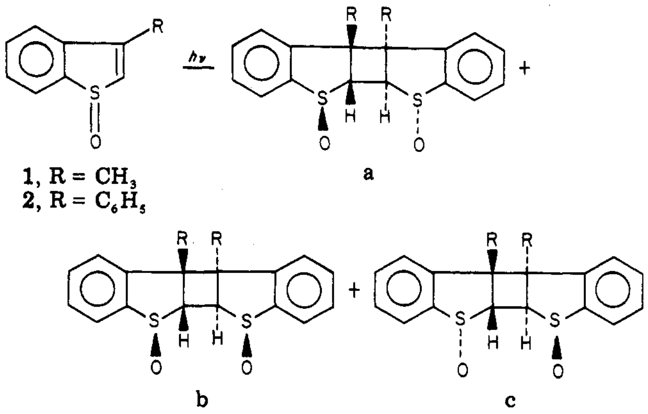
	dimer	chemical shift[a]
3-MeBTO (1)	**1a**	4.73 (s, 2 H), 1.17 (s, 6 H), 7.4–8 (m, 8 H)
	1b	4.47 (d, 1 H, $^{AB}J = 6$), 3.67 (d, 1 H, $^{AB}J = 6$), 1.03 (s, 3 H), 1.40 (s, 3 H), 7.4–8 (m)
	1c	3.24 (s, 2 H), 1.35 (s, 6 H), 7.3–8.15 (m, 8 H)
3-PhBTO (2)	**2a**	5.50 (s, 2 H)
	2b	4.15 (d, 1 H, $^{AB}J = 9$), 5.17 (d, 1 H, $^{AB}J = 9$)
2-PhBTO (4)	**4a** or **4c**	6.05 (s, 2 H)

[a] Chemical shifts are given in parts per million and *J* values in hertz.

contraction or to the rearrangement into cyclic sulfenates as in the case of *cis*- and *trans*-1,3-dihydro-2-thiaphenalene 2-oxides and analogues,[6,7] of substituted thiochromanone sulfoxides,[8-10] and of aliphatic sulfoxides;[11-13] deoxygenation with reduction to sulfide in the case of diphenyl sulfoxides.[14] In the course of our studies on the reactivity of sulfoxides in the benzo[*b*]thiophene series with respect to the hydrodesulfuration reaction[15] and cycloaddition processes[16] we have explored the photoreactivity of these compounds.[17] As in this series, the benzo[*b*]thiophene *S*-oxide is not isolable;[18] it is only possible to examine the influence of the substituent in the 2- or 3-position. A reaction mechanism consistent with the experimental data will be presented.

Photoproducts. Solutions of sulfoxides were irradiated at 313 nm or in the presence of benzophenone at 366 nm. Table I gives a survey of the experiments and indicates the product distribution for each compound as determined after irradiation by ^{1}H NMR analysis (Table II).

The stereochemistry of the dimers is determined by oxidation[21] of the sulfoxides to the corresponding sulfones, which were previously identified.[19,20] All the photodimers are anti head to head (hth) without any trace of the head to tail (htt) dimer. 3-CH_3BTO (**1**) gives the three dimers **1a–c** previously described[17] which differ only by the stereochemistry of the S=O sulfoxide bonds. According to the literature[22,23] there is no significant solvent polarity effect on the product distribution of the dimers.



1, R = CH_3
2, R = C_6H_5

For 3-PhBTO (**2**) the yield of photodimerization is low, leading to the unstable compounds **2a–c**. The photoreactivities of 3-Br- and 3-ClBTO were not studied because of formation of tars during the irradiation procedure.

For the 2-substituted compounds the results are different. 2-MeBTO (**3**) led to the deoxygenated compound **3d** (2-MeBT) and to tars with no trace of dimerization. We checked that this formation was not due to the unstability of the dimers by synthesizing the corresponding sulfide dimers hth and htt by reduction of the corresponding sulfones[24] and reoxidation to the **3a–c** and **3′a–c** sulfoxides. All these compounds were perfectly stable and isolable.

The irradiation of **3** gives essentially a photoreduction with no dimerization.

For the 2-phenylbenzothiophene sulfoxide **4** there was essentially formation of one dimer (**4a** or **4c**, 60%, only one singlet for H_3 and $H_{3'}$ in the ^{1}H NMR spectrum) along

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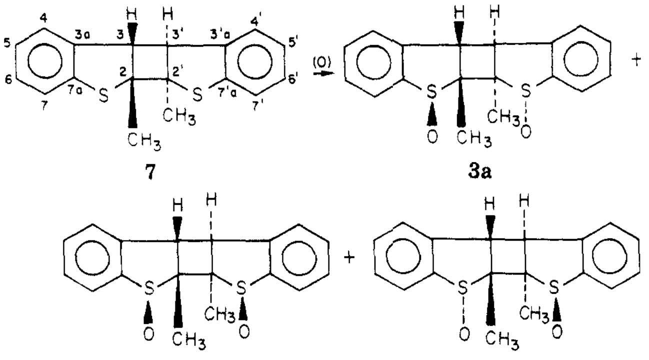
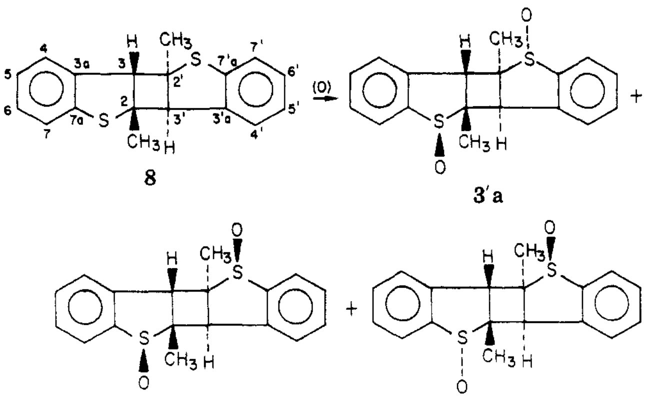


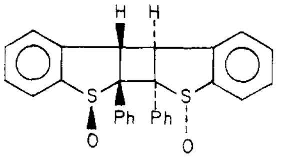
7 3a

3b 3c

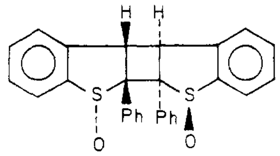


8 3'a

3'b 3'c



4a



4c

with the formation of small amounts (~10%) of the corresponding sulfide. The anti stereochemistry of the hth dimer was determined by oxidation to the corresponding sulfone.[20] It was impossible by all means, acidic or photochemical,[17] to epimerize the S=O bond. This absence of reactivity was probably due to the steric effect of the phenyl groups α to the S=O.

The irradiation of 2,3-Me_2BTO (5) led only to the corresponding sulfide with a significant amount of tars.

As previously mentioned for the 3-Br or 3-Cl compounds, the corresponding 2-compounds **6** were unstable under the photochemical conditions, with immediate formation of tars.

The lack of solubility for dimers of 2-Ph- and 3-PhBTO precluded any further study of the process. For this reason and only kinetic photochemical study we attempted was on the photodimerization of the 3- and 2-methylbenzo[*b*]thiophene sulfoxides **1** and **3**.

Photochemical Deoxygenation of 2-Methylbenzo[*b*]thiophene 1-Oxide (3). The photodeoxygenation of **3** at 313 nm was studied as a function of the substrate concentration in benzene as solvent. The data conformed to a linear relationship between $1/\phi$ and $1/C$. The correlation coefficient, the intercept, and the slope are given in Table III. The mixture analysis has been determined by ^{1}H NMR with dioxane as an internal reference.

The increase of ϕ with the concentration of **3** is in accordance with a mechanism in which two molecules of sulfoxide lead to the sulfide and one molecule of oxygen. This mechanism has been proposed in the case of the photochemical deoxygenation of the sulfoxide of the dibenzothiophene.[25]

Table III. Concentration Dependence for Quantum Yield of the Photodeoxygenation of 3 at 313 nm in Benzene Solution[a]

10^2(concn), M	ϕ^b	$1/C$	$1/\phi$
2.24	0.028	44.64	35.71
4.13	0.055	24.21	18.18
5.76	0.068	17.36	14.71
7.48	0.076	13.37	13.16
9.00	0.082	11.11	12.20

[a] For $1/\phi = f(1/C)$, $r = 0.9899$, slope $s = 0.7$, and intercept $i = 3$. [b] For each concentration the ϕ value is at least the mean of four determinations.

Table IV. Concentration Dependence for Quantum Yield[a,b] of the Photodimerization of 1 at 313 nm in Benzene Solution

10^2(concn), M	ϕ^c	$1/C$	$1/\phi_{dim} = 2/\phi$
1.84	0.108	54.35	18.52
2.39	0.136	41.84	14.71
3.98	0.206	25.13	9.71
5.63	0.290	17.76	6.85
8.68	0.380	11.52	5.26

[a] For $1/\phi_{dim} = f(1/C)$, $r = 0.9993$, $s = 0.31 \pm 0.02$, and $i = 1.6 \pm 0.6$. [b] $\phi_{dim} = \phi(\text{3-Me-BTO})^2$. [c] For each concentration, four measurements were performed.

Table V. Quantum Yields of Dimerization of 1 in the Presence of Cyclooctatetraene (COT) at 313 nm in Benzene Solution[a,d]

10^3[COT], M	$\phi_{dim}{}^b$	$\phi^\circ{}_{dim}{}^c/\phi_{dim}$
1.99	0.051	1.33
4.10	0.043	1.58
8.65	0.033	2.06
18.97	0.022	3.09
41.22	0.013	5.23

[a] For $\phi^\circ{}_{dim}/\phi_{dim} = f\{Q\}$, $r = 0.9998$, slope $s = 99 \pm 4$, and intercept $i = 1.2 \pm 0.1$. [b] For each concentration in COT the ϕ value corresponds to the mean value of at least four determinations. [c] $\phi^\circ{}_{dim} = 0.068$ in every case. [d] [Sulfoxide] = 2.39×10^{-2} M in every case.

Different experiments performed in order to trap the liberated oxygen for determining its nature were unsuccessful.

In the presence of cyclooctatetraene (COT) as quencher it was not possible to establish any relationship between the quantum yield and the sulfoxide concentration, due to the effect of the liberated oxygen which reacts with the cyclooctatetraene. With benzophenone as sensitizer the reaction was faster, but here again no relationship has been found. These two partial results seem, however, to be in favor of passage through an excited triplet state.

Photodimerization of 3-MeBTO (1). Concentration Dependence. The photodimerization of **1** at 313 nm was studied as a function of substrate concentration in benzene solution. The data (Table IV) conformed to a linear relationship between $1/\phi_{dim}$ and $1/C$. The correlation coefficient, the intercept, and the slope of the line are indicated. The mixture analysis has been determined by ^{1}H NMR, with dioxane as an internal reference, and U.V. spectra at 320nm.

Quenching of Photodimerization. Investigation of cyclooctatetraene (COT) quenching of the dimerization of **1** in benzene gave data (Table V) that produced a Stern–

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Volmer relationship (eq 1) according to Scheme I.[26]

$$\phi^\circ_{\mathrm{dim}}/\phi_{\mathrm{dim}} = 1 + \frac{k_q[\mathrm{COT}]}{k_d + k_r[M]} \qquad (1)$$

Scheme I

$$\mathrm{M} \xrightarrow{h\nu} {}^1\mathrm{M}$$

$${}^1\mathrm{M} \xrightarrow{k_1} \mathrm{M}$$

$${}^1\mathrm{M} \xrightarrow{k_2} {}^3\mathrm{M}$$

$${}^3\mathrm{M} \xrightarrow{k_d} \mathrm{M}$$

$${}^3\mathrm{M} + \mathrm{COT} \xrightarrow{k_q} \mathrm{M} + {}^3\mathrm{COT}$$

$${}^3\mathrm{M} + \mathrm{M} \xrightarrow{k_r} \mathrm{T}\cdots\mathrm{T} \text{ etc. ... (Scheme II)}$$

The quantum yields have been obtained by using the ^{1}H NMR method with dioxane as an internal reference for the mixture analysis.

As in the case of the corresponding sulfone,[20] the very efficient quenching implies that the dimers arise from a triplet state.

Sensitized Dimerization. The 366-nm irradiation of 1 and benzophenone in benzene solution was explored. The quantum yield of the sensitized dimerization was studied as a function of the concentration of 3-Me-BTO (1). The results conformed to a linear relationship (Table VI).

Discussion

The very efficient quenching by COT of the unique hth anti dimer implies that as in the case of the corresponding sulfone, 3-MeBTO$_2$,[20] the photodimerization proceeds from a triplet state precursor according to general Scheme II,[26]

Scheme II

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S} \text{ (rate} = I_a)$$

$${}^1\mathrm{S} \xrightarrow{k_1} {}^3\mathrm{S} \text{ (rate} = k_1[{}^1\mathrm{S}])$$

$${}^1\mathrm{S} \xrightarrow{k_2} \text{(rate} = k_2[{}^1\mathrm{S}])$$

$${}^3\mathrm{S} \xrightarrow{k_3} \mathrm{S} \text{ (rate} = k_3[{}^3\mathrm{S}])$$

$$\mathrm{M} + {}^3\mathrm{S} \xrightarrow{k_4} {}^3\mathrm{M} + \mathrm{S} \text{ (rate} = k_4[\mathrm{M}][{}^3\mathrm{S}])$$

$${}^3\mathrm{M} \xrightarrow{k_d} \mathrm{M} \text{ (rate} = k_d[{}^3\mathrm{M}])$$

$${}^3\mathrm{M} + \mathrm{M} \xrightarrow{k_r} \mathrm{T}\cdots\mathrm{T} \text{ (rate} = k_r[{}^3\mathrm{M}][\mathrm{M}])$$

$$\mathrm{T}\cdots\mathrm{T} \xrightarrow{k_5} 2\mathrm{M} \text{ (rate} = k_5[\mathrm{T}\cdots\mathrm{T}])$$

$$\mathrm{T}\cdots\mathrm{T} \xrightarrow{k_6} \text{hth dimer (rate} = k_6[\mathrm{T}\cdots\mathrm{T}])$$

where S, ^{1}S, and ^{3}S refer to the ground, singlet, and triplet excited states of the sensitizer, M and ^{3}M refer to the ground and triplet states of the reactant, and T···T the metastable intermediate precursor of the unique dimer.[26]

Applying the steady-state approximations to the appropriate intermediates, the kinetic relationship in the absence or in presence of the sensitizer is given by eq 2,

$$1/\phi_{\mathrm{dim}} = 1/\alpha\phi_{\mathrm{isc}} + k_d/k_r\alpha\phi_{\mathrm{isc}}[\mathrm{M}] \qquad (2)$$

where α is the fraction of the intermediate T···T converted to the dimer and ϕ_{isc} the yield of the intersystem conversion between the excited singlet and the triplet of the sulfoxide or the sensitizer. On the assumption that the sulfoxide 1 should present the same behavior as the corresponding sulfone,[19] i.e., that the energy transfer from the triplet of the benzophenone was 100% efficient,[27] it is possible to calculate from eq 2 an α value of 0.91 (Table VI). The substitution of this value in 2 and application to the results in the absence of sensitizer (Table IV) leads to a value of ϕ_{isc} for the intersystem conversion $^1\mathrm{M} \rightarrow {}^3\mathrm{M}$ of 0.68.

Table VI. Concentration Dependence of Quantum Yield of Sensitized 3-MeBTO Dimer Formation in Benzene Solution at 366 nm

10^2[sulfoxide],[b] M	ϕ[a]	$1/C$	$1/\phi_{\mathrm{dim}} = 2/\phi$
2.29	0.292	43.67	6.84
3.82	0.449	26.18	4.45
6.12	0.614	16.34	3.26
8.67	0.764	11.53	2.62

[a] For each concentration ϕ is the mean of at least four determinations. For $1/\phi_{\mathrm{dim}} = f(1/[\mathrm{sulfoxide}])$, $r = 0.9997$, $s = 0.13 \pm 0.008$, and $i = 1.1 \pm 0.2$. [b] [Benzophenone] = 2.08×10^{-2} M in every case.

From eq 2 and from the slope of the Stern–Volmer equation (eq 1) with a k_q value fo 1.2×10^{10} M^{-1} s^{-1},[19] the results of the quantum yields in the presence or in the absence of inhibition (Tables IV and V) led to the values of $k_d = 10^8$ s^{-1} and $k_r = 5.6 \times 10^8$ m^{-1} s^{-1}.

The k_r value is higher than the value found for the sulfones.[19,20,22] This result could be related to the decrease in the ground state of the aromatic character of the C_2C_3 double bond from the sulfoxide to the sulfone.[28]

On the basis of the previous experimental data and discussions,[19,20,22] in the photodimerization of the sulfone analogues the behavior of the sulfoxides seems to be identical. The data agree well with the association of a molecule in the ground state with a molecule in a triplet state. The so-formed complex would give a tertiary 1,4-diradical stabilized by the presence of the sulfoxide group before proceeding to product. Moreover, due to the steric hindrance of the methyl group in the 3-position this diradical could give the preferential formation of the hth photodimer.

Experimental Section

Instrumentation. UV spectra were recorded on Gilford 250 and Unicam SP-800 spectrophotometers. Infrared spectra were measured on a Perkin-Elmer 720 instrument. ^{1}H NMR spectra were obtained at 20 °C from Varian A-60, Varian EM-360, and Bruker WP-80 spectrophotometers. ^{13}C NMR spectra of solutions were recorded at 20 °C on a Bruker HX-90 NMR instrument operating at 22.63 MHz and on a Bruker WP-80 operating at 20.115 MHz in the Fourier transform mode. Mass spectral measurements were made on an CEC 21-110C spectrophotometer. Melting points were obtained on a Buchi apparatus.

Materials. 2- and 3-substituted benzo[*b*]thiophene 1-oxides 1–6 were prepared as previously described from corresponding sulfides.[17,21,29] Bisulfides 7 and 8 were readily obtained by reduction with $AlLiH_4$[24] of the corresponding already described disulfones.[20] Head to head bisulfide 7: ^{1}H NMR (CDCl$_3$) δ 7.43–7.1 (m, 8 H), 4.23 (s, 2 H), 1.37 (s, 6 H). Head to tail bisulfide

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8: ^{1}H NMR ($CDCl_3$) δ 7.63–7.1 (m, 8 H), 3.97 (s, 2 H), 1.88 (s, 6 H).

Oxidation of 7 and 8 by *m*-chloroperbenzoic acid[20] leads to the mixture of dimers **3a–c** and **3′a–c**, respectively. These dimers can be separated by thin-layer preparative chromatography on SiO_2; they were identified by cyclobutanic hydrogen atoms and methyl signals in the ^{1}H NMR ($CDCl_3$): **3a**, δ 4.13 (2 H), 1.1 (6 H); **3b**, δ 4.77 (1 H), 3.70 (1 H), 1.25 (3 H), 1.05 (3 H); **3c**, δ 4.66 (2 H), 1.32 (6 H); **3′a**, δ 4.45 (2 H), 2.0 (6 H); **3′b** δ 4.23 (1H), 4.10 (1 H), 2.15 (3 H), 1.88 (3 H); **3′c**, δ 4.37 (2 H), 2.07 (6 H).

Irradiations. Preparative irradiations were carried out in a 300-mL-capacity photolysis vessel equipped with a nitrogen inlet and Pyrex immersion well. The solutions were previously purged with dry nitrogen for 30 min and then irradiated with a Type 125W Philips HPK mercury arc lamp. Direct irradiations at 313 nm were performed through a K_2CrO_4/K_2CO_3 filter solution[26] circulating around the immersion well. Irradiations at 366 nm for sensitization studies were carried out with the lamp emission filtered by 0.7 M $Cu(NO_3)_2$ solution.[23]

Direct irradiations for concentration, quenching, and sensitization studies were carried out with a Hanovia 450-W mercury arc lamp in a merry-go-round apparatus[30] with interference filters allowing the selection of individual bands. Pyrex tubes (10 × 100 mm) were filled with 3.5 mL of the solution to be irradiated; the samples were then degassed (10^{-6} torr) by using several freeze–thaw cycles before the tubes were sealed. All runs were carried out under low-conversion conditions. After irradiation the amount of unreacted monomer was determined simultaneously by quantitative spectrophotometric UV analysis and by quantitative ^{1}H NMR analysis with dioxane as an internal reference.

Actinometry. The actinometer used was the benzophenone–benzhydrol system according to the described method.[31] Actinometer solutions were irradiated in parallel with the reaction mixtures.

Preparative Dimerization of 3-MeBTO (1). Direct irradiation of **1** (6.08 mM) in 280 mL of dry benzene at 313 nm for 15 h gave (50%) of a mixture of the two dimers **1a** and **1b** with a **1a** to **1b** ratio of 5:3 and a small amount of the third dimer **1c**. After evaporation of the solvent under vacuum, these dimers were separated by thin-layer preparative chromatography on SiO_2 (eluent ether–methanol, 95:5).

Sensitized irradiation of **1** at 366 nm for 4 h, with benzophenone as the sensitizer, gave the same isomers in the same amount with an overall yield of 80%. Anal. Calcd for $C_{18}H_{16}O_2S_2$: C, 65.85; H, 7.41. Found: C, 65.7; H, 7.5.

1a: F 224–226 °C; IR ($CDCl_3$) 1060, 1040, 1025 cm^{-1}; mass spectrum (70 eV), *m/e* 328, 312, 296, 148; ^{13}C NMR ($CDCl_3$); 9 peaks) δ 22.4 (CH_3), 51.5 (C_2, $C_{2'}$), 57.0 (C_3, $C_{3'}$), 125.4 (C_6, $C_{6'}$), 128.0 (C_7, $C_{7'}$), 129.8 (C_4, $C_{4'}$), 132.4 (C_5, $C_{5'}$), 145.1 and 146.2 (C_{3a}, $C_{3'a}$, C_{7a}, $C_{7'a}$).

1b: F 250 °C dec; IR ($CDCl_3$) 1055–1045 cm^{-1}; mass spectrum (70eV), *m/e* 328, 311 148; ^{13}C NMR ($CDCl_3$; all the carbons are different, giving 18 different peaks) δ 23.8, 24.2 (CH_3), 57.6, 58.1 (C_2, $C_{2'}$), 56.4, 60.1 (C_3, $C_{3'}$), 126.0, 126.6, (C_6, $C_{6'}$), 128.2, 128.5 (C_7, $C_{7'}$), 129.7, 130.1 (C_4, $C_{4'}$), 132.3, 132.6 (C_5, $C_{5'}$), 143.9, 144.4, 146.0, and 147.2 (C_{3a}, $C_{3'a}$, C_{7a}, $C_{7'a}$).

1c: F 230 °C; IR ($CDCl_3$) 1055–1040 cm^{-1}.

Preparative Dimerization of 3-PhBTO (2). Irradiation of **2** (1.33 mM in 280 mL of benzene) at 366 nm, with benzophenone as the sensitizer, led to a mixture of dimers. It was very difficult to separate the more stable dimers **2a** and **2b** by SiO_2 thick-layer chromatography because of their lack of solubility in all common organic solvents. **2a** and **2b** were identified by their ^{1}H NMR spectra (CF_3COOH–$CDCl_3$).

Mixture of the dimers **2a–c**: IR ($CDCl_3$) 1060–1040 cm^{-1}; mass spectrum (70eV), *m/e* 452, 433, 404, 209. Anal. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.33; H, 4.42. Found: C, 73.9; H, 4.4.

Irradiation of 2-MeBTO (3). Direct irradiation of **3** (2.81 mM) at 313 nm and sensitized irradiation at 366 nm, with benzophenone as the sensitizer, were performed in 280 mL of dry benzene. After removal of the solvent, the products of the reaction were separated by chromatography on SiO_2, leading to 10% of 2-methylbenzothiophene (**3d**) and 50% of unreacted sulfoxide **3**.

Irradiation of 2-PhBTO (4). Irradiation of **4** (0.88 mM) in benzene solution (280 mL) was carried out for 4 h at 366 nm, with benzophenone as the sensitizer. Evaporation of the solvent under vacuum and chromatography on SiO_2 gave the corresponding sulfide **4d** (5%), the head to head dimer **4a** (or **4c**; 60%), and the unreacted sulfoxide **4**: IR (KBr) 1070, 1035, 1030 cm^{-1}; mass spectrum (70 eV), *m/e* 452, 338, 232, 216. Anal. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.33; H, 4.42. Found: C, 73.9; H, 4.5.

Irradiation of 2,3-Me$_2$BTO (5). Direct irradiation and sensitized irradiation of **5** (2.8 mM) in benzene solution (280 mL) were performed at 313 and at 366 nm, respectively. Removal of the solvent and chromatography on SiO_2 gave 180 mg (35%) of the corresponding sulfide **5d**.

Registry No. 1, 51500-43-7; **1a**, 67282-05-7; **1b**, 67336-09-8; **1c**, 67336-10-1; **2**, 70445-87-3; **2a**, 78592-67-3; **2b**, 78655-25-1; **2c**, 78655-26-2; **3**, 33945-86-7; **3a**, 78592-68-4; **3b**, 78655-27-3; **3c**, 78655-28-4; **3′a**, 78592-69-5; **3′b**, 78655-29-5; **3′c**, 78655-30-8; **4**, 70445-86-2; **4** HTH dimer, 78592-70-8; **5**, 70445-88-4; **6** (2-Cl), 57147-28-1; **6** (2-Br), 57147-27-0; **6** (3-Cl), 63724-95-8; **6** (3-Br), 57147-26-9; **7**, 78592-71-9; 8, 78592-72-0.

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[30] The measurements have been made in the Laboratoire des Composês Azotês Polyfonctionnels, Université Paul Sabatier, Toulouse (Professor A. Lattes and Dr. J. C. Micheau).

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Mannich Reaction Product of Dihydrocodeinone[1]

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The Mannich reaction with dihydrocodeinone (1) was previously reported to give the dimeric product 7,7′-methylenebis(dihydrocodeinone) (2). Investigation revealed that this structural assignment was incorrect. The product formed, dimer 5, [3-methoxy-17-methyl-4,5α-epoxy-6,7-didehydromorphinan[6,7-*e*]-3,4-dihydropyran-2-spiro-7′-(3′-methoxy-17′-methyl-4′,5′α-epoxymorphinan-6′-one)], results from a Diels–Alder 1,4-cycloaddition between two molecules of 7-methylenedihydrocodeinone (4).

Rapoport and Small[2] reported that the Mannich reaction with dihydrocodeinone (1) unexpectedly gave the dimeric product 7,7′-methylenebis(dihydrocodeinone) (2). The isolation of the intermediate Mannich base 3 or the corresponding eliminated 7-methylene compound 4 (see

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