Evidence of Transannular Bonding Interaction between Two Sulfur Atoms on Photolysis of Naphtho[1,8-*ef*][1,4]dithiepins

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Naphtho[1,8-*ef*][1,4]dithiepins **5** were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins **3** with diethyl diazomalonate in the presence of copper acetylacetonate. The X-ray crystallographic analysis of 2,3-dihydro-2,2-bis(ethoxycarbonyl)-3-phenylnaphtho[1,8-*ef*][1,4]dithiepin (**5a**) revealed that the S···S distance is shorter than the sum of their van der Waals radii, indicating that compounds **5** have a strong through-space interaction between the two sulfur atoms. Direct irradiation of **5** with a 500 W high-pressure mercury lamp (313 nm) at room temperature gave the corresponding olefins **6** and naphtho[1,8-*cd*]-1,2-dithiole (**1**) quantitatively. The quantum yields of the consumption of **5a** and the formation of **6a** and **1** were 0.34. The mechanism of this reaction was investigated by examining the effect of sensitization and light intensity. The results indicate that the reaction may proceed by a one-photon process from an excited singlet state. *Ab initio* calculations were carried out on model compound **7**, and it was shown that the excitation to the S_1 state causes a bonding interaction between the two sulfur atoms, making the reaction possible.

Introduction

Transannular interaction or through-space interaction has often been observed between two or more heteroatoms that are arranged appropriately in one molecule.[1−5] Such an interaction manifests itself in a low ionization potential (in gas phase), a low anodic peak potential (in solution), or reactivities. Considerable lone-pair−lone-pair interactions between sulfur atoms in mesocyclic bissulfides such as 1,5-dithiocane (1,5-dithiacyclooctane) were elucidated by photoelectron spectroscopy (PES).[2,3]

The existence of the proximity effect between the two sulfur and selenium atoms in 1,8-dichalcogen-substituted naphthalenes is indicated by their unusually low oxidation potentials as compared with those of normal sulfides and selenides, *i.e.*, 1,8-bis(methylthio)naphthalene 0.70 V, 1-(methylthio)naphthalene 0.97 V, 1,8-bis(methylseleno)naphthalene 0.48 V, and 1-(methylseleno)naphthalene 0.82 V, by cyclic voltammetry measurement using Ag/AgNO$_3$ in CH$_3$CN as a reference electrode.[3,4i] When these sulfur or selenium compounds and their corresponding monooxides were treated with strong acids or acid anhydrides such as concentrated sulfuric acid or trifluoromethanesulfonic anhydride [(CF$_3$SO$_2$)$_2$O], they gave the corresponding dithia and diselena dications *via* probably the initial formation of cation radicals, and the dithia or diselena dications were treated with water to give the corresponding sulfoxides or selenoxides in high yields.[3,4f,g,i]

Recently, we have reported that photochemical reactions using cyclic 1,8-bis(alkylthio)- and 1,8-bis(alkylseleno)naphthalenes provide reactive species by releasing thermodynamically stable naphtho[1,8-*cd*]-1,2-dithiole and naphtho[1,8-*cd*]-1,2-diselenole. For example, photodecomposition of naphtho[1,8-*de*]-1,3-dithiin 1-oxides, 1-*N*-tosyl-sulfilimines, and 1-bis(ethoxycarbonyl)methylides provided quantitatively the corresponding carbonyl compounds, *N*-tosylaldimines, and olefins, respectively, together with naphtho[1,8-*cd*]-1,2-dithiole.[6] Furthermore, *o*-quinodimethane is readily generated from photolysis of 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin.[7] We suggested that the photodecomposition of these compounds proceeded by the interaction between the two sulfur or selenium atoms at the 1,8-positions of naphthalene. However, only limited, direct experimental evidence of the S···S interaction has been presented so far. In further extension of these studies, we prepared and photolyzed naphtho[1,8-*ef*][1,4]dithiepins **5** and carried out *ab initio* calculations of **7** as a model compound. We now report the evidence of the through-space bonding interaction between the two sulfur atoms on photolysis of **5**.

Results and Discussion

Preparation of Naphtho[1,8-*ef*][1,4]dithiepins 5. Naphtho[1,8-*ef*][1,4]dithiepins **5** were prepared according

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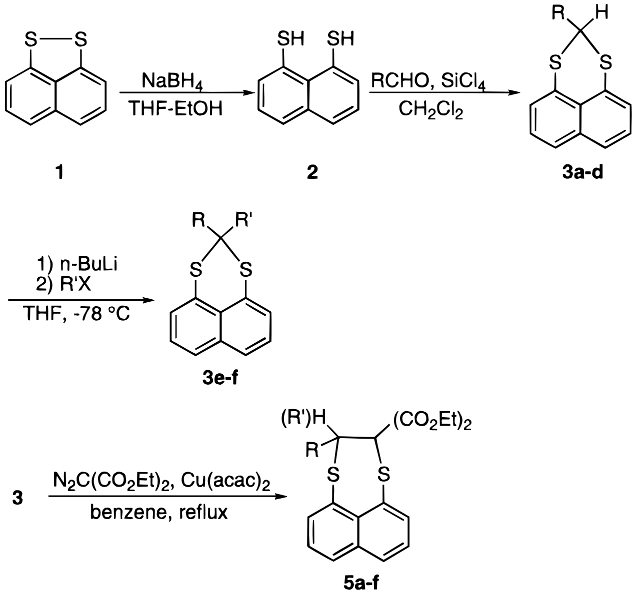
Scheme 1



to the following procedures shown in Scheme 1. Naphtho[1,8-*cd*]-1,2-dithiole (**1**) and 1,8-naphthalenedithiol (**2**) were prepared according to the method reported in the literature.[8,9] 2-Substituted naphtho[1,8-*de*]-1,3-dithiins **3a**−**d** were prepared by the reactions of **2** and aldehydes in the presence of $SiCl_4$ in CH_2Cl_2 in high yields.[10] However, 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiins **3e**,**f** were obtained in poor yields on analogous treatment of ketones and **2**. Therefore, compounds **3e**,**f** were prepared from the reaction of 2-lithiated **3a** with electrophiles such as methyl iodide or benzyl bromide. Treatment of naphtho[1,8-*de*]dithiins **3** with diethyl diazomalonate in the presence of copper acetylacetonate in benzene under reflux conditions gave the corresponding naphtho[1,8-*ef*][1,4]dithiepins **5**, which may be formed from the corresponding sulfonium ylides by the Stevens-type rearrangement.[11] In fact, 2-substituted naphtho-[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylides **4a** and **4b** could be isolated by the reaction of **3a** or **3b** with diethyl diazomalonate in the presence of copper acetylacetonate[6] and these sulfonium ylides underwent the Stevens-type rearrangement to give the corresponding ring-expanded compounds **5a** and **5b**. However, compounds **5c**−**f** were not obtained under similar reaction conditions. Interestingly, similar treatment of **3d** with diethyl diazomalonate did not yield the allylic rearrangement compounds[12] but gave the Stevens-type rearrangement compound **5d**.

X-ray Crystallographic Analysis of 2,3-Dihydro-2,2-bis(ethoxycarbonyl)-3-phenylnaphtho[1,8-*ef*][1,4]-dithiepin (5a). The detailed structural analysis of **5a** was performed by X-ray crystallographic analysis. Selected bond distances, bond angles, and torsional angles of **5a** are collected in Tables 1−3. The ORTEP drawing of **5a** is depicted in Figure 1. The naphthalene ring in compound **5a** is appreciably twisted about the C(5)−C(10) axis. The exocyclic bonds of S(1)−C(1) and S(2)−C(9) are splayed outward, and the sulfur atoms in the 1,8-positions of naphthalene are displaced above and below the average plane of the naphthalene ring. More substantial twisting of the naphthalene ring has been observed in 1,8-disubstituted derivatives with bulky substituents.[13] The S(1)···S(2) distance of **5a** is 3.132 Å,

Table 1. Selected Bond Distances (Å) for Compound 5a[a]

S(1)−C(1)	1.774(4)	C(4)−C(5)	1.435(6)
S(1)−C(11)	1.830(4)	C(5)−C(6)	1.393(7)
S(2)−C(9)	1.782(4)	C(5)−C(10)	1.434(6)
S(2)−C(12)	1.819(3)	C(6)−C(7)	1.321(9)
C(1)−C(2)	1.382(5)	C(7)−C(8)	1.419(8)
C(1)−C(10)	1.420(6)	C(8)−C(9)	1.365(6)
C(2)−C(3)	1.378(7)	C(9)−C(10)	1.434(6)
C(3)−C(4)	1.328(8)	C(11)−C(12)	1.562(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The atom-labeling scheme is shown in Figure 1.

Table 2. Selected Bond Angles (deg) for Compound 5a[a]

C(1)−S(1)−C(11)	103.0(2)	C(5)−C(6)−C(7)	122.1(5)
C(9)−S(2)−C(12)	108.0(2)	C(6)−C(7)−C(8)	120.3(5)
S(1)−C(1)−C(2)	112.8(3)	C(7)−C(8)−C(9)	120.5(5)
S(1)−C(1)−C(10)	126.3(3)	S(2)−C(9)−C(8)	114.8(3)
C(2)−C(1)−C(10)	120.9(4)	S(2)−C(9)−C(10)	124.0(3)
C(1)−C(2)−C(3)	121.6(4)	C(8)−C(9)−C(10)	120.3(4)
C(2)−C(3)−C(4)	119.9(4)	C(1)−C(10)−C(5)	116.6(4)
C(3)−C(4)−C(5)	122.0(4)	C(1)−C(10)−C(9)	126.5(4)
C(4)−C(5)−C(6)	121.4(5)	C(5)−C(10)−C(9)	117.0(4)
C(4)−C(5)−C(10)	118.8(4)	S(1)−C(11)−C(12)	111.8(2)
C(6)−C(5)−C(10)	119.8(4)	S(2)−C(12)−C(11)	112.8(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The atom-labeling scheme is shown in Figure 1.

Table 3. Selected Torsional Angles (deg) for Compound 5a[a]

S(1)−C(1)−C(10)−C(9)	2.2	C(2)−C(3)−C(4)−C(5)	0.2
C(1)−C(10)−C(9)−S(2)	17.1	C(3)−C(4)−C(5)−C(6)	−177.7
C(10)−C(9)−S(2)−C(12)	−73.8	C(4)−C(5)−C(6)−C(7)	−178.1
C(9)−S(2)−C(12)−C(11)	47.4	C(5)−C(6)−C(7)−C(8)	1.5
S(1)−C(11)−C(12)−S(2)	36.5	C(6)−C(7)−C(8)−C(9)	−0.22
C(1)−S(1)−C(11)−C(12)	−92.0	C(7)−C(8)−C(9)−C(10)	−2.9
C(11)−S(1)−C(1)−C(10)	48.8	C(8)−C(9)−C(10)−C(1)	−174.8
C(2)−C(1)−C(10)−C(9)	−177.1	C(1)−C(10)−C(5)−C(4)	−5.4
C(10)−C(1)−C(2)−C(3)	0.3	C(9)−C(10)−C(5)−C(4)	175.2
C(1)−C(2)−C(3)−C(4)	−2.3		

[a] The atom-labeling scheme is shown in Figure 1.

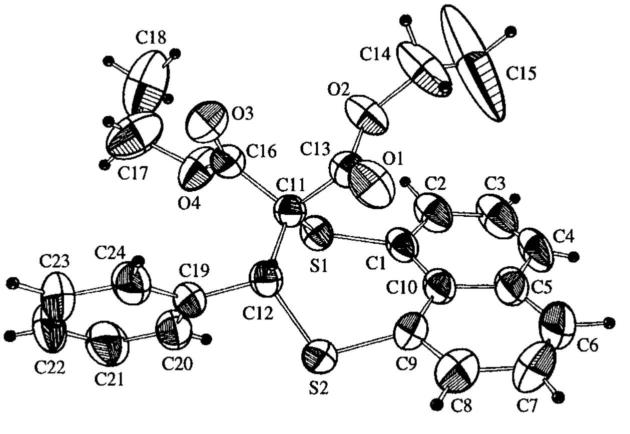


Figure 1. ORTEP drawing of **5a**.

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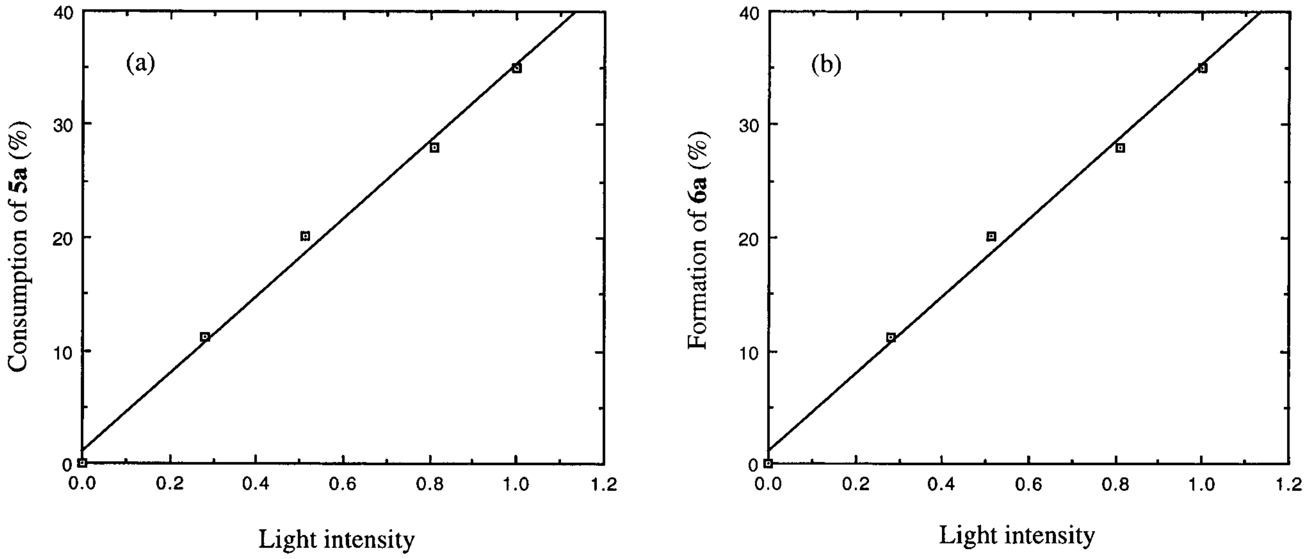
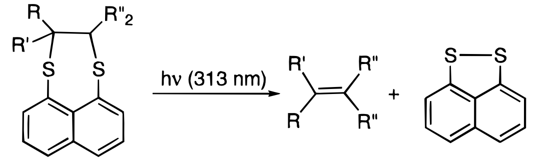


Figure 2. Light intensity dependence on the consumption of **5a** (a) and the formation of **6a** (b) (4.61×10^{-3} M **5a** in CH_2Cl_2).

Table 4. Irradiation of Compound 5 in CH_2Cl_2[a]



5 **6** **1**

R'' = CO_2Et

	R	R′	yield of **6**/%[b]	yield of **1**/%[b]
5a	Ph	H	>99 (92)[c]	>99 (100)[c]
5b	*p*-Tol	H	>99 (91)[c]	>99 (97)[c]
5c	PhCH=CH	H	>99 (91)[c]	>99 (99)[c]
5d	2-furyl	H	>99 (96)[c]	>99 (98)[c]
5e	Ph	CH_3	>99 (96)[c]	>99 (99)[c]
5f	Ph	$C_6H_5CH_2$	>99 (97)[c]	>99 (98)[c]

[a] 500 W high-pressure Hg lamp, $\lambda = 313$ nm, substrates (0.23 mmol), CH_2Cl_2 (5 mL). [b] Yields were determined by HPLC and ^1H NMR spectroscopy. [c] Isolated yields.

which is significantly shorter than the sum of their van der Waals radii (3.70 Å), being indicative of the existence of the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene.

Photolysis of Naphtho[1,8-*ef*][1,4]dithiepins 5. Direct irradiation of compounds **5** in deoxygenated CH_2Cl_2 was carried out in a cylindrical quartz tube using a high-pressure mercury lamp (500 W, 313 nm) at room temperature to give the corresponding olefins **6** and naphtho[1,8-*cd*]-1,2-dithiole (**1**) quantitatively (Table 4). Polar and nonpolar solvents including ethanol, acetonitrile, THF, CH_2Cl_2, $CHCl_3$, and hexane were examined on photoreaction of **5a**; photodecomposition reactions gave **6a** and **1** quantitatively regardless of the solvents used.

The consumption of **5a** and the formation of products **6a** and **1** were unaffected by the addition of benzophenone as a triplet sensitizer and isoprene as a triplet quencher, indicating that the reaction may proceed *via* an excited singlet state, perhaps the lowest excited singlet (S_1) state. The quantum yields of the consumption of **5a** and the formation of **6a** and **1** at room temperature under similar photolysis conditions were measured by comparison with fulgide actinometry to be 0.34, respectively.[14]

The effect of light intensity on photolysis of compound **5a** was studied in order to understand whether the reaction proceeds by a one-, two-, or multi-photon process. The loss of **5a** and the formation of **6a** were proportional to the first power of the 313 nm light as shown in Figure 2. These results imply that the reaction proceeds by a one-photon process.

***Ab Initio* Calculations of 2,3-Dihydronaphtho[1,8-*ef*][1,4]dithiepin (7).** As it was suggested that the photodecomposition of **5** proceeds *via* the S_1 state, we carried out *ab initio* calculations of model compound **7** in the S_1 state as well as in the ground state (S_0). The RHF method was applied to the S_0 state with the STO-3G*,[15] 3-21G(*),[16] and 6-31G* [17] basis sets and the CIS method to the S_1 state with the STO-3G* basis set.

Selected structural parameters of the optimized S_0 and S_1 structures are shown in Table 5, and three-dimensional views of the STO-3G* optimized structures are shown in Figure 3 in order to visualize the structural relaxation after the excitation. All basis sets gave similar structures for S_0. The S···S distance was calculated to be 3.060, 3.149, and 3.202 Å by the STO-3G*, 3-21G(*), and 6-31G* calculations, respectively. These values are close to the corresponding value (3.132 Å) in Figure 1. Moreover, the above-mentioned structural features observed for **5a** are reasonably reproduced. As shown in Figure 4, the HOMO of **7** is essentially an out-of-phase combination of the so-called σ^*_{S-S} orbital and the HOMO of naphthalene, and the LUMO of **7** is essentially the LUMO of naphthalene. As expected, the S_1 state calculated at the S_0 geometry is mainly (72%) composed of the HOMO → LUMO single excitation. We calculated four low-lying singlet excited states at the S_0 geometry; the oscillator strength for S_1 was the largest among these states, and it is plausible that the photodecomposition proceeds *via* the S_1 state. Since the σ^*_{S-S} orbital is

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Table 5. Optimized Geometries for the S_0 and S_1 States of 7[a]

	S_0			S_1
	STO-3G*	3-21G(*)	6-31G*	STO-3G*
Interatomic Distances (Å)				
S(1)−C(1)	1.759	1.784	1.788	1.721
S(1)−C(11)	1.789	1.815	1.812	1.806
S(2)−C(9)	1.761	1.784	1.788	1.696
S(2)−C(12)	1.784	1.813	1.812	1.815
C(1)−C(2)	1.366	1.365	1.367	1.409
C(1)−C(10)	1.453	1.437	1.439	1.419
C(2)−C(3)	1.418	1.405	1.407	1.386
C(3)−C(4)	1.350	1.352	1.354	1.378
C(4)−C(5)	1.430	1.416	1.417	1.420
C(5)−C(6)	1.432	1.419	1.421	1.413
C(5)−C(10)	1.412	1.420	1.419	1.434
C(6)−C(7)	1.349	1.350	1.351	1.387
C(7)−C(8)	1.420	1.408	1.411	1.376
C(8)−C(9)	1.365	1.364	1.365	1.423
C(9)−C(10)	1.455	1.443	1.445	1.431
C(11)−C(12)	1.558	1.543	1.528	1.566
S(1)···S(2)	3.060	3.149	3.202	2.516
Interatomic Angles (deg)				
C(1)−S(1)−C(11)	99.7	100.5	101.6	103.0
C(9)−S(2)−C(12)	101.7	103.6	104.9	104.2
S(1)−C(1)−C(2)	115.5	114.5	113.9	119.8
S(1)−C(1)−C(10)	125.3	125.5	126.0	119.4
C(2)−C(1)−C(10)	119.2	120.0	120.1	120.8
C(1)−C(2)−C(3)	122.4	122.1	122.2	119.3
C(2)−C(3)−C(4)	119.5	119.4	119.2	121.3
C(3)−C(4)−C(5)	120.7	120.7	120.7	121.5
C(4)−C(5)−C(6)	119.1	118.8	118.5	123.4
C(4)−C(5)−C(10)	120.5	120.7	120.9	118.0
C(6)−C(5)−C(10)	120.4	120.6	120.7	118.6
C(5)−C(6)−C(7)	120.8	120.9	121.0	121.0
C(6)−C(7)−C(8)	119.4	119.3	119.1	121.6
C(7)−C(8)−C(9)	122.5	122.2	122.3	119.7
S(2)−C(9)−C(8)	115.5	114.8	114.3	120.5
S(2)−C(9)−C(10)	124.9	124.7	124.9	119.7
C(8)−C(9)−C(10)	119.1	119.9	120.0	119.8
C(1)−C(10)−C(5)	117.7	116.8	116.7	119.1
C(1)−C(10)−C(9)	124.5	126.3	126.6	121.6
C(5)−C(10)−C(9)	117.8	116.9	116.7	119.2
S(1)−C(11)−C(12)	113.3	113.1	113.9	105.3
S(2)−C(12)−C(11)	113.6	113.6	114.4	104.8
Dihedral Angles (deg)				
S(1)−C(1)−C(10)−C(9)	4.5	6.0	6.1	−3.6
C(1)−C(10)−C(9)−S(2)	10.3	14.8	16.4	7.5
C(10)−C(9)−S(2)−C(12)	−73.4	−74.4	−73.2	−80.0
C(9)−S(2)−C(12)−C(11)	60.6	50.5	46.6	80.7
S(1)−C(11)−C(12)−S(2)	24.5	35.5	38.7	7.0
C(1)−S(1)−C(11)−C(12)	−90.1	−93.0	−92.2	−90.7
C(11)−S(1)−C(1)−C(10)	53.1	46.8	44.0	73.6
C(2)−C(1)−C(10)−C(9)	−175.2	−176.1	−175.9	177.6
C(10)−C(1)−C(2)−C(3)	−1.5	−0.8	−0.8	0.1
C(1)−C(2)−C(3)−C(4)	−1.7	−3.1	−3.3	−0.6
C(2)−C(3)−C(4)−C(5)	2.4	2.6	2.8	−0.6
C(3)−C(4)−C(5)−C(6)	178.9	−178.8	−178.9	−177.1
C(4)−C(5)−C(6)−C(7)	−177.7	−179.0	−178.8	177.3
C(5)−C(6)−C(7)−C(8)	1.0	2.2	2.3	1.6
C(6)−C(7)−C(8)−C(9)	−1.5	−1.3	−1.5	0.1
C(7)−C(8)−C(9)−C(10)	−0.3	−2.3	−2.1	−1.5
C(8)−C(9)−C(10)−C(1)	−178.4	−174.3	−174.2	−174.9
C(1)−C(10)−C(5)−C(4)	−3.3	−5.3	−5.6	−2.5
C(9)−C(10)−C(5)−C(4)	176.0	175.6	175.3	−178.8

[a] The atom-labeling scheme is shown in Figure 3.

antibonding between the two sulfur atoms, the excitation to S_1 causes a bonding character between them. Indeed, the geometry optimization for S_1 resulted in a shortening of the S···S distance by *ca.* 0.5 Å. Moreover, the naphthalene moiety is not so distorted in the optimized S_1 structure compared with the S_0 structure, since the repulsive interaction between the two sulfur atoms in S_0 is changed to a bonding interaction. At the optimized S_1 structure, the HOMO is largely localized between the two sulfur atoms, and the contribution of the HOMO → LUMO single excitation to the S_1 state is 91%.

As to the photodecomposition reactivity, we note the following four points. (1) Upon the $S_0 \rightarrow S_1$ excitation, the repulsive interaction between the two sulfur atoms becomes a bonding one, and a "four-membered ring" is formed. Disappearance of the S···S repulsion is the first requisite for the reaction to occur. In the S_0 state, not only is the reaction symmetry-forbidden as shown in Figure 5 but the two sulfur atoms cannot approach each other due to the lone-pair−lone-pair repulsion. (2) The S_1 state is not essentially concerned with the S−C bonds to be broken but mainly with the S···S moiety and the naphthalene ring, and the reaction is symmetry-forbidden also in the S_1 state (σ^*_{S-S} and the naphthalene LUMO have the same symmetry). The energy of the S_1 state is raised on the initial stage of the concerted elongation of the two S−C bonds. However, the energy of a higher excited state ("S_n") which has a $\sigma_{S-C}{}^- \rightarrow \sigma^*_{S-C}{}^+$ doubly excited character is lowered. Avoided crossings occur between excited states along the reaction coordinate, and as may be seen from Figure 6, the barrier on the S_1 surface is expected to be much lower than that in S_0. The photoreaction pathway shown in Figure 6 is consistent with the observed quantum yield, 0.34. The naphthalene ring is of significance in that it gives rise to the excited state of a relatively low energy. (3) The stabilization of the S_1 state due to the structural relaxation amounts to 20.6 kcal mol^{-1}. A part of the resulting high excess energy can be used to override the reaction barrier. (4) The shortening of the S···S distance raises the energy levels of $\sigma_{S-C}{}^-$ and σ^*_{S-S} and lowers that of $\sigma^*_{S-C}{}^+$. This may favor the reaction.

The relaxed S_1 state can be regarded as an S···S radical cation plus a naphthalene radical anion, and our proposed mechanism of the photodecomposition may remind one of the fragmentation of the radical cation of 1,5-dithiocane (1,5-dithiacyclooctane) generated under mass spectroscopic conditions into the 1,2-dithiolane radical cation and cyclopropane and similar reactions of other mesocyclic bissulfides.[18] These reactions are also symmetry-forbidden, but they were observed under mass spectroscopic conditions where the parent radical cation has a high excess energy. The 1,5-dithiocane radical cation is an unusually stable, long-lived species.[19]

Our photoreaction may also be related to the loss of ethylene from the thiirane dimer radical cation.[20] While our reaction and the above-mentioned fragmentation of mesocyclic bissulfide radical cations are symmetry-forbidden, the decomposition of the thiirane dimer radical cation is symmetry-allowed. This difference originates from the relative orientation of the S···S bond and the forming C−C single or double bond. In the case of the thiirane dimer radical cation, they are perpendicular to each other, while in our case and in the case of the mesocyclic bissulfide radical cations, they are parallel with each other.

Conclusion

Compounds **5** were photolyzed by a 500 W high-pressure mercury lamp to give **6** and **1** quantitatively. These reactions proceeded *via* an excited singlet state as

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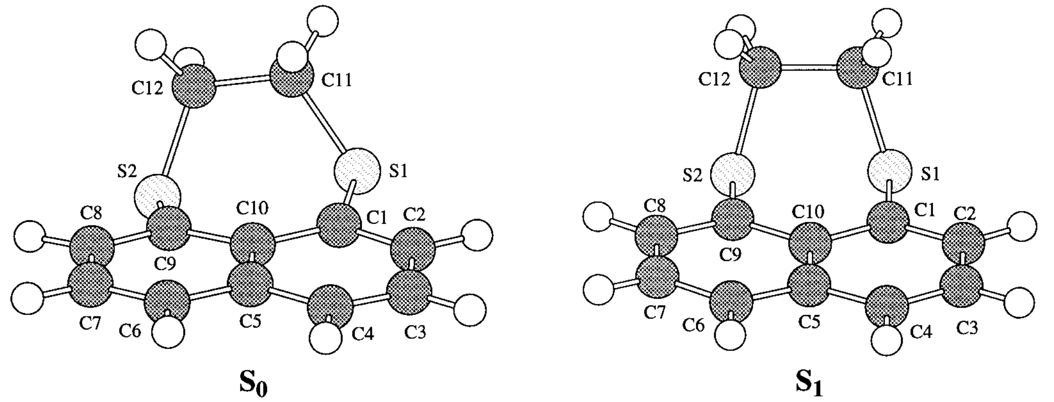

Figure 3. Three-dimensional view for RHF/STO-3G* optimized S_0 structure (left) and CIS/STO-3G* optimized S_1 structure (right) of **7**.

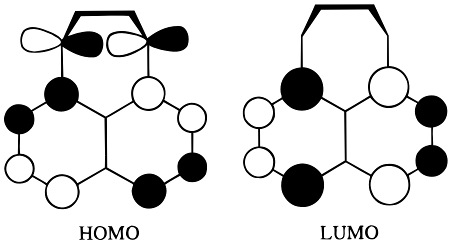

Figure 4. Schematic representation of HOMO and LUMO of **7**. The orbital energies of HOMO are −5.34, −7.68, and −7.56 eV, and those of LUMO are 5.57, 2.22, and 2.32 eV by STO-3G*, 3-21G(*), and 6-31G* calculations, respectively.

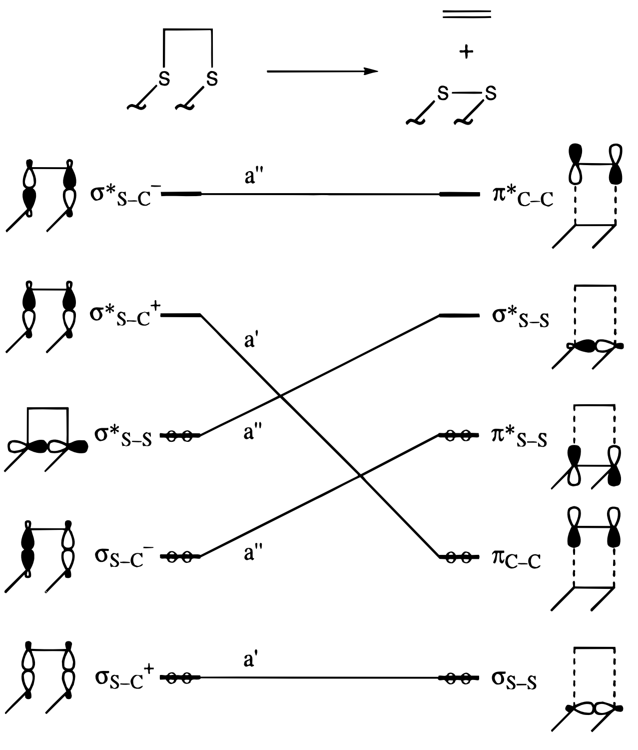

Figure 5. An MO correlation diagram which explains that the thermal decomposition of a $-S-CH_2-CH_2-S-$ moiety to give $-S-S-$ and ethylene is symmetry-forbidden (a C_s symmetry is assumed). The lone-pair orbitals other than σ^*_{S-S} and π^*_{S-S} are not included for clarity.

a one-photon process. *Ab initio* calculations of model compound **7** showed that the excitation to the S_1 state causes the S···S bonding interaction, and this is related to the clean photodecomposition of **5**. Such an interaction is also expected to play an important role in the related photochemical reactions.[6,7]

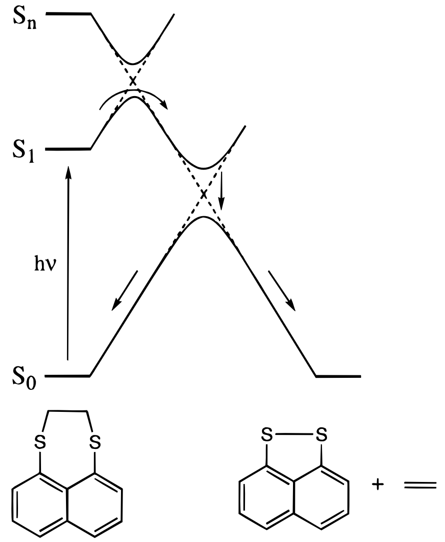

Figure 6. A schematic state correlation diagram between **7** and **1** + ethylene. The proposed photodecomposition pathway is also shown. The ground state S_0 of the reactant is described by $(\sigma_{S-C}{}^{+})^2(\sigma_{S-C}{}^{-})^2(\sigma^*_{S-S})^2(\pi^*_{Np})^0(\sigma^*_{S-C}{}^{+})^0$ where π^*_{Np} is the LUMO of naphthalene (see also Figure 5). The lowest excited singlet state S_1 is approximately described by $(\sigma_{S-C}{}^{+})^2(\sigma_{S-C}{}^{-})^2(\sigma^*_{S-S})^1(\pi^*_{Np})^1(\sigma^*_{S-C}{}^{+})^0$. "$S_n$" represents an excited state to which the electronic configuration $(\sigma_{S-C}{}^{+})^2(\sigma_{S-C}{}^{-})^0(\sigma^*_{S-S})^2(\pi^*_{Np})^0(\sigma^*_{S-C}{}^{+})^2$ largely contributes.

Experimental Section

Photolysis, quantum yield, sensitization, and intensity effect experiments were performed by irradiation with a 500 W ultrahigh-pressure mercury lamp equipped with a glass filter and monochromator. All photoreactions were monitored and quantified by HPLC or ^1H NMR. X-ray data collection was performed on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer (23 ± 1 °C), and calculations for structure solution and refinement were perfomed on a VAX 3100 computer using SDP/VAX. Elemental analyses were carried out by Chemical Analysis Center at this University.

Naphtho[1,8-*cd*]-1,2-dithiole (**1**) was prepared according to the method reported in the literature.[8] 1,8-Naphthalenedithiole was prepared by reduction of **1** with $NaBH_4$ in ethanol−THF.[9]

Synthesis of Naphtho[1,8-*de*]-1,3-dithiins 3a−d. General Procedure.[10] To a well-stirred solution of 5 mmol of carbonyl compound and 5 mmol of 1,8-naphthalenedithiol (**1**) in 20 mL of CH_2Cl_2 at −20 °C was added dropwise 5 mmol of tetrachlorosilane. The solution was warmed up to room temperature and monitored by TLC. When the reaction was complete (within 2 h), the solution was quenched with 10 mL of 5% sodium bicarbonate solution and extracted with CH_2Cl_2 (3 × 100 mL). After the solution was dried with magnesium sulfate and the solvent removed, the residue was separated by silica-gel column chromatography (eluent, tetrachloromethane) and then recrystallization from ethyl acetate−hexane gave the pure product.

2-Phenylnaphtho[1,8-*de*]-1,3-dithiin (3a): yield 98%; mp 124−125 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 5.42 (s, 1H), 7.36−7.49 (m, 7H), 7.55−7.58 (m, 2H), 7.70−7.73 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 46.83, 125.27, 125.48, 125.91, 127.71, 128.84, 129.02, 129.06, 132.04, 135.06, 136.51; MS (*m/z*) 280 (M^+). Anal. Calcd for $C_{17}H_{12}S_2$: C, 72.82, H, 4.31. Found: C, 72.71, H, 4.21.

2-*p*-Tolylnaphtho[1,8-*de*]-1,3-dithiin (3b): yield 97%; mp 135−136 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.37 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.42−7.46 (m, 4H), 7.68 (d, J = 7.8 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.26, 46.58, 125.25, 125.45, 125.84, 127.60, 128.12, 129.69, 132.22, 133.42, 135.02, 138.99; MS (*m/z*) 294 (M^+). Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43, H, 4.79. Found: C, 73.48, H, 4.70.

2-(3-Phenyl-2-propenyl)naphtho[1,8-*de*]-1,3-dithiin (3c): yield 88%; mp 148−149 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 5.07 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 1H), 6.39 (dd, J_1 = 15.4 Hz, J_2 = 8.4 Hz, 1H), 6.85 (dd, J_1 = 15.4 Hz, J_2 = 1.1 Hz, 1H), 7.26−7.41 (m, 9H), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H), 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 43.76, 124.21, 125.61, 126.36, 126.41, 126.76, 127.66, 128.36, 128.61, 129.81, 134.38, 134.91, 135.71; MS (*m/z*) 306 (M^+). Anal. Calcd for $C_{19}H_{14}S_2$: C, 74.47, H, 4.60. Found: C, 74.25, H, 4.57.

2-(2-Furyl)naphtho[1,8-*de*]-1,3-dithiin (3d): yield 87%; mp 67−68 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 5.33 (s, 1H), 6.31 (dd, J_1 = 3.2 Hz, J_2 = 1.9 Hz, 1H), 6.35 (d, J = 3.2 Hz, 1H), 7.36−7.40 (m, 2H), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H), 7.70 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 38.60, 109.04, 110.82, 125.46, 125.61, 126.34, 127.84, 129.76, 134.91, 142.73, 150,08; MS (*m/z*) 270 (M^+). Anal. Calcd for $C_{15}H_{10}O_1S_2$: C, 66.64, H, 3.73. Found: C, 66.50, H, 3.67.

Synthesis of 2,2-Disubstituted Naphtho[1,8-*de*]-1,3-dithiins 3e,f. General Procedure. *n*-Butyllithium (1.3 mL of 1.67 N solution in hexane, 2.2 mmol) was added dropwise at −78 °C to a solution of 2-phenylnaphtho[1,8-*de*]-1,3-dithiin (**5a**) (408 mg, 2.0 mmol) in THF (20 mL) and stirred for 1 h. To this solution was added electrophiles (2.2 mmol) for 1 h at −78 °C with stirring, and then the solution was warmed up to room temperature and monitored by TLC. After the reaction and usual workup process, the products were separated by silica-gel column chromatography using carbon tetrachloride as eluent and then recrystallization from ethyl acetate−hexane to give the pure product.

2-Methyl-2-phenylnaphtho[1,8-*de*]-1,3-dithiin (3e): yield 97%; mp 116−117 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.09 (s, 3H), 7.25−7,30 (m, 1H), 7.33−7.39 (m, 4H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2H), 7.67 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2H), 7.82−7.84 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 30.39, 51.86, 125.23, 125.71, 126.13, 127.48, 127.60, 128.12, 128.50, 131.36, 134.75, 141.90; MS (*m/z*) 294 (M^+). Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43, H, 4.79. Found: C, 73.42, H, 4.75.

2-Benzyl-2-phenylnaphtho[1,8-*de*]-1,3-dithiin (3f): yield 84%; mp 137−138 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.55 (s, 2H), 6.73 (d, J = 7.1 Hz, 2H), 7.12 (t, J = 7.1 Hz, 2H), 7.16−7.22 (m, 4H), 7.34 (t, J = 7.3 Hz, 2H), 7.48 (dd, J_1 = 7.3 Hz, J_2 = 1.0 Hz, 2H), 7.61−7.66 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 49.33, 57.32, 125.73, 126.42, 126.52, 126.97, 127.46, 127.55, 127.98, 128.05, 128.46, 130.05, 130.80, 134.61, 134.86, 140.54; MS (*m/z*) 370 (M^+). Anal. Calcd for $C_{24}H_{18}S_2$: C, 77.80, H, 4.90. Found: C, 77.66, H, 4.78.

Synthesis of Naphtho[1,8-*ef*][1,4]dithiepins 5a−f. General Procedure. A mixture of 2-substituted- or 2,2-substituted-naphtho[1,8-*de*]dithiins **3** (1 mmol) and diethyl diazomalonate (1 mmol) in benzene (5 mL) was refluxed for 48 h in the presence of 15 mg of copper acetylacetonate. After cooling, the solvent was evaporated. The residues were purified by silica-gel column chromatography (eluent, ethyl acetate−hexane) and recrystallization from dichloromethane−hexane to give the pure products **5**.

2,3-Dihydro-2,2-bis(ethoxycarbonyl)-3-phenylnaphtho-[1,8-*ef*][1,4]dithiepin (5a): yield 66%; mp 139−140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87−0.92 (m, 6H), 3.56−3.67 (m, 1H), 3.82−3.91 (m, 3H), 5.72 (s, 1H), 7.25−7.33 (m, 5H), 7.44−7.47 (m, 2H), 7.70−7.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.29, 13.65, 59.43, 62.25, 74.56, 125.63, 125.81, 128.11, 128.20, 128.89, 129.58, 129.95, 131.27, 133.67, 133.82, 134.08, 135.67, 135.83, 137.25, 165.68, 167.65; IR (KBr) 1742, 1721, 1241, 1218 cm^{-1} (CO_2); MS (*m/z*) 438 (M^+). Anal. Calcd for $C_{24}H_{22}O_4S_2$: C, 65.73, H, 5.06. Found: C, 65.63, H, 5.03.

2,3-Dihydro-2,2-bis(ethoxycarbonyl)-3-*p*-tolylnaphtho-[1,8-*ef*][1,4]dithiepin (5b): yield 72%; mp 144−145 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88−0.95 (m, 6H), 3.21 (s, 3H), 3.65−3.69 (m, 1H), 3.83−3.91 (m, 3H), 5.69 (s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.26−7.32 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.71−7.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.40, 13.71, 21.12, 59.14, 62.30, 62.33, 74.65, 125.67, 125.90, 127.75, 128.85, 129.78, 129.97, 131.27, 133.74, 133.92, 134.19, 134.26, 135.67, 135.90, 138.10, 165.80, 167.77; IR (KBr) 1738, 1301, 1238, 1195 cm^{-1} (CO_2); MS (*m/z*) 452 (M^+). Anal. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.35, H, 5.34. Found: C, 66.38, H, 5.30.

2,3-Dihydro-2,2-bis(ethoxycarbonyl)-3-(3-phenyl-2-propenyl)naphtho[1,8-*ef*][1,4]dithiepin (5c): yield 72%; oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 4.09−4.16 (m, 2H), 4.29−4.37 (m, 2H), 4.76 (d, J = 8.7 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.50 (dd, J_1 = 15.6 Hz, J_2 = 8.7 Hz, 1H), 7.18−7.38 (m, 7H), 7.69−7.71 (m, 2H), 7.83−7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 14.00, 59.01, 62.30, 62.57, 70.06, 124.51, 125.45, 125.96, 126.58, 127.89, 128.39, 128.44, 128.62, 131.67, 132.24, 133.48, 133.91, 135.42, 136.19, 136.31, 137.48, 166.29, 168.53; IR (KBr) 1735, 1272, 1241, 1218 cm^{-1} (CO_2); MS (*m/z*) 464 (M^+). Anal. Calcd for $C_{26}H_{24}O_4S_2$: C, 67.22, H, 5.21. Found: C, 67.34, H, 5.33.

2,3-Dihydro-2,2-bis(ethoxycarbonyl)-3-(2-furyl)naphtho[1,8-*ef*][1,4]dithiepin (5d): yield 68%; mp 91−92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 4.05−4.09 (m, 1H), 4.13−4.23 (m, 3H), 5.47 (s, 1H), 6.28−6.30 (m, 2H), 7.30−7.37 (m, 3H), 7.71−7.77 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.71, 13.96, 53.80, 62.41, 62.76, 70.64, 108.94, 110.58, 125.51, 125.97, 128.04, 129.06, 132.23, 132.31, 133.63, 135.19, 132.26, 137.43, 141.97, 150.00, 165.80, 167.96; IR (KBr) 1742, 1721, 1255, 1195 cm^{-1} (CO_2); MS (*m/z*) 428 (M^+). Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 61.66, H, 4.70. Found: C, 61.65, H, 4.61.

2,2-Bis(ethoxycarbonyl)-3-methyl-3-phenylnaphtho-[1,8-*ef*][1,4]dithiepin (5e): yield 82%; mp 139−140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.76 (t, J = 7.1 Hz, 3H), 0.98 (t, J = 7.1 Hz, 3H), 2.52 (s, 3H), 3.48−3.67 (m, 4H), 7.295−7.39 (m, 5H), 7.77−7.83 (m, 4H), 7.99−8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.41, 13.70, 25.10, 61.50, 62.11, 63.76, 78.95, 125.34, 125.35, 126.01, 127.78, 128.29, 128.73, 130.53, 131.24, 132.10, 134.38, 135.81, 141.38, 165.04, 165.68; IR (KBr) 1729, 1238, 1185 cm^{-1} (CO_2); MS (*m/z*) 452 (M^+). Anal. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.35, H, 5.34. Found: C, 66.23, H, 5.32.

2,2-Bis(ethoxycarbonyl)-3-benzyl-3-phenylnaphtho-[1,8-*ef*][1,4]dithiepin (5f): yield 66%; mp 176−177 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (t, J = 6.9 Hz, 3H), 1.03 (t, J = 6.9 Hz, 3H), 3.39−3.43 (m, 2H), 3.83 (d, J = 15.0 Hz, 1H), 3.90−4.05 (br s, 2H), 4.54 (d, J = 15.0 Hz, 1H), 7.13−7.20 (m, 5H), 7.21−7.32 (m, 5H), 7.72−7.78 (m, 4H), 7.90−7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.12, 13.75, 42.12, 61.82, 62.27, 69.59, 80.29, 125.37, 126.08, 126.17, 127.17, 127.43, 127.52, 130.24, 130.39, 130.80, 130.93, 131.88, 131.97, 133.84, 135.09, 133.35, 134.55, 137.43, 139.65, 165.40, 165.99; IR (KBr) 1744, 1717, 1241, 1212 cm^{-1} (CO_2); MS (*m/z*) 528 (M^+). Anal. Calcd for $C_{31}H_{28}O_4S_2$: C, 70.43, H, 5.34. Found: C, 70.19, H, 5.25.

General Photolysis Procedure. A solution of naphtho-[1,8-*ef*][1,4]dithiepins (0.23 mmol) in solvent (10 mL) was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high-pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The reaction progress was monitored by HPLC or ^{1}H NMR spectroscopy. After irradiation, the solvent was evaporated and the residue was purified by preparative HPLC, and the products were characterized by NMR and GC-MS spectroscopies.

6a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.29 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 4.28−4.37 (m, 4H), 7.37−7.40 (m, 3H), 7.44−7.47 (m, 2H), 7.74 (s, 1H); MS (*m*/*z*) 248 (M$^+$).

6b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.31 (t, $J = 7.1$ Hz, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 2.37 (s, 3H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.70 (s, 1H); MS (*m*/*z*) 262 (M$^+$).

6c: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.27−1.41 (m, 12H), 4.23−4.40 (m, 8H), 6.62−6.67 (m, 1H), 7.00−7.07 (m, 2H), 7.23−7.42 (m, 8H), 7.49−7.54 (m, 4H), 7.79−7.82 (m, 1H); MS (*m*/*z*) 274 (M$^+$).

6d: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.32 (t, $J = 7.1$ Hz, 3H), 1.37 (t, $J = 7.1$ Hz, 3H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.40 (q, $J = 7.1$ Hz, 2H), 6.50 (dd, $J_1 = 3.5$ Hz, $J_2 = 1.7$ Hz, 1H), 6.70 (d, $J = 3.5$ Hz, 1H), 7.45 (s, 1H), 7.52 (d, $J = 1.7$ Hz, 1H); MS (*m*/*z*) 238 (M$^+$).

6e: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.95 (t, $J = 7.1$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 3H), 2.44 (s, 3H), 3.96 (q, $J = 7.1$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 7.23−7.26 (m, 2H), 7.32−7.37 (m, 3H); MS (*m*/*z*) 262 (M$^+$).

6f: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (t, $J = 7.1$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 3H), 3.94 (q, $J = 7.1$ Hz, 2H), 4.16 (s, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 7.10−7.14 (m, 2H), 7.15−7.20 (m, 3H), 7.22−7.26 (m, 3H); MS (*m*/*z*) 338 (M$^+$).

Quantum Yields. The measurement of the quantum yield was carried out using the output of a 500 W high-pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The fulgide, (*E*)-α-(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride, which has a quantum yield of 0.20 for its photocolouration at 313 nm in toluene was used as an actinometer.[14] Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Sample and actinometer cells were sequentially irradiated. The actinometer cells were used to determine the photo flux, which was then used to convert the rate of loss of the material into a quantum yield. Quantum yield was determined from the solution that began at concentration of 6 mM, and conversions were kept under 5%. The measurement of quantum yields was repeated several times by HPLC detection.

Effect of Light Intensity. The measurement of the light intensity effect was carried out using the output of a 500 W high-pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The light intensity was attenuated by using a quartz filter (313 nm; 27%, 52%, and 83%). Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from the solutions that began at concentration 6 mM, and irradiation times were kept under 1 h. The measurement of yields was repeated several times by HPLC detection.

X-ray Analysis of 5a.[24] X-ray diffraction analysis on **5a** was carried out on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer. The structure of **5a** $C_{24}H_{22}O_4S_2$ (formula weight 438.57) was determined from a monoclinic crystal of dimension 0.5 × 0.5 × 0.3 mm (space group $P2_1/c$), with unit cell $a = 9.460(2)$ Å, $b = 15.673(6)$ Å, $c = 14.933(3)$ Å, $\beta = 105.05(2)°$, $V = 2138.0$ Å^3. It has four molecules per cell, $\rho = 1.36$ g/cm^3, $\mu = 2.7$ cm^{-1}, $F(000) = 920$. The cell dimensions were determined from the setting angles of 25 reflections with $4 < \theta < 21°$ using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 4056 reflections were measured ($2\theta < 50°$) using the $\omega - 2\theta$ step scan technique. All data processing was performed on a Micro VAX 3100 computer by using the MolEN structure-solving program obtained from Enraf Nonius Corp., Delft, The Netherlands. An empirical absorption correction based on series of ψ scans was also applied to the data. The structure was refined by full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and the weight w is defined as 1.0 for all observed reflections. All hydrogen atoms were located, and their positions were refined in least-squares; their isotropic thermal parameters were held fixed at 4.0 Å. The final R and R_w values were 0.056 and 0.053, respectively.

***Ab Initio* Calculations.** *Ab initio* calculations were carried out on a HP735/125 workstation. Spartan 3.1[21] was used for the RHF calculations of the S$_0$ state and Gaussian 92[22] for the CIS calculations of excited states. The STO-3G*,[15] 3-21G(*),[16] and 6-31G*[17] basis sets were used for the S$_0$ state, while only the STO-3G* basis set was used in the excited-state calculations. All these basis sets include d polarization functions on S. The STO-3G* basis set was successfully used for related molecules.[23]

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[24] The author has deposited atomic coordinates for this structure 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, U.K.