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Effect of Through-Space Interaction on the Photolytic Desulfurization or Deselenization and Intramolecular Cyclization Reactions of 1,9-Disubstituted Dibenzochalcogenophenes

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1,9-Dithia and 1,9-diselena substituents in dibenzochalcogenophenes **1** are in close proximity within the van der Waals S−S and Se−Se contacts and hence have a strong through-space interaction. Photolysis of the compounds **1** with a 400 W high-pressure mercury lamp in benzene produces triphenyleno[4,5-*bcd*]chalcogenophenes **2** and tribenzo[*bc,e,hi*][2,7]dichalcogenaazulenes **3** in high yields, except for the dibenzofuran derivative, via photoexcitation, sequential desulfurization or deselenization, and intramolecular cyclization. In the reaction, 1,9-bis(phenylthio)dibenzofuran (**1e**) exhibits lower reactivity as compared with other dibenzothiophene and dibenzoselenophene derivatives. The X-ray crystallographic analysis of 1,9-bis(phenylseleno)dibenzoselenophene (**1a**), 1,9-bis(phenylseleno)dibenzothiophene (**1b**), and 1,9-bis(phenylthio)dibenzoselenophene (**1c**) demonstrated that their structures are distorted as is also that of 1,9-bis(phenylthio)dibenzothiophene (**1d**),[1] while dibenzofuran derivative **1e** was found to be a nearly planar molecule. The structure and reactivity relationship of compounds **1a**−**e** was examined in the photolytic reactions by comparing their interheteroatomic distances at the 1,9 positions and their oxidation potentials. Furthermore, compounds **1a**−**e** afforded the corresponding monosulfoxides and bis-sulfoxides on oxidation with *m*-chloroperbenzoic acid which were photolyzed readily to give also **2** and **3**.

Introduction

It is well known that the formation of dications and cation radicals via transannular interaction has often been observed between two or more heteroatoms that are arranged appropriately in one molecule.[2] The transannular σ-bond formation has been reported between the two heteroatoms such as a combination of N−N, S−S, and Se−Se atoms in the oxidation of diazabicyclo[3.3.3]nonane,[3a] 1,5-dithiacyclooctane,[3b] and 1,5-diselenacyclooctane;[3c] their diaza, dithia, and diselena dication salts are actually isolated, and their structures have been determined by X-ray crystallographic analysis (Figure 1).

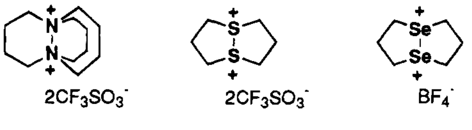
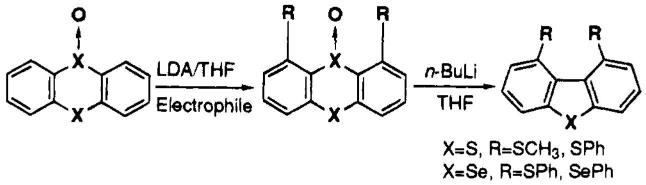


Figure 1.

Scheme 1



Recently, we have reported that 1,9-disubstituted dibenzochalcogenophenes (**1**) bearing two sulfur or selenium atoms in close proximity were prepared by the ligand coupling reactions of corresponding 4,6-disubstituted chalcogenanthrene 5-oxides with organolithium reagents (Scheme 1).[4] The X-ray crystallographic analysis of 1,9-bis(phenylthio)dibenzothiophene (**1d**) revealed that the distance between the two sulfur atoms located at 1,9 positions is 3.012 Å which is substantially shorter than the van der Waals contact of sulfur atoms (3.70 Å).[1,5] The compound **1d** was found to generate the corresponding dithia dication on dissolution in concentrated sulfuric acid-d_2 which was identified by measurement of ^{1}H-NMR spectrum.[1] Similarly, 1,9-bis(phenylseleno)dibenzoselenophene (**1a**) and 1,9-bis(phenylthio)dibenzoselenophene (**1c**) produced the corresponding diselena and dithia dications on treatment with concentrated sulfuric acid.[5] In the course of our studies with respect to the through-space interaction of compounds **1**, we have succeeded in the first preparation of dibenzo[*bc,fg*][1,4]dithiapentalene by demethylation and desulfurization reactions from photolysis and thermolysis of 1,9-bis(methylthio)dibenzothiophene.[6] On the other hand, photolysis of 1,9-bis(phenylthio)dibenzothiophene (**1d**) was found to proceed via concomitant desulfurization and ring contraction reactions to give triphenyleno[4,5-*bcd*]thiophene (**2b**) and tribenzo[*bc,e,hi*][2,7]dithiaazulene (**3d**).[7] Compound **2b**

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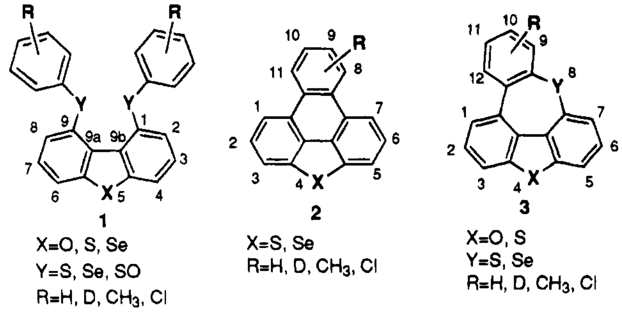


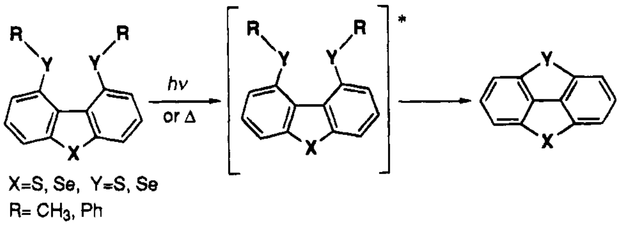
1
X=O, S, Se
Y=S, Se, SO
R=H, D, CH$_3$, Cl

2
X=S, Se
R=H, D, CH$_3$, Cl

3
X=O, S
Y=S, Se
R=H, D, CH$_3$, Cl

Figure 2.

Scheme 2



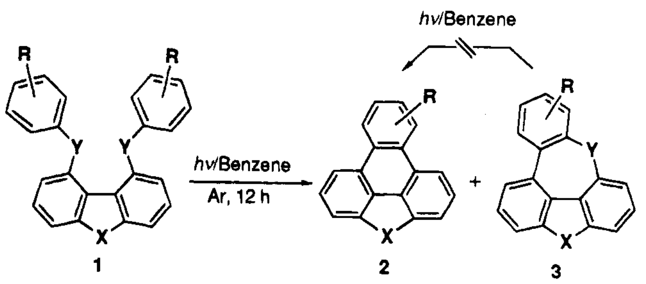
X=S, Se, Y=S, Se
R= CH$_3$, Ph

was prepared by conventional procedures from expensive triphenylene as a starting material.[8] In this paper we present that the photolysis of 1,9-bis(arylthio)- or 1,9-bis(arylseleno)dibenzochalcogenophenes **1** proceeds via desulfurization or deselenization and ring contraction reactions to give triphenyleno[4,5-*bcd*]chalcogenophenes **2** and tribenzo[*bc,e,hi*][2,7]dichalcogenaazulenes **3** as shown in Figure 2. The structure and reactivity relationship in the photolysis of compounds **1a**–**e** is also reported on the basis of the comparison of the structures by X-ray crystallographic analysis and of the measurement of their oxidation potentials. Furthermore, the photolytic reactions of the monosulfoxides and bis-sulfoxides which can be obtained by oxidation of **1c**–**e** on treatment with *m*-chloroperbenzoic acid (*m*CPBA) are also reported.

Results and Discussion

Photolysis of 1,9-Disubstituted Dibenzochalcogenophenes 1. Recently, we reported the preparation of a new type of dibenzo[*bc,fg*][1,4]dichalcogenapentalene derivatives by the photolysis and thermolysis of 1,9-bis(methylthio)dibenzothiophene and 1,9-bis(phenylthio)- or 1,9-bis(phenylseleno)dibenzoselenophenes (Scheme 2). The formation of these unexpected thia or selenapentalene derivatives is attributed to the activation of the dibenzochalcogenophene derivatives via the through-space interaction between the two sulfur or selenium atoms at 1,9 positions providing the feasibility of the S–C or Se–C bond fission. In order to accumulate data on the activation of the molecules and clarify the effects of through-space interaction worked between the two heteroatoms on the reactions of **1** involving bond scission, photolysis of compounds **1** was carried out with a 400 W high-pressure mercury lamp in benzene under argon for 12 h. In the case of photolysis of the compound **1d**, the desulfurized and cyclized products, triphenyleno[4,5-*bcd*]thiophene (**2b**) and tribenzo[*bc,e,hi*][2,7]dithiaazulene (**3d**), were obtained in 72 and 26% yields, respectively (Scheme 3). Similarly, on photolysis of selenium analogs **1a** and **1c**, deselenization or desulfurization and cyclization reactions proceeded simultaneously to give triphenyleno[4,5-*bcd*]selenophene (**2a**) in 81 and 77% yields, respectively. On the other hand, both 1,9-bis(phenylseleno)dibenzothiophene (**1b**) and 1,9-bis(phenylthio)dibenzofuran (**1e**) were prepared from 4,6-bis(phenylseleno)thianthrene 5-oxide and 1,9-bis(phenylthio)phenoxathiin 10-oxide in moderate yields not by ligand coupling reaction with alkyl- or aryllithium but by treatment with Grignard reagent and CuCl$_2$, and the photolysis of **1b** and **1e** was performed with a high-pressure mercury lamp.[4] Photolysis of **1b** proceeded similarly as **1a**, **1c**, and **1d** to give **2b** and tribenzo[*bc,e,hi*][2,7]thiaselenaazulene (**3b**) in 75 and 6% yields together with diphenyl diselenide. On the identical photolysis of **1e** for 12 h, the starting **1e** was recovered in 79% yield together with 1-(phenylthio)dibenzofuran (12%) and a trace amount of tribenzo[*bc,e,hi*][2,7]oxathiaazulene (**3e**). Though the reaction of **1e** was continued for 60 h, 1-(phenylthio)dibenzofuran (33%) and **3e** (12%) were obtained together with the starting **1e** (54%). These results are summarized in Table 1.

Scheme 3



1
X=O, S, Se
Y=S, Se
R=H, D, CH$_3$, Cl

2
X=S, Se
R=H, D, CH$_3$, Cl
54-81%

3
X=O, S
Y=S, Se
R=H, D, CH$_3$, Cl
11-30%

The low photochemical reactivity of dibenzofuran **1e** may be attributed to the lack of through-space interaction between the 1,9-dithia substituents; this is in marked contrast with the strong interaction between the two substituents of **1a**–**d**. In fact, the compounds **1a**, **1c**, and **1d** were found to generate readily the stable dithia or diselena dications on dissolution in concentrated sulfuric acid-d_2 by measurement of their ^{1}H and ^{77}Se-NMR spectra, and the dithia or diselena dications of **1a**, **1c** and **1d** were treated with water to give 1-(phenylseleninyl)-9-(phenylseleno)dibenzoselenophene (**4a**), 1-(phenylsulfinyl)-9-(phenylthio)dibenzoselenophene (**4c**), and 1-(phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**4d**) in 81, 75, and 87% yields, respectively.[1,5] On the other hand, dibenzofuran derivative (**1e**) was found to be very unstable in the concentrated sulfuric acid, and the corresponding dithia dication was not observed at all in the ^{1}H-NMR spectrum. Compound **1e** did not give 1-(phenylsulfinyl)-9-(phenylthio)dibenzofuran (**4e**) but a complex mixture of the product after treatment with concentrated sulfuric acid and water. This different reactivity of **1e** as compared to the dibenzothiophene or dibenzoselenophene derivatives **1a**–**d** may be rationally explained to be due to the strength of the interaction between the two substituents. Hence it is worthy of examination for the structures of compounds **1a**–**e**, since the structure of **1a**–**e** influenced their reactivity. Both unsubstituted dibenzothiophene and dibenzoselenophene have completely planar structures but the dibenzothiophene ring of the compound **1d** has been disclosed by X-ray analysis

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Table 1. Photolysis of Compounds 1 in Benzene

	X	Y	R	product	yield (%)	product	yield (%)
1a	Se	Se	H	**2a**	81	**3a**	0
1b	S	Se	H	**2b**	75	**3b**	6
1c	Se	S	H	**2a**	77	**3c**	0
1d	S	S	H	**2b**	72	**3d**	26
1e	O	S	H	**2e**	0	**3e**	trace
1f	S	S	*o*-D[a]	**2f** (8-D)	75[b]	**3f** (9-D)	22[c]
1g	Se	S	*o*-D[a]	**2g** (8-D)	62[d]	**3g** (9-D)	0
1h	S	S	*o*-CH_3	**2h** (8-CH_3)	69	**3h** (9-CH_3)	24
1i	S	S	*p*-CH_3	**2i** (9-CH_3)	67	**3i** (11-CH_3)	30
1j	S	S	*m*-CH_3	**2h+2i**	54[e]	*f*	–
1k	S	S	*p*-Cl	**2k** (9-Cl)	81	**3k** (11-Cl)	11
1l	S	S	2,5-Xyl	**2l** (8,11-CH_3)	61	**3l** (9,12-CH_3)	32

[a] Deuterium contents (D) are 99% in both the phenylthio groups. [b] D = 45%. [c] D = 46%. [d] D = 52%. [e] **2f**:**2g** = 1:1. [f] Complex mixture.

Table 2. Interheteroatom Distances (Å), Partial Torsional Angles (deg), Oxidation Potentials (V), and UV Spectra of 1,9-Disubstituted Dibenzochalcogenophenes[a]

	X	Y	distances (Å) Y–Y	angles (deg) C1–C9b–C9a–C9	E_p (V)	UV, λ_{max} (nm)
1a	Se	Se	3.072	19.5	0.54	307 (sh), 338, 357, 374
1b	S	Se	3.098	19.9	0.63	308 (sh), 350, 365
1c	Se	S	2.973	22.6	0.85	306 (sh), 361, 377
1d	S	S	3.012	20.7	0.86	306 (sh), 354, 369
1e	O	S	3.190	5.3	1.02	289, 298, 327, 338 (sh)
4d	S	S,SO	3.016	19.1	–	306 (sh), 352, 366
4e	O	S,SO	–	–	–	301, 338 (sh)
5e	O	SO	–	–	–	306
5e′	O	SO	3.093	2.3	–	308

[a] The oxidation potentials were determined by the cyclic voltammetry in CH_3CN using a Pt electrode vs Ag/0.01 M $AgNO_3$ as a reference electrode. The UV spectra were measured in CH_2Cl_2 as a solvent.

to have a distorted conformation from the planar form.[1,9] Therefore, X-ray crystallographic analysis of the compounds **1a–c** and **1e** was performed and their structures as determined were compared with that of the compound **1d**.[10] The dibenzoselenophene ring of **1a** is considerably distorted from the normal planar form due to the steric repulsion between the two phenylseleno substituents attached at the 1,9 positions, and the two phenyl rings are located in an anti orientation. The structures of compounds **1b–d** were found by X-ray crystallographic analysis to be roughly identical with that of **1a**. On the other hand, the structure of **1e** is markedly contrasted with that of **1a–d**. Apparently, the dibenzofuran ring of **1e** is a nearly planar form as compared with sulfur or selenium analogs **1a–d**. The X-ray structural data of compounds **1a–e**, namely, the distances between the two chalcogen atoms at 1,9 positions, and the torsional angles at C1–C9b–C9a–C9 positions are listed in Table 2 for comparison.[4] The distances between the two sulfur atoms and two selenium atoms of the compounds **1a–d** are within the van der Waals contact (S: 3.70 Å, Se: 4.00 Å).[5] The S-S distance of **1e** is markedly longer than those of **1c** and **1d** as shown in Table 2. This may be due to the shorter distance of the O–C bond of the dibenzofuran ring (**1e**: 1.378 Å) than that of the S–C and Se–C bonds of dibenzothiophene (**1d**: 1.746 Å) and dibenzoselenophene rings (**1c**: 1.897 Å). These results suggest that dibenzoselenophene and dibenzothiophene derivatives are more distorted as compared with the dibenzofuran derivative and hence the through-space interaction of the two substituents strongly influences these photolytic reactions and progresses readily the desulfurization and deselenization reactions. Though it was reported that a photolytic sulfur extrusion reaction was found to occur from dialkyl sulfides such as dibenzyl sulfide and 7-thiabicyclo[2.2.1]heptane in the presence of trialkyl phosphite, our reaction is a first example of the photolytic desulfurization or deselenization reactions, free from trialkyl phosphite, which are progressed by repulsion and through-space interaction between the two chalcogen atoms.[11,12]

It was reported that the compounds bearing two substituents in close proximity have electric repulsion between the substituents and the strain of the molecules is relaxed by removing the electric replusion. For example, Staab et al. have reported that the pK_a values of several proton sponge compounds such as 4,5-bis(dimethylamino)fluorene, 1,10-bis(dimethylamino)phenanthrene, and 1,9-bis(dimethylamino)dibenzothiophene are related to their structures, and the degree of the repulsive forces worked between the two nitrogen lone electron pairs.[13] On the other hand, the S–S distance at the 1,9 positions and the torsional angle at C1–C9b–C9a–C9 of a sulfonium salt of 1,9-bis(methylthio)dibenzothiophene were found to be 2.85 Å and 15.5° by X-ray crystallographic analysis, suggesting that the lone pair repulsion between the two sulfur atoms should be decreased by oxidation of one sulfur atom.[14]

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(10) The X-ray crystallographic analysis of compounds **1a**, **1c**, **1d**, and **4d** were carried out by Prof. F. Iwasaki. The authors have deposited atomic coordinates for **1a–e**, **4b,d**, and **5e′** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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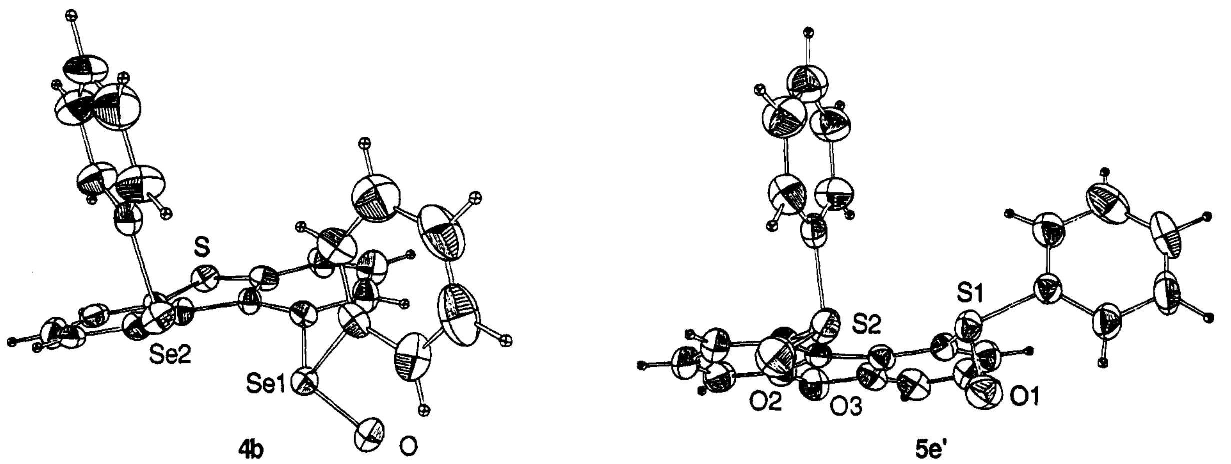


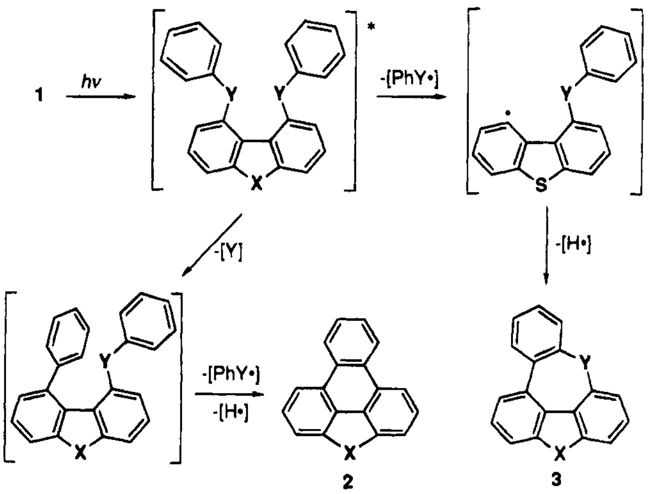
4b **5e'**

Figure 3. ORTEP drawings of **4b** and **5e'**.

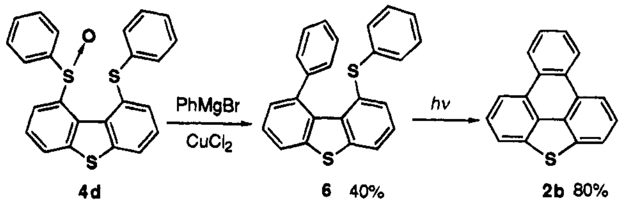
If the steric and electronic repulsions between the two chalcogen atoms in **1a–e** play important roles particularly for n-π^* excitation in these photocyclization reactions, feasibility for the photocyclization reactions can be correlated with their oxidation potentials. Hence, the oxidation potentials of **1a–e** were measured with a cyclic voltammetry in acetonitrile at 20 °C, using a Pt electrode, Ag/0.01 M $AgNO_3$ as a reference electrode (electrolyte: 0.1 M $NaClO_4$; scan rate: 200 mV/s). As shown in Table 2, compounds **1a–d** have lower oxidation potentials and absorb longer wavelength light in UV spectra than dibenzofuran derivative **1e**. These results reveal that the distorsional forces of the dibenzothiophene or dibenzoselenophene rings should be stronger as compared with that of the dibenzofuran ring due to steric repulsion between the two chalcogen atoms attached at the 1,9 positions. Furthermore, the photolytic reactions of 2,8-bis(phenylthio)dibenzothiophene (E_p = 1.09 V, vs Ag/$AgNO_3$) and 1-(phenylthio)dibenzothiophene (E_p = 1.12 V, vs Ag/$AgNO_3$) did not proceed under similar reaction condition, supporting the inference that a proximate effect between the two arylthio or arylseleno substituents should be essential for initiation of these cyclization reactions.[15]

As shown in Table 2, the distance between the two sulfur atoms at the 1,9 positions and the torsional angle at C1–C9b–C9a–C9 positions are 3.016 Å and 19.1° in **4d**, and the formation of dithia dication derived from **4d** in concentrated sulfuric acid was confirmed by ^{1}H-NMR, revealing that the sulfenyl and sulfinyl groups at the 1,9-positions in the compound **4d** are in close proximity.[4] Furthermore, Se–Se spin coupling has been observed in the ^{77}Se-NMR spectra of compound **4a** and 1-(phenylseleninyl)-9-(phenylseleno)dibenzothiophene (**4b**) as shown in the following coupling constants: **4a**: 372.0 Hz; **4b**: 367.5 Hz, suggesting that the two selenium atoms at the 1,9 positions in **4a** and **4b** have an electronic through-space interaction. The Se–Se distance at the 1,9 positions and the torsional angle at the C1–C9b–C9a–C9 positions of **4b** were determined by X-ray crystallographic analysis as 3.088 Å and 17.4° (Figure 3).

Scheme 4



Scheme 5



When the dithiaazulene **3d** was photolyzed under similar conditions as described above, neither desulfurization nor ring contraction reaction was observed and the starting **3d** was recovered quantitatively, suggesting that **2b** was obtained directly from the photolysis of **1d** and not via **3d** (Scheme 3). Therefore, the compounds **2** and **3** should be produced via different pathways. Since the formation of diphenyl disulfide and elemental sulfur was detected by mass spectrometry in the photolysis of **1d**, and the desulfurization reaction of **3d** was not observed, we predicted that concomitant desulfurization and phenylthio radical extrusion reactions from the excited **1d** initially proceed via the photolysis of **1d**, and a subsequent cyclization reaction gave the compounds **2b** and **3d** (Scheme 4). In fact, 1-(phenylthio)-9-phenyldibenzothiophene (**6**) which was prepared from compound **4d** on treatment with PhMgBr and $CuCl_2$ was photolyzed with a high-pressure mercury lamp for 12 h to produce **2b** in 80% yield (Scheme 5).

In order to clarify whether the origin of the benzene ring condensed to the products comes from one of the 1,9-disubstituted phenyl groups or the benzene used as the

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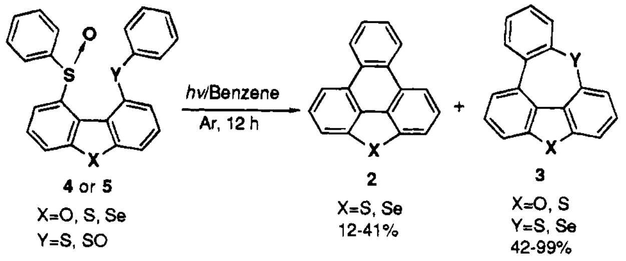
[14] Kimura, T.; Nakayama, H.; Furukawa, N. *Chem. Lett.* **1994**, 27.

[15] 2,8-Bis(phenylthio)dibenzothiophene (quantitatively) and 1-(phenylthio)dibenzothiophene (90%) were recovered in the photolytic condition.

Scheme 6



solvent, photolysis of **1c** in *p*-xylene and ortho deuteriated compounds **1f,g** in benzene was carried out. When **1c** was photolyzed in *p*-xylene, no *p*-xylene incorporation was observed in the product. Furthermore, 1,9-bis(*o*-monodeuteriated phenylthio)dibenzothiophene (**1f**) (D content: 99%) was photolyzed similarly as described above to give 8-deuteriated triphenylenothiophene (**2f**) (75%, D content: 45%) and 9-deuteriated tribenzodithiaazulene (**3f**) (22%, D content: 46%) as shown in Table 1. On the photolysis of selenium analog **1g**, compound **2g** was obtained in 62% yield (D content: 52%). These results reveal that in the photolytic reaction of compounds **1**, ca. 50% deuterium labeled at the ortho positions of compounds **1** remains in the products. Since no deuterium scramble was observed in the present reaction conditions, the photolysis of compounds **1** can be used for general preparation of substituted **2** and **3**. For example, the photolysis of 1,9-bis(*o*-tolylthio)dibenzothiophene (**1h**) produced 8-methyltriphenylenothiophene (**2h**) and 9-methyltribenzodithiaazulene (**3h**) in 69 and 24% yields, respectively, while on the photolysis of para-substituted arylthio derivatives **1i** and **1k**, 9-methyl- and 9-chlorotriphenylenothiophene (**2i** and **2k**), and 10-methyl- and 10-chlorotribenzodithiaazulene (**3i** and **3k**) were obtained (**2i**: 67%, **2k**: 81% and **3i**: 30%, **3k**: 11%).[7] Furthermore, 8,11-dimethyl derivatives **2l** and **3l** were also obtained in 61 and 32% yields, respectively, on the photolysis of 1,9-bis(2,5-xylylthio)dibenzothiophene (**1l**) together with di(2,5-xylyl) disulfide (64%). These results are summarized in Table 1.

Photolysis of Sulfinyl Derivatives. In order to compare the photolytic reactivity by changing the oxidation state of the sulfur atom at the 1,9-disubstituents, compounds **1** were converted to the corresponding monosulfoxides **4** and bis-sulfoxides **5** and these compounds were subjected to photolysis in a similar manner as described above (Scheme 6). These oxidized compounds **4** and **5** were found to be rather unstable compared with the corresponding phenylthio derivatives **1** and gradually decomposed at room temperature without shielding. Photolysis of **4d** was carried out by the identical procedure as described above to give **2b** and **3d** in 41 and 57% yields, while on photolysis of 1,9-bis(phenylsulfinyl)dibenzothiophene (**5d**) and its diastereoisomer **5d′** under identical condition, compounds **2b** and **3d** were obtained. Interestingly, though only a trace amount of **3e** was obtained by photolysis of **1e**, 1-(phenylsulfinyl)-9-(phenylthio)dibenzofuran (**4e**) was found to undergo photochemical decomposition to give **3e** in 99% yield. Furthermore, on irradiation of both 1,9-bis(phenylsulfinyl)dibenzofuran (**5e**) and its diastereoisomer **5e′**, compound **3e** was also obtained in 91 and 68% yields, respectively. These results are summarized in Table 3. The structural analysis of one diastereomer of dibenzofuran derivative **5e′** was carried out by X-ray crystallographic analysis and the configuration was determined to be the meso form (*R,S* and *S,R* configurations), and hence the other **5e** should be a racemic mixture of *S,S* and *R,R* configurations (Figure 3). It was revealed by the X-ray crystallographic analysis that the S−S distance of **5e′** is 3.093 Å and the S2−O1 distance is 3.343 Å (van der Waals contact: S−O: 3.25 Å). Furthermore, the meso isomer **5e′** was found to be rather unstable compared with **5e**, suggesting that the repulsion of two oxygen atoms or two phenyl groups in the compound **5e′** should be stronger than those in compound **5e**.

Table 3. Photolysis of Compounds 4 and 5 in Benzene

	X	Y	Y′	product	yield (%)	product	yield (%)
4c	Se	S	SO	**2a**	91	**3a**	0
4d	S	S	SO	**2b**	41	**3d**	57
4e	O	S	SO	**2e**	0	**3e**	95
5d	S	SO	SO	**2b**	31	**3d**	42
5d′	S	SO	SO	**2b**	12	**3d**	50
5e	O	SO	SO	**2e**	0	**3e**	99
5e′	O	SO	SO	**2e**	0	**3e**	68

Table 4. Oxidation Potentials (E_p)[a]

	E_p (V)		E_p (V)
2a	0.99	**2i**	1.03
2b	1.11	**2k**	1.15
2h	1.08	**2l**	1.23

[a] The cyclic voltammograms for the products were irreversible and their peak potentials were determined by the cyclic voltammetry in CH_3CN using a Pt electrode; E_p vs Ag/0.01 M $AgNO_3$; scan rate: 200 mV/s.

Electrochemical Properties of Triphenyleno[4,5-*bcd*]thiophenes. Recently, we reported that dibenzo[*bc,fg*][1,4]dithiapentalene has a completely planar form and has a comparable similar physical property to polythiophene derivatives. Hence the oxidation potentials of **2a−l** obtained were determined by cyclic voltammetry as described above and their values are shown in Table 4. Interestingly, the intensities of the electric current of compounds **2b,h,i,k,l** increase gradually with repeated scannings of the electric potential between 0 to 1.20 V, suggesting that new polythiophene derivatives are produced on the electrode surface (Figure 4).

Conclusion

Compounds **1** were photolyzed by a 400 W high-pressure mercury lamp in benzene to produce **2** and **3** and these reactions proceeded without trialkyl phosphite via photoexitation, desulfurization or deselenization reaction, and cyclization reaction. It was revealed that the photolytic reactivity of compounds **1** related to their structure and electrochemical properties. Furthermore, photolysis of the corresponding sulfinyl compounds also proceeded to give the cyclization products.

Experimental Section

IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. NMR spectra were measured with $CDCl_3$ on a Hitachi R-600, a JEOL JNM-EX270, a Bruker ARX-400, and a Bruker AM-500 spectrometer. Mass spectra were obtained with a JEOL JMX SX102 mass spectrometer. X-ray data collection was performed on a Enraf-Nonius CAD4 computer controlled κ axis diffractometer (23 ± 1 °C), and calculations for structure solution and refinement were performed on a VAX computer using SDP/VAX. For oxidation potential, a Hokuto Denko Co. Model HB-104 apparatus was used.

1,9-Bis(arylthio)dibenzothiophene (1d, 1f, and 1h−k). These compounds were prepared by a ligand coupling reaction of corresponding 4,6-bis(arylthio)thianthrene 5-oxide.[1]

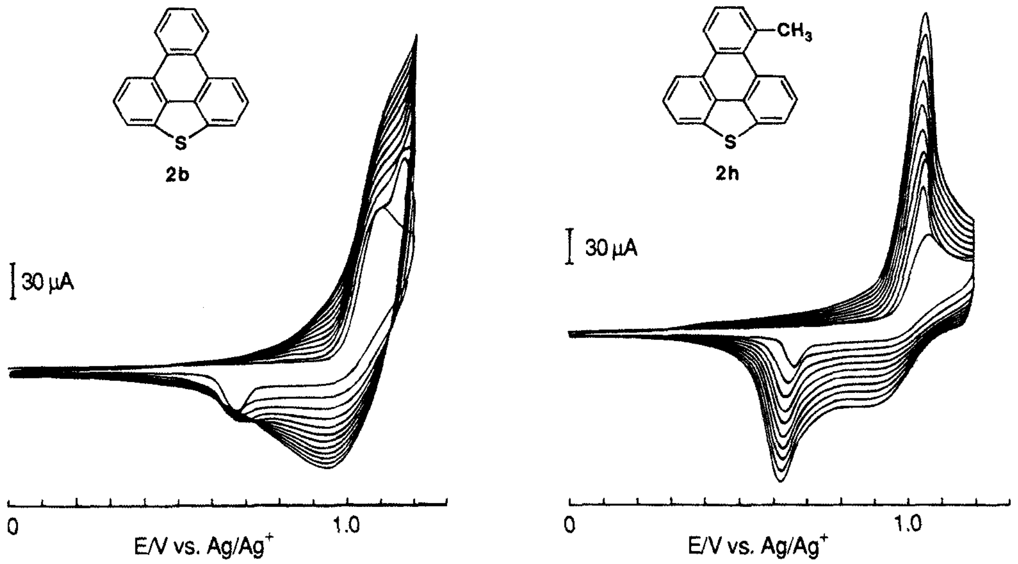


Figure 4. Cyclic voltammograms of **2b** and **2h**.

1,9-Bis(phenylseleno)dibenzoselenophene (1a) and 1,9-Bis(phenylthio)dibenzoselenophene (1c). These compounds were prepared from corresponding 4,6-disubstituted selenanthrene 5-oxide.[6c] The crystal data for **1a**: monoclinic, space group $P2_1/n$, a = 18.094(2) Å, b = 8.1571(6) Å, c = 13.723(1) Å, β = 96.505(0)°, V = 2012.4(3) Å^3, z = 4, ϱ = 1.795 gcm^{-3}, μ (Mo Kα) = 5.461 mm^{-1}, R = 0.0664 (R_w = 0.0655); the crystal data for **1c**: monoclinic, space group $P2_1/n$, a = 17.899(3) Å, b = 8.086(2) Å, c = 13.631(2) Å, β = 96.33(1)°, V = 1960.8(7) Å^3, z = 4, ϱ = 1.513 gm^{-3}, μ (Mo Kα) = 2.100 mm^{-1}, R = 0.0457 (R_w = 0.0700).

1,9-Bis(ortho-monodeuteriated phenylthio)dibenzoselenophene (1g). The compound **1g** was prepared by the method similar to the synthesis of **1c** using 2,2′-bis-deuteriated diphenyl disulfide.

4,6-Bis(phenylseleno)thianthrene 5-oxide: mp 202–203 °C; ^{1}H-NMR (500 MHz) δ 7.19 (dd, J = 7.9 Hz, 1.1 Hz, 2H), 7.24 (t, J = 7.9 Hz, 2H), 7.32–7.38 (m, 6H), 7.57–7.61 (m, 4H), 7.60 (dd, J = 7.9 Hz, 1.1 Hz, 2H); MS (m/z) 544 (M$^+$). Anal. Calcd for $C_{24}H_{16}OS_2Se_2$: C, 53.14; H, 2.97%. Found: C, 52.89; H, 3.04%.

1,9-Bis(phenylthio)phenoxathiin 10-Oxide. Phenoxathiin 10-oxide (864 mg, 4.0 mmol) dissolved in THF (40 mL) was lithiated with 0.109 M LDA (80 mL, 8.72 mmol) at −78 °C for 2 h under N_2 atmosphere.[16] Then diphenyl disulfide (4.26 g, 19.5 mmol) was added. After stirring for 3 h at −78 °C and for 12 h at −20 °C, the solution was treated with H_2O (1.5 mL). The solvent was evaporated and the residue was extracted with CH_2Cl_2 (3 × 100 mL) and then purified by column chromatography (silica gel; CH_2Cl_2:ethyl acetate = 25:1) to give 1,9-bis(phenylthio)phenoxathiin 10-oxide and 1-(phenylthio)phenoxathiin 10-oxide in 55% (944 mg) and 16% (289 mg) yields, respectively. 1,9-Bis(phenylthio)phenoxathiin 10-oxide: mp 182–183 °C; ^{1}H-NMR δ 7.18–7.53 (m, 16H); IR (KBr) 1035 cm^{-1} (SO); MS (m/z) 416 (M$^+$ − 16). Anal. Calcd for $C_{24}H_{16}O_2S_3$: C, 66.64; H, 3.73%. Found: C, 66.74; H, 3.71%. 1-(Phenylthio)phenoxathiin 10-oxide: mp 133–134 °C; ^{1}H-NMR δ 7.14–7.85 (m, 12H); IR (KBr) 1042 cm^{-1} (SO); MS (m/z) 308 (M$^+$ − 16). Anal. Calcd for $C_{18}H_{12}O_2S_2$: C, 66.64; H, 3.73%. Found: C, 66.29; H, 3.73%.

4,6-Bis(2,5-xylylthio)thianthrene 5-Oxide. Thianthrene 5-oxide (2.32 g, 10 mmol) dissolved in THF (100 mL) was lithiated with 0.5 M LDA (50 mL, 25 mmol) for 3 h at −78 °C. To this solution was added bis(2,5-xylylthio) disulfide (6.9 g, 25 mmol) and stirred for 12 h at −20 °C. After treatment with water and usual workup, the reaction mixture was purified with column chromatography (silica gel, CH_2Cl_2) and with preparative HPLC to give 4,6-bis(2,5-xylylthio)thianthrene 5-oxide (2.57 g, 51%): ^{1}H-NMR (270 MHz) δ 2.26 (s, 6H), 2.39 (s, 6H), 6.86 (dd, J = 7.8 Hz, 1.2 Hz, 2H), 7.09–7.23 (m, 6H), 7.24 (t, J = 7.8 Hz, 2H), 7.54 (dd, J = 7.8 Hz, 1.2 Hz, 2H); HRMS (m/z) calcd for $C_{28}H_{24}OS_4$: 504.0710, found 504.0660 (M$^+$).

1,9-Bis(phenylseleno)dibenzothiophene (1b). To a THF (60 mL) solution of 1,9-bis(phenylseleno)thianthrene 5-oxide (485 mg, 0.9 mmol) was added 0.5 M PhMgBr/THF (20 ml, 10 mmol) dropwise. The solution was stirred for 2 h, anhydrous $CuCl_2$ (1.34 g, 10 mmol) was added, and then the solution was stirred for 12 h. The solution was treated with water. After usual workup, the reaction mixture was purified by column chromatography (silica gel; hexane:CCl_4 = 3:1) to give 1,9-bis(phenylseleno)dibenzothiophene (322 mg, 73%): mp 176–176.5 °C; ^{1}H-NMR (500 MHz) δ 6.99–7.10 (m, 10H), 7.34 (t, J = 7.7 Hz, 2H), 7.74 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 7.7 Hz, 2H); ^{13}C-NMR (125 MHz) δ 122.1, 126.7, 127.6, 127.7, 128.9, 131.4, 134.3, 137.1, 138.2, 140.3; ^{77}Se-NMR (76 MHz) 422.1; MS (m/z) 496 (M$^+$). Anal. Calcd for $C_{24}H_{16}SSe_2$: C, 58.31; H, 3.26%. Found: C, 58.10; H, 3.18%; the crystal data; monoclinic, space group $P2_1/n$, a = 13.618(1) Å, b = 8.112(0) Å, c = 18.063(1) Å, β = 96.40(1)°, V = 1983.0 Å^3, z = 4, ϱ = 1.66 gcm^{-3}, μ (Mo Kα) = 38.0 cm^{-1}, R = 0.029 (R_w = 0.030).

1,9-Bis(phenylthio)dibenzofuran (1e). To a THF (50 mL) solution of 1,9-bis(phenylthio)phenoxathiin 10-oxide (216 mg, 0.500 mmol) was added 0.25 M EtMgBr/THF (20 mL, 5.0 mmol) dropwise. The solution was stirred for 3 h, anhydrous $CuCl_2$ (1.01 g, 7.50 mmol) was added, and then the solution was stirred for 6 h. The solution was treated with aqueous NH_4Cl solution (50 mL). After usual workup, the reaction mixture was purified by column chromatography (silica gel; CCl_4) to give 1,9-bis(phenylthio)dibenzofuran (108 mg, 56%): mp 123–124 °C; ^{1}H-NMR (270 MHz) δ 7.18 (dd, J = 8.2 Hz, 0.8 Hz, 2H), 7.24–7.29 (m, 10H), 7.33 (t, J = 8.2 Hz, 2H), 7.46 (dd, J = 8.2 Hz, 0.8 Hz, 2H); MS (m/z) 384 (M$^+$). Anal. Calcd for $C_{24}H_{16}OS_2$: C, 74.97; H, 4.19%. Found: C, 74.78; H, 4.36%; the crystal data; monoclinic, space group $P2_1/n$, a = 10.142(3) Å, b = 12.611(2) Å, c = 14.592(4) Å, β = 92.55(1)°, V = 1864.4 Å^3, z = 4, ϱ = 1.37 gcm^{-3}, μ = 2.8 cm^{-1}, R = 0.034 (R_w = 0.033).

1,9-Bis(2,5-xylylthio)dibenzothiophene (1l). 4,6-Bis(2,5-xylylthio)thianthrene 5-oxide (2.3 g, 4.6 mmol) dissolved in THF (200 mL) was treated with 1.60 M n-butyllithium (12.5 mL, 20 mmol) at −78 °C. After usual workup and purification by column chromatography (silica gel, CH_2Cl_2) and by preparative HPLC, **1l** was obtained (797 mg, 38%): mp 138–140 °C; ^{1}H-NMR (500 MHz) δ 1.97 (s, 3H), 2.16 (s, 3H), 6.89 (d, J = 7.8 Hz, 2H), 6.94 (s, 2H), 6.96 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.33 (dd, J = 7.4 Hz, 1.2 Hz, 2H), 7.68 (dd, J = 7.4 Hz, 1.2 Hz, 2H); MS (m/z) 456 (M$^+$). Anal. Calcd for $C_{28}H_{24}S_3$: C, 73.64; H, 5.30%. Found: C, 73.56; H, 5.25%.

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[16] Shirley, D. A.; Lehto, E. A. *J. Am. Chem. Soc.* **1955**, *77*, 1841. Gilman; H.; Eidt, S. H. *Ibid.* **1956**, *78*, 3848.

Oxidation of 1,9-Bis(phenylthio)dibenzothiophene (1d). To a solution of **1d** (1.454 g, 3.635 mmol) in 150 mL CH_2Cl_2 was added *m*-CPBA (899 mg, 3.647 mmol, assay ≥ 70%) in 100 mL CH_2Cl_2 for 2h at −78 °C. The solution was stirred for 12 h at −20 °C and treated with NH_3 gas. After filtration, the solution was evaporated and the residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:ethyl acetate = 5:1) to give **4d** (1.113 mg, 74%),[1] **5d** (84 mg, 5%), **5d′** (87 mg, 6%). **5d**: mp 300 °C dec; ^{1}H-NMR (500 MHz) δ 7.45−7.46 (m, 6H), 7.68 (t, J = 7.8 Hz, 2H), 7.73−7.75 (m, 4H), 7.87 (d, J = 7.8 Hz, 2H), 8.05 (d J = 7.8 Hz, 2H); IR (KBr) 1035 cm^{-1} (SO). Anal. Calcd for $C_{24}H_{16}O_2S_3$: C, 66.64; H, 3.73%. Found: C, 66.18; H, 3.57%. **5d′**: mp 265−266 °C; ^{1}H-NMR (500 MHz) δ 7 33−7.36 (m, 6H), 7.47−7.49 (m, 4H), 7.61 (t, J = 7.8 Hz, 2H), 7.89 (dd, J = 7.8 Hz, 0.8 Hz, 2H), 7.99 (dd, J = 7.8 Hz, 0.8 Hz, 2H); IR (KBr) 1038 cm^{-1} (SO). Anal. Calcd for $C_{24}H_{16}O_2S_3$: C, 66.64; H, 3.73%. Found: C, 66.62; H, 3.65%.

Oxidation of 1,9-Bis(phenylseleno)dibenzoselenophene (1a). **1a** (152 mg, 0.281 mmol) was dissolved in concd H_2SO_4 (3 mL) and the solution was stirred for 24 h. Then the solution was poured into ice−water and extracted with CH_2Cl_2 (5 × 40 mL). The extract was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:ethyl acetate = 6:1) to give **4a** (118 mg, 75%). **4a**: mp 184 °C dec; ^{1}H-NMR (270 MHz) δ 6.85−6.91 (m, 2H), 7.08−7.15 (m, 3H), 7.38 (t, J = 7.8 Hz, 1H), 7.39−7.46 (m, 3H), 7.50 (t, J = 7.8 Hz, 1H), 7.78 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.81 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.82−7.88 (m, 2H), 7.95 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.96 (dd, J = 7.8 Hz, 1.1 Hz, 1H); ^{77}Se-NMR (51 MHz) δ 420.7, 482.4, 894.1; IR (KBr) 812 cm^{-1} (SeO); MS (m/z) 558 (M$^+$); HRMS (m/z) calcd for $C_{24}H_{16}O^{80}Se_2{}^{78}Se$ 557.8714, found 557.8673 (M$^+$). Anal. Calcd for $C_{24}H_{16}OSe_3$: C, 51.73; H, 2.89%. Found: C, 51.07; H, 2.97%.

Oxidation of 1,9-Bis(phenylthio)dibenzoselenophene (1c). **1c** (11 mg, 0.025 mmol) was dissolved in concd H_2SO_4 (3 mL) and the solution was stirred for 24 h. Then the solution was poured into ice−water and extracted with CH_2Cl_2 (3 × 40 mL). The extraction was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:ethyl acetate = 6:1) to give **4c** (9 mg, 79%). **4c**: mp 238 °C dec; ^{1}H-NMR (270 MHz) δ 6.71−6.75 (m, 2H), 7.05−7.10 (m, 3H), 7.34−7.41 (m, 3H), 7.42 (t, J = 7.8 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.64−7.68 (m, 2H), 7.68 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.77 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.93 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.96 (dd, J = 7.8 Hz, 1.1 Hz, 1H); ^{77}Se-NMR (51 MHz) δ 569.9; IR (KBr) 1027 cm^{-1} (SO); MS (m/z) 464 (M$^+$); HRMS (m/z) calcd for $C_{24}H_{16}OS2^{80}Se$ 463.9808, found 463.9841 (M$^+$). Anal. Calcd for $C_{24}H_{16}OS_2Se$: C, 62.20; H, 3.48%. Found: C, 61.62; H, 3.46%.

Oxidation of 1,9-Bis(phenylseleno)dibenzothiophene (1b). To a solution of **1b** (240 mg, 0.49 mmol) in 100 mL of CH_2Cl_2 was added *m*-CPBA (141 mg, 0.49 mmol, assay≥60%) in 50 mL of CH_2Cl_2 for 2 h at −20 °C. The solution was stirred for 20 h at −20 °C and treated with NH_3 gas. After filtration, the solution was evaporated and the residue was purified by column chromatography (silica gel; CH_2Cl_2, CH_2Cl_2:ethyl acetate = 1:1, and then CH_2Cl_2:ethanol = 1:1) to give **4b** (176 mg, 71%). **4b**: mp 203 °C dec; ^{1}H-NMR (500 MHz) δ 6.83−6.88 (m, 2H), 7.09−7.13 (m, 3H), 7.34−7.44 (m, 3H), 7.45 (t, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.79−7.81 (m, 2H), 7.82 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.94 (d J = 7.8 Hz, 1H), 7.95 (d J = 7.8 Hz, 1H), 7.98 (dd, J = 7.8 Hz, 1.1 Hz, 1H); ^{13}C-NMR (125 MHz) 123.2, 124.0, 125.3, 127.0, 127.1, 127.8, 128.5, 128.6, 129.1, 129.4, 129.5, 130.5, 133.6, 133.9, 136.2, 136.6, 140.4, 141.5, 141.9, 144.9; ^{77}Se-NMR (76 MHz) 409.4, 890.7; IR (KBr) 816 cm^{-1} (SeO); HRMS (m/z) calcd for $C_{24}H_{16}OS^{80}Se_2$ 511.9256, found 511.9272 (M$^+$). Anal. Calcd for $C_{24}H_{16}OSSe_2$: C, 56.48; H, 3.16%. Found: C, 56.25; H, 3.09%; the crystal data; monoclinic, space group $P2_1/n$, a = 10.063(1) Å, b = 9.022(1) Å, c = 21.981(3) Å, β = 93.50(1)°, V = 1992.0 Å^3, z = 4, ϱ = 1.70 gcm^{-3}, μ (Mo Kα) = 37.9 cm^{-1}, R = 0.045 (R_w = 0.046).

Oxidation of 1,9-Bis(phenylthio)dibenzofuran (1e). Method A: **1e** (267 mg, 0.70 mmol) was oxidized with *m*-CPBA (242 mg, 0.70 mmol, assay ≥ 50%) as described above to give **4e** (212 mg, 73%) together with a trace amount of **5e** and **5e′**. Method B: **1c** (384 mg, 1.0 mmol) was oxidized with *m*-CPBA (690 mg, 2.0 mmol, assay ≥ 50%) as described above to give **5e** (265 mg, 63%) and **5e′** (117 mg, 28%). **4e**: mp 160−161 °C ; ^{1}H-NMR (270 MHz) δ 7.03−7.11 (m, 2H), 7.16−7.31 (m, 6H), 7.42 (dd, J = 7.6 Hz, 1.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.55−7.60 (m, 2H), 7.62 (dd, J = 7.6 Hz, 1.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.72 (dd, J = 7.6 Hz, 1.4 Hz, 1H), 8.17 (dd, J = 7.6 Hz, 1.4 Hz, 1H); MS (m/z) 400 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_2S_2$: C, 71.97; H, 4.03%. Found: C, 71.94; H, 3.94%. **5e′**: mp 254−258 °C; ^{1}H-NMR (270 MHz) δ 7.24−7.38 (m, 10H), 7.72 (t, J = 7.8 Hz, 2H), 7.84 (dd, J = 7.8 Hz, 1.4 Hz, 2H), 7.90 (dd, J = 7.8 Hz, 1.4 Hz, 2H); IR (KBr) 1040 cm^{-1} (SO); HRMS (m/z) calcd for $C_{24}H_{16}O_3S_2$ 416.0541, found 416.0483 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_3S_2$: C, 69.21; H, 3.87%. Found: C, 69.18; H, 3.76%; the crystal data for **5e′**; monoclinic, space group $P2_1/n$, a = 10.578(0) Å, b = 12.640(1) Å, c = 14.405(1) Å, β = 93.34(28)°, V = 1922.8 Å^3, z = 4, ϱ = 1.44 gm^{-3}, μ (Mo Kα) = 2.9 cm^{-1}, R = 0.040 (R_w = 0.041). **5e**: mp 248−254 °C; ^{1}H-NMR (270 MHz) δ 7.37−7.44 (m, 6H), 7.59−7.65 (m, 4H), 7.77 (t, J = 7.0 Hz, 2H), 7.82 (dd, J = 7.0 Hz, 1.9 Hz, 2H), 8.15 (dd, J = 7.0 Hz, 1.9 Hz, 2H); IR (KBr) 1042 cm^{-1} (SO); HRMS (m/z) calcd for $C_{24}H_{16}O_3S_2$ 416.0541, found 416.0524 (M$^+$).

1-(Phenylthio)-9-phenyldibenzothiophene (6). To a THF (50 mL) solution of **4d** (180 mg, 0.43 mmol) was added 0.86 M PhMgBr/THF (10 mL, 8.6 mmol) dropwise. After stirring for 5 h, anhydrous $CuCl_2$ (1.156 g, 8.6 mmol) was added and the solution was stirred for 12 h. Then the solution was treated with aqueous NH_4Cl solution. After usual work-up, the reaction mixture was purified by column chromatography (silica gel; CH_2Cl_2) and preparative HPLC to give **6** in 40% yield. **6**: ^{1}H-NMR (500 MHz) δ 6.75−6.79 (m, 2H), 7.02−7.09 (m, 3H), 7.14 (dd, J = 7.2 Hz, 1.0 Hz, 1H), 7.26 (t, J = 8.2 Hz, 1H), 7.36−7.41 (m, 1H), 7.42−7.70 (m, 5H), 7.52 (t, J = 7.2 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.80 (dd, 7.2 Hz, 1.0 Hz, 1H); ^{13}C-NMR (125 MHz) δ 126.4, 126.7, 126.8, 127.1, 128.3, 128.5, 128.7, 129.1, 130.4, 130.6, 132.5, 134.5, 135.9, 139.0, 140.3, 141.0, 141.1, 144.3; M; HRMS (m/z) calcd for $C_{24}H_{16}S_2$: 368.0693, found 368.0667 (M$^+$).

Photolysis of 1,9-Bis(phenylthio)dibenzothiophene (1d). **1d** (40 mg, 0.10 mmol) was placed in a glass tube and benzene (10 mL) was added under argon. The solution was irradiated with a 400 W high pressure mercury lamp for 12 h at 20 °C. After distillation of the solvent, the reaction mixture was purified by column chromatography (silica gel, CH_2Cl_2) and preparative HPLC, and then **2b** and **3d** were obtained in 72 and 26% yields, respectively. **2b**: mp 196.5−197.0 °C (lit.[8] 190−191 °C); ^{1}H-NMR (270 MHz) δ 7.72−7.80 (m, 2H), 7.88 (t, J = 7.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 8.49 (d, J = 7.8 Hz, 2H), 8.71−8.79 (m, 2H); MS (m/z) 258 (M$^+$). **3d**: ^{1}H-NMR (270 MHz) δ 7.32−7.41 (m, 3H), 7.42 (t, J = 7.8 Hz, 1H), 7.50 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.67−7.72 (m, 1H), 7.74−7.79 (m, 2H), 7.90 (dd, J = 7.8 Hz, 1.1 Hz, 1H); HRMS (m/z) calcd for $C_{18}H_{10}S_2$ 290.0224, found 290.0216 (M$^+$).

Photolysis of 1,9-Bis(phenylseleno)dibenzoselenophene (1a). **1a** (54.1 mg, 0.10 mmol) was treated similarly as described above to give **2a** (24.8 mg, 81%). **2a**: mp 184−185 °C; ^{1}H-NMR (270 MHz) δ 7.71−7.79 (m, 2H), 7.81 (t, J = 7.8 Hz, 2H), 8.11 (d, J = 7.8 Hz, 2H), 8.53 (d, J = 7.8 Hz, 2H), 8.70−8.77 (m, 2H); ^{13}C-NMR (67 MHz) δ 117.9, 123.6, 124.0, 126.9, 127.7, 130.2, 130.5, 133.4, 138.8; ^{77}Se-NMR (51 MHz) δ 458.1; MS (m/z) 306 (M$^+$). Anal. Calcd for $C_{18}H_{10}Se$: C, 70.83; H, 3.30%. Found: C, 70.71; H, 3.23%.

Photolysis of 1,9-Bis(phenylthio)dibenzoselenophene (1c). **1c** (53 mg, 0.12 mmol) was treated similarly as described above to give the compound **2a** (28 mg, 77%).

Photolysis of 1,9-Bis(phenylseleno)dibenzothiophene (1b). **1b** (51 mg, 0.1 mmol) was photolyzed similarly for 24 h as described above to give the compounds **2b** and **3b** in 75 and 6% yields. **3b**: ^{1}H-NMR (500 MHz) δ 7.26 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 7.33 (dt, J = 7.4 Hz, 1.6 Hz, 1H), 7.38 (dt, J = 7.8 Hz, 1.7 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.82 (dd, J = 7.4 Hz, 1.6 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H); HRMS (m/z) calcd for $C_{18}H_{10}SSe$ 337.9668, found 337.9685 (M^+).

Photolysis of 1,9-Bis(phenylthio)dibenzofuran (1e). **1e** (39 mg, 0.10 mmol) in 10 mL of benzene was irradiated as described above for 12 h to give a trace amount of tribenzo[*bc,e,hi*][2,7]oxathiaazulene (**3e**) and 1-(phenylthio)dibenzofuran. **3e**: ^{1}H-NMR (270 MHz) δ 7.15−7.12 (m, 1H), 7.28−7.44 (m, 4H), 7.5−7.68 (m, 4H), 7.72−7.78 (m, 1H); HRMS (m/z) calcd for $C_{18}H_{10}OS$ 274.0452, found 274.0428 (M^+). 1-(Phenylthio)dibenzofuran: ^{1}H-NMR (270 MHz) δ 7.18−7.61 (m, 11H), 8.29−8.35 (m, 1H); MS (m/z) 276 (M^+).

Photolysis of 1,9-Bis(ortho-monodeuteriated phenylthio)dibenzothiophene (1f). **1f** was photolyzed similarly to give **2f** (75%, D content = 45%) and **3f** (22%, D content = 46%). Deuterium contents were determined by mass spectrometry.

Photolysis of 1,9-Bis(ortho-monodeuteriated phenylthio)dibenzoselenophene (1g). **1g** was photolyzed similarly to give **2g** (62%, D content = 52%).

Photolysis of 1,9-Bis(*o*-tolylthio)dibenzothiophene (1h). **2h**: mp 169 °C; ^{1}H-NMR (500 MHz) δ 3.20 (s, 3H), 7.56 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.83 (t, 7.9 Hz, 1H), 8.03(d, J = 7.7 Hz, 1H), 8.06 (d, J = 7.7 Hz, 1H), 8.44 (d, J = 7.9 Hz, 1H), 8.68 (d, J = 7.7 Hz, 1H), 8.74 (d, J = 7.9 Hz, 1H); MS (m/z) 272 (M^+). Anal. Calcd for $C_{19}H_{12}S$: C, 83.79; H, 4.44%. Found: C, 83.56; H, 4.58%. **3h**: ^{1}H-NMR (270 MHz) δ 2,75 (s, 3H), 7.14 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.33 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.55 (dd, J = 7.6 Hz, 1.1 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.75 (dd, J = 7.6 Hz, 1.1 Hz, 1H), 7.78 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 7.88 (dd, J = 7.8 Hz, 1.1 Hz, 1H); HRMS (m/z) calcd for $C_{19}H_{12}S_2$ 304.0380, found 304.0384 (M^+).

Photolysis of 1,9-Bis(*p*-tolylthio)dibenzothiophene (1i). **2i**: mp 151−152 °C; ^{1}H-NMR (500 MHz) δ 2.67 (s, 3H), 7.58 (d, J = 8.2 Hz, 1H), 7.859 (t, 7.8 Hz, 1H), 7.864 (t, J = 7.8 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 8.44 (d, J = 7.8 Hz, 1H), 8.47 (d = 7.8 Hz, 1H), 8.53 (s, 1H), 8.62 (d, J = 8.2 Hz, 1H); ^{13}C-NMR (125 MHz) δ 21.8, 116.8, 117.0, 119.6, 119.9, 124.0, 124.2, 126.9, 127.0, 128.1, 128.6, 128.8, 129.0, 130.52, 130.54, 130.9, 137.4, 138.8, 138.9; MS (m/z) 272 (M^+). Anal. Calcd for $C_{19}H_{12}S$: C, 83.79; 4.44. Found: C, 83.16; H, 4.38. **3i**: ^{1}H-NMR (270 MHz) δ 2.39 (s, 3H), 7.16 (s, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.50 (dd, J = 7.6 Hz, 0.8 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.89 (dd, J = 7.6 Hz, 0.8 Hz, 1H); HRMS (m/z) calcd for $C_{19}H_{12}S_2$ 304.0380, found 304.0342 (M^+).

Photolysis of 1,9-Bis(*m*-tolylthio)dibenzothiophene (1j). Photolysis of **1j** produced a 1:1 mixture of **2h** and **2i** in 54% yield.

Photolysis of 1,9-Bis[(*p*-chlorophenyl)thio]dibenzothiophene (1k). **2k**: mp 167 °C; ^{1}H-NMR (270 MHz) δ 7.63 (dd, J = 8.6 Hz, 2.2 Hz, 1H), 7.83 (t, J = 7.8 Hz, 2H), 8.04 (dd, J = 7.8 Hz, 3.0 Hz, 2H), 8.31 (dd, J = 7.8 Hz, 3.0 Hz, 2H), 8.53 (d, J = 8.6 Hz, 2H), 8.56 (d, 2.2 Hz, 1H); MS (m/z) 292 (M^+). Anal. Calcd for $C_{18}H_9SCl$: C, 73.84; H, 3.10%. Found: C, 73.70; H, 3.01%. **3k**: ^{1}H-NMR (500 MHz) δ 7.33 (d, J = 6.8 Hz, 1H), 7.34 (s, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 6.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H); HRMS (m/z) calcd for $C_{18}H_9S_2{}^{35}Cl$ 323.9834, found 323.9857 (M^+).

Photolysis of 1,9-Bis(2,5-xylylthio)dibenzothiophene (1l). **2l**: mp 190−191 °C; ^{1}H-NMR (270 MHz) δ 3.16 (s, 6H), 7.46(s, 2H), 7.80 (t, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H), 8.66 (d, J = 8.1 Hz, 2H); MS (m/z) 286 (M^+). Anal. Calcd for $C_{20}H_{14}S$: C, 83.88; H, 4.93%. Found: C, 83.52; H, 4.80%. **3l**: ^{1}H-MNR (270 MHz) δ 1.99 (s, 3H), 2.73 (s, 3H), 7.13 (ABq, J = 7.7 Hz, 1H), 7.22 (ABq, J = 7.7 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.51 (dd, J = 7.8, 1.0 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.59 (dd, J = 7.3, 1.4 Hz, 1H), 7.77 (dd, J = 7.8, 1.0 Hz, 1H), 7.85 (dd, J = 7.3, 1.4 Hz, 1H); HRMS (m/z) calcd for $C_{20}H_{14}S_2$ 318.0537, found 318.0550 (M^+).

Photolysis of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzothiophene. **4d** (43 mg, 1.0 mmol) was photolyzed in CH_2Cl_2 (10 mL) for 44 h to give **2b** (11 mg, 41%) and **3d** (17 mg, 57%).

Photolysis of 1,9-Bis(phenylsulfinyl)dibenzothiophene. **5d** (43 mg, 0.1 mmol) was photolyzed in benzene (10 mL) for 12 h to give **2b** (8 mg, 31%) and **3d** (12 mg, 42%).

Photolysis of 1,9-Bis(phenylsulfinyl)dibenzothiophene. **5d′** (42 mg, 0.1 mmol) was photolyzed in benzene (10 mL) for 24 h to give **2b** (3 mg, 12%) and **3d** (14 mg, 50%).

Photolysis of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzoselenophene. **4c** (15 mg, 0.03 mmol) was photolyzed in CH_2Cl_2 (5 mL) for 12 h to give **2a** (9 mg, 91%).

Photolysis of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzofuran. **4e** (20 mg, 0.05 mmol) was photolyzed in CH_2Cl_2 (5 mL) for 12 h to give **3e** (13 mg, 95%).

Photolysis of 1,9-Bis(phenylsulfinyl)dibenzofuran. **5e** (20 mg, 0.05 mmol) was photolyzed in CH_2Cl_2 (5 mL) for 12 h to give **3e** (13 mg, 99%).

Photolysis of 1,9-Bis(phenylsulfinyl)dibenzofuran. **5e′** (20 mg, 0.05 mmol) was photolyzed in CH_2Cl_2 (5 mL) for 12 h to give **3e** (9 mg, 68%).

Photolysis of 1-(Phenylthio)-9-phenyldibenzothiophene. **6** (58 mg, 0.16 mmol) was photolyzed in benzene for 6 h to give **2b** (80%).

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Supplementary Material Available: Characterization data and copies of ^{1}H-NMR spectra of various compounds (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.