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**Studies on Formation, Structures, and Reactivities  
of Sterically Congested  
Aromatic Compounds Bearing Sulfur Atoms**

**1992**

**Takeshi Kimura**

**Submitted in partial fulfillment of the requirements  
for the degree of Doctor of Science,  
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## CHAPTER 1

### GENERAL INTRODUCTION

## General Introduction

Recently, heteroatoms belonging to the third to the fifth row of the periodic table have attracted considerable attention in organic chemistry. Particularly, organic sulfur compounds have been interested in their biological activities. In the numerous organic sulfur compounds, sulfoxides have long been considered to be more important since they have high and characteristic reactivities as compared to other organic sulfur compounds. For examples, it has been found that diaryl or alkyl aryl sulfoxides undergo facile o-lithiation of the aromatic rings, and unusual ligand coupling and ligand exchange reactions.<sup>1</sup>

On the other hand, it is well known that the two or more heteroatoms which are arranged appropriately in space are able to interact intramolecularly with each other, called transannular interaction. As typical examples, nitrogen, sulfur and selenium atoms attached to the 1,5- or 1,6-positions in the eight or ten membered rings interact intramolecularly and form a  $\sigma$ -bond between the heteroatoms by oxidation.<sup>2,3,4</sup> Similarly, in the several compounds containing heteroatoms as the substituents, unusually strong attractive interactions or bond formations between the heteroatoms are observed when they are situated at the appropriate positions.

In this thesis, the author wishes to summarize the results on the new ligand coupling reactions of sterically congested sulfoxides and formation of dithia dications via transannular interactions between the two sulfur functional groups.

Furthermore, the author also describes the formation of triphenylenothiophene and novel dibenzodithiopentalene by thermolysis and photolysis of dibenzothiophene derivatives.

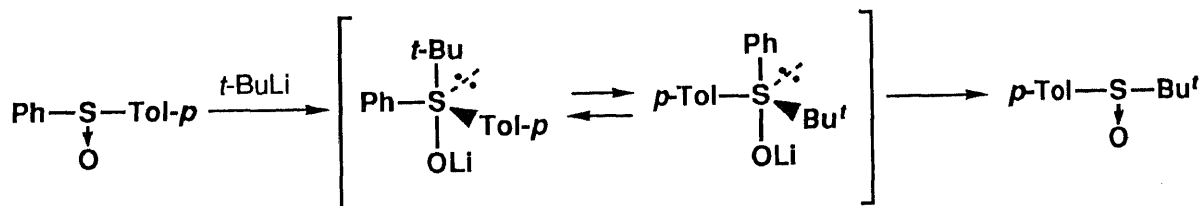
### **Reactions of Sulfoxides with Organometallic Reagents**

It is well known that sulfoxides react with organometallic reagents such as organolithium or Grignard reagents affording the four different reaction pathways.<sup>1</sup> One involves nucleophilic substitution with the Walden inversion at the sulfinyl sulfur atom ("ligand exchange"). A second one is a concomitant ligand exchange and disproportionation. A third one is a ligand coupling reaction and a fourth reaction is an ortho lithiation. In this section these reactions are briefly described.

#### Ligand Exchange and Disproportionation Reactions.

Sulfoxides have been known to undergo facile ligand exchange reactions upon treatment with organolithium or Grignard reagents. In the exchange reactions using alkyl aryl sulfoxides or haloalkyl aryl sulfoxides, the most electronegative ligand is usually replaced by organometallic reagents to give dialkyl sulfoxides with complete inversion of the sulfur center. On the other hand, reactions of diaryl sulfoxides with organometallic reagents used to give essentially ligand exchange products but the results are mechanistically ambiguous and hence have been discussed for many years.

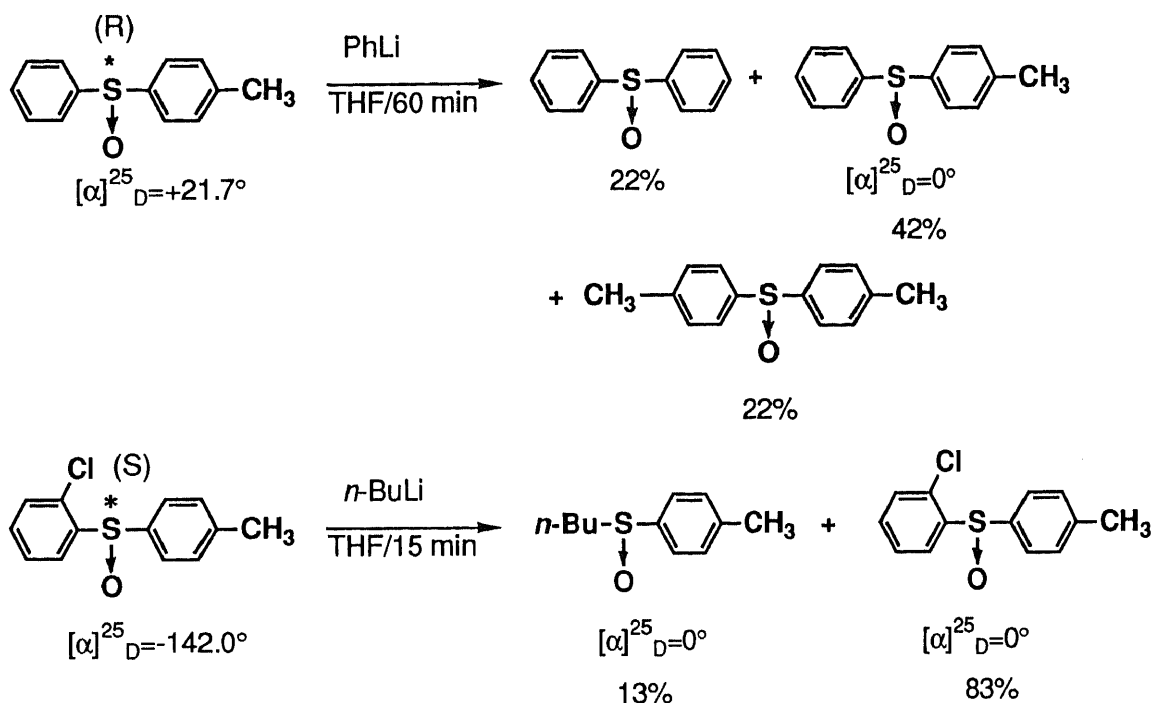
### Ligand Exchange Reaction



$$\begin{array}{c}
 \text{Ph}-\text{S}-\text{Tol-}p \\
 \downarrow \text{O}
 \end{array}
 \xrightleftharpoons{\text{PhLi}}
 \left[ \begin{array}{c} \text{Ph} \\ | \\ \text{Ph}-\text{S} \\ | \quad \swarrow \\ \text{OLi} \quad \text{Tol-}p \end{array} \right]
 \xrightleftharpoons{p\text{-TolLi}}
 \begin{array}{c}
 \text{Ph}-\text{S}-\text{Ph} \\
 \downarrow \text{O}
 \end{array}$$
  

$$\begin{array}{c}
 \text{Ph}-\text{S}-\text{Tol-}p \\
 \downarrow \text{O}
 \end{array}
 \xrightleftharpoons{p\text{-TolLi}}
 \left[ \begin{array}{c} \text{Tol-}p \\ | \\ \text{Ph}-\text{S} \\ | \quad \swarrow \\ \text{OLi} \quad \text{Tol-}p \end{array} \right]
 \xrightleftharpoons{\text{PhLi}}
 \begin{array}{c}
 p\text{-Tol}-\text{S}-\text{Tol-}p \\
 \downarrow \text{O}
 \end{array}$$

4

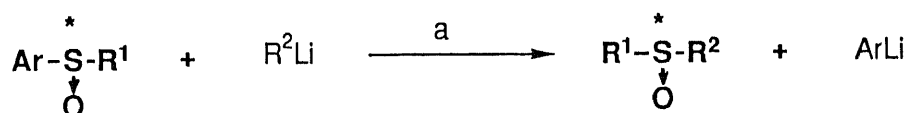


Scheme 1-2

These exchange reactions are believed to proceed via an  $S_N2$ -type process involving  $\sigma$ -sulfuranes as intermediates or simple transition states. For example, the reaction of phenyl *p*-tolyl sulfoxide with phenyllithium gives a mixture of three sulfoxides, namely, phenyl *p*-tolyl, diphenyl and di-*p*-tolyl sulfoxides in the 2:1:1 statistical ratio as ligand exchange products.<sup>5</sup> The stereochemistry of this facile disproportionation reaction was investigated using optically active (R)-phenyl *p*-tolyl sulfoxide or (S)-*o*-chlorophenyl *p*-tolyl sulfoxide to result in the formation of the completely racemized starting sulfoxide (Scheme 1-2).<sup>5</sup>

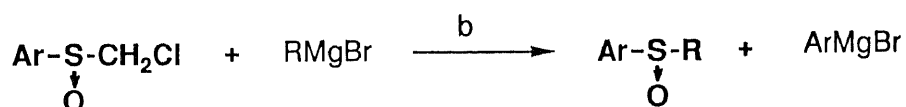
Meanwhile, the simple ligand exchange reactions of sulfoxides have been utilized to provide several new organolithium or Grignard reagents that are difficult to generate

by conventional procedures.<sup>6a,7,8</sup> Furthermore, this simple exchange reaction was applied to the synthesis of optically pure sulfoxides (Scheme 1-3<sup>6b,c</sup> and 1-4<sup>6d</sup>).



a) dimethoxyethane or ether

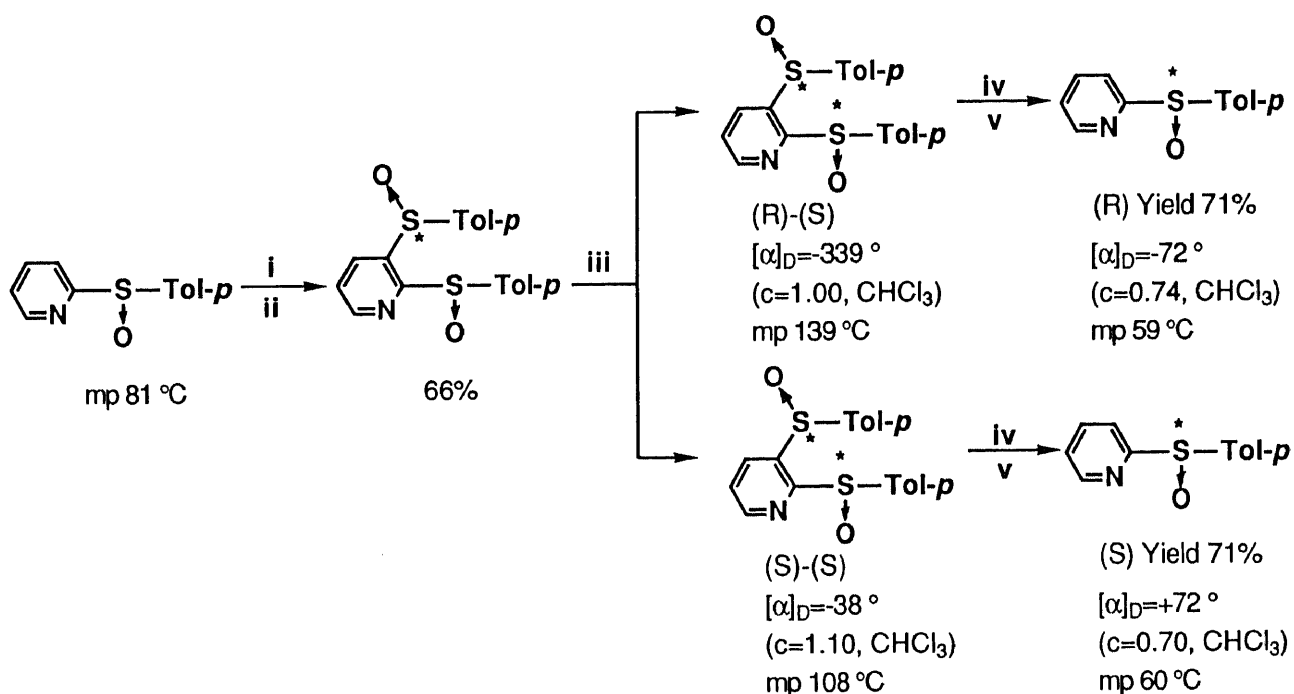
Ar: *p*-Tol, Ph; R<sup>1</sup>: CH<sub>3</sub>, *n*-Bu; R<sup>2</sup>: CH<sub>3</sub>, *n*-Bu, *t*-Bu



b) ether or THF

Ar: *p*-Tol, Ph; R: Et, *i*-Pr

Scheme 1-3



i: LDA, THF, -78 °C; ii: *p*-Tol-SO-*i*-Ment, -95 °C; iii: separation by column chromatography;  
iv: *p*-TolMgBr, THF, -90 °C; v: H<sub>2</sub>O.

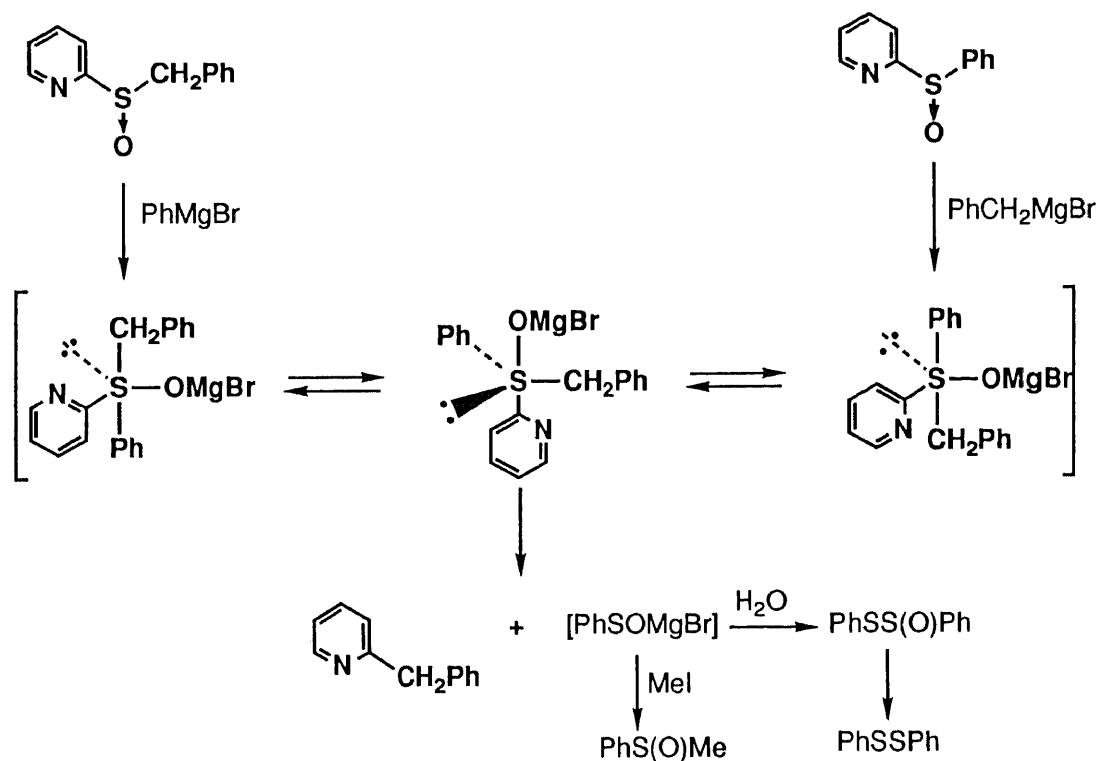
Scheme 1-4



## Ligand Coupling Reactions

As an alternative nucleophilic substitution reaction on the sulfur atom of sulfoxides with organometallic reagents, ligand coupling reactions have been reported.<sup>9</sup> When sulfoxides bearing electronegative ligands such as pyridyl group were treated with organolithium or Grignard reagents the coupling reactions were observed between the two ligands to give the corresponding biaryls or pyridylaryls in good yields. In the reactions tetracoordinate sulfurane should be formed as an intermediate (Scheme 1-5).<sup>5,7,9</sup>

### Ligand Coupling Reaction

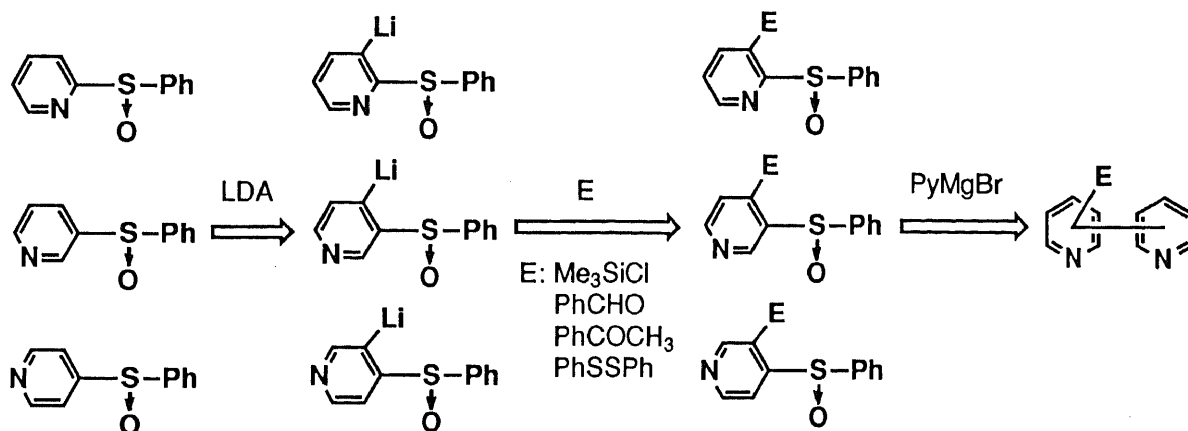


Scheme 1-5

There are two different types of bonding orbitals in sulfuranes as well as other hypervalent species having a trigonal bipyramidal (TB) structure; one is an apical bond and the other is an equatorial bond. The apical positions are occupied by electronegative ligands using p orbital of the central sulfur atom, whereas the equatorial positions which are composed of  $sp^2$  hybridized orbitals, are presumed to be taken up by electron donating substituents. The ligand coupling reactions presumably take place by the initial nucleophilic attack of the organolithium reagents on the sulfur atom resulting in the formation of an unstable  $\sigma$ -sulfurane as an intermediate. On the mechanism of ligand coupling, it is considered that the two electronegative ligands can couple in the sulfurane. In the TB structure of sulfurane, one ligand occupied at the apical position and another one at the equatorial positions can interchange their positions by pseudo rotation or turnstile rotation and thus the two ligands come close together for coupling.<sup>6d,e</sup>

In the coupling reactions the stereochemistry of the carbon atom attached at the coupling center reveals the retention of its configuration indicating that the reaction should proceed via a concerted front side attack of the one ligand on the other by forming a three membered transition state or intermediate without bond breaking.

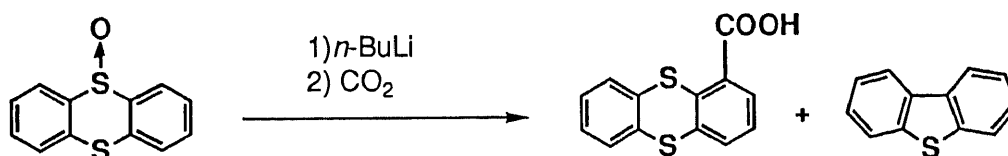
These coupling reactions have been used for synthesis of numerous symmetric and unsymmetric bipyridines which are difficult to synthesis by usual methods (Scheme 1-6).<sup>6a</sup>



Scheme 1-6

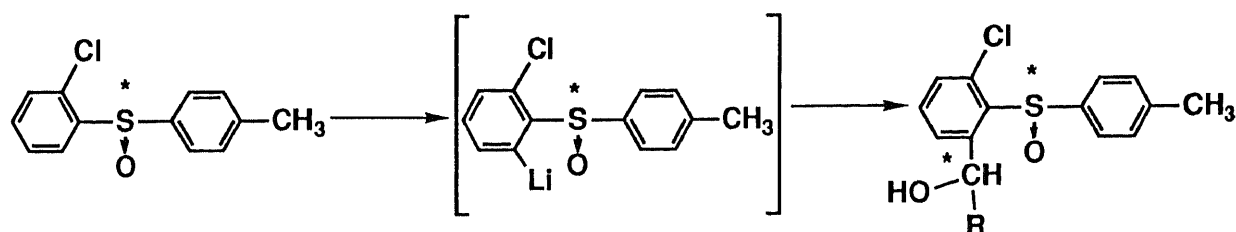
### o-Lithiation Reactions

The regio specific introduction of the suitable substituents into the aromatic ring has been an important technique in synthetic organic chemistry. There are many substituents which can control the regiochemistry of lithiations on aromatic rings.<sup>6a,6d,11</sup> However, there are a few reports using sulfinyl moiety as an directed o-lithiation in the aromatic ring. Gilman et al. found that the lithiation of thianthrene-5-oxide with *n*-butyllithium gave not only the desired o-lithiation product but also the ligand coupling and reduction product simultaneously (Scheme 1-7).<sup>10</sup>



Scheme 1-7

Recently, highly regiospecific ortho lithiation of diaryl sulfoxides bearing phenyl or pyridyl group was performed using lithiumdiisopropylamide (LDA) as a base instead of *n*-butyllithium to give the desired *o*-lithiated products in high yields (Scheme 1-8).<sup>11</sup>

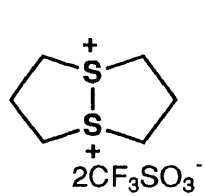
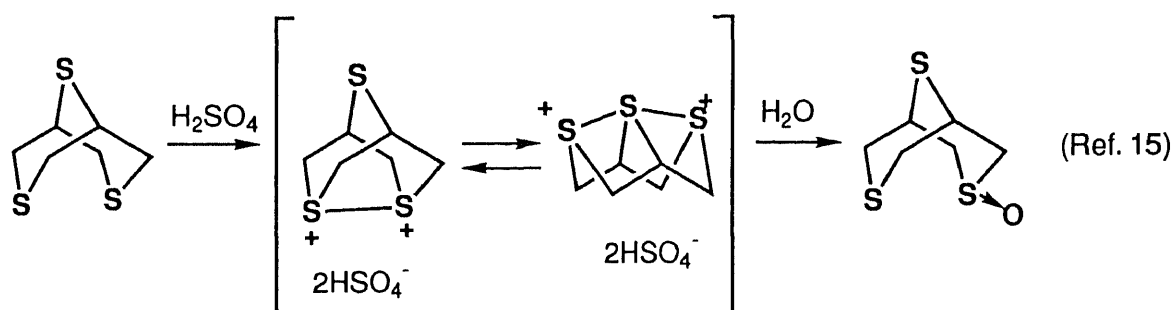
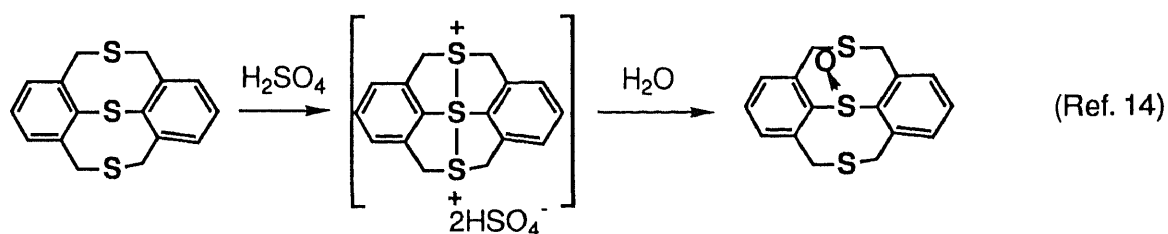
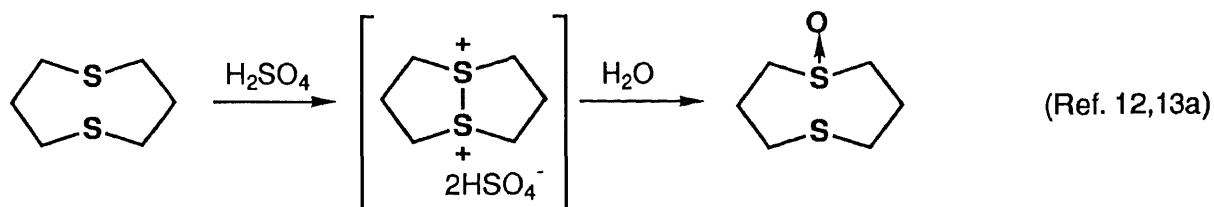
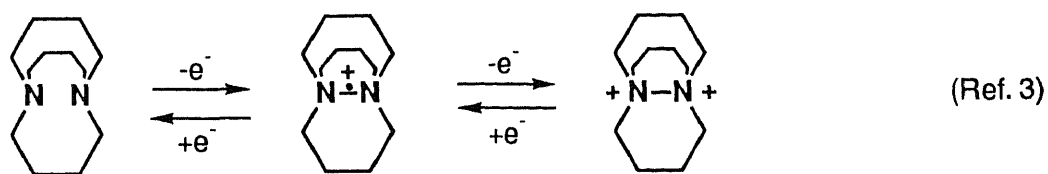


aldehyde	Product R	yield(%)	diastereomer ratio
C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub>	95	66:34
<i>p</i> -TolCHO	<i>p</i> -Tol	96	65:35
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	96	65:35
<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	91	63:37

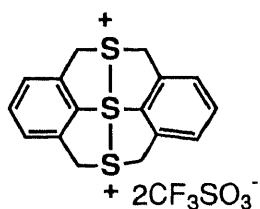
Scheme 1-8

### Transannular Interactions of Heteroatoms

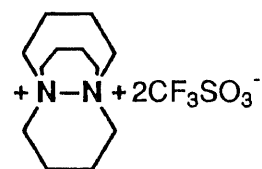
It is well known that the two or more heteroatoms which are arranged appropriately in space are able to interact intramolecularly with each other.<sup>2,3,4</sup> In general, attractive force is more important than the repulsive force in the transannular interaction between the heteroatoms. For instance in 1,5-diheteroatom substituted cyclic compounds, if one removes one or two electrons from one heteroatom, the lone pair electrons on the other heteroatoms participate to make a  $\sigma$ -bonding for stabilization to produce a new cation radical or



(Ref. 13)



(Ref. 14)



(Ref. 3)

Scheme 9. Several Dications

dication. Recently, transannular  $\sigma$ -bond formation between heteroatoms such as a combination of N-N,<sup>3</sup> S-S<sup>12,13a</sup> and S-S-S<sup>14,15</sup> has been reported and their dication salts are actually isolated and their structures have been determined by X-ray crystallographic analysis (Scheme 1-9).<sup>2,3,13</sup> On the other hand, sterically congested two or more heteroatoms substituted at the suitable positions in the aromatic ring have been found to provide exceptionally strong transannular interaction between them. The two apparently different factors which govern this transannular effect are; i) the steric strain in these systems due to bulkiness or lone pair repulsion of the substituted groups and hence works as the destabilizing repulsive effect for orbital overlapping of the heteroatoms, ii) if two heteroatoms are located within their van der Waals radii,  $\sigma$ -bond is readily formed between them upon one or two electron oxidation thus providing a considerable relaxation of the steric strain to convert repulsive force into attractive force. Staab and his coworkers employed the systematic variation of the structures of numerous aromatic compounds bearing nitrogen substituents on the effect of base strength shown in Table 1-1, and correlated well the base strength with the interactions between the two nitrogen atoms as a function of steric factor, in particular of the geometry and the bond length of the N-H-N bonds formed by proton-uptake by means of X-ray structural analysis. On the other hand, the oxidation reactions of cyclic compounds having the nearby two heteroatoms (N or S) proceed via different manners compared with that of the corresponding acyclic compounds. Here

these unusual proximity properties are discussed in detail as the results of steric interactions between the two heteroatoms.

#### Proton Sponges: N-H-N Interaction

Both acidity and basicity represent the two characteristic properties of compounds. Many informations on the dissociation constants of organic acids and bases have been described as decisive roles in the theoretical understanding of chemical bonding in organic compounds. Obviously, the strengths of acid and base depend on the structural and electronic factors of the molecules such as inductive, mesomeric, and steric effects. On the other hand, the report by Alder et al. in 1968 on unusually high basicity of a relatively simple organic compound such as **4** as compared to **1**, **2**, and **3** was the subject of considerable attention (Fig. 1-1).<sup>16,17</sup>

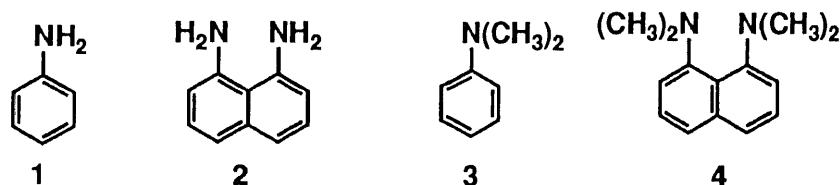


Fig. 1-1

They described that aniline **1** and 1,8-diaminonaphthalene **2** have similar basicities of typical aromatic amines, whereas 1,8-bis(dimethylamino)naphthalene **4** has a basicity of ten million times higher than that of dimethylaniline **3**.

The increase in basicity by increasing the bulkiness around the two amino groups in the peri positions is considered to be

due to the two factors which work together in the identical direction; firstly the two dialkylamino groups increasingly forces the molecules into an suitable arrangement for trapping protons. Essentially, the repulsion between the two nitrogen lone pairs at the 1,8-positions gives a destabilizing effect for the free bases; secondary the protonation on the one nitrogen atom yields a monocation in which a particularly stable intramolecular hydrogen bond bridging the two amino nitrogen atoms is formed because of the sterically fixed short N-N distance. This latter effect removes the destabilizing "lone pair" interaction and thus causes a considerable decrease in the steric strain.

In these studies, the sterically congestive effects are essentially limited to such compounds as those belonging to the class of the peridisubstituted naphthalenes. On the other hand, Staab et al. have synthesized analogously several other diamines such as **5-8** bearing two congested amino groups in space and studied the basicities and determination of the structures for these compounds.<sup>18-21</sup> Various structural factors could be responsible for the observed values in the basicity as in the series of compounds, **4** ( $pK_a=12.1$ ), **5** (12.8),<sup>19</sup> **6** (11.5),<sup>20</sup> **7** (11.9) and **8** (11.8) (Table 1-1).<sup>21</sup>



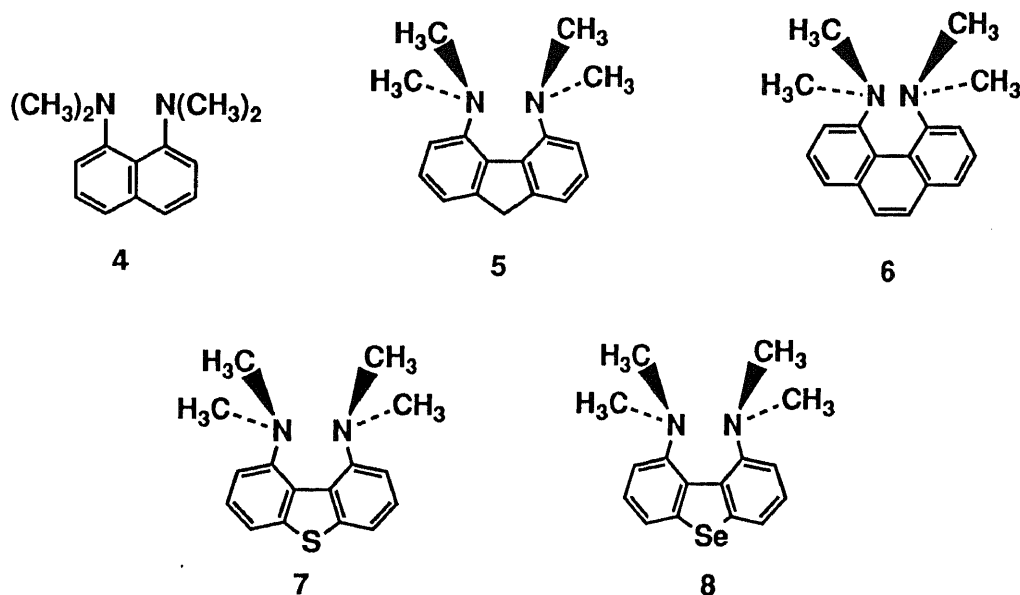
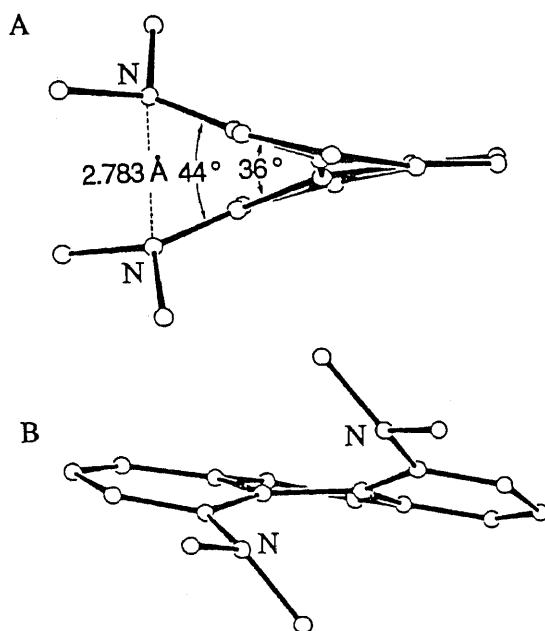
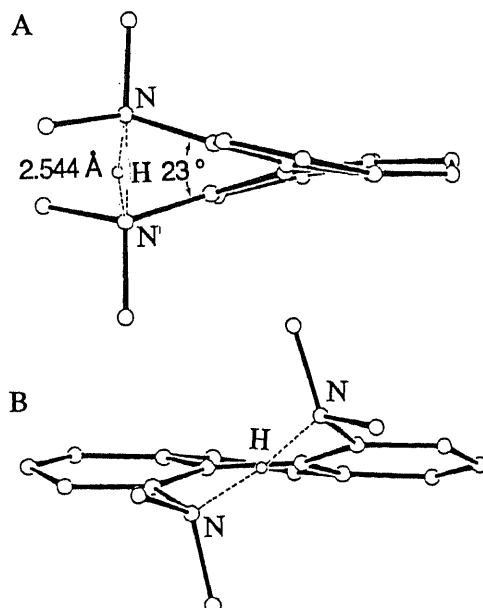
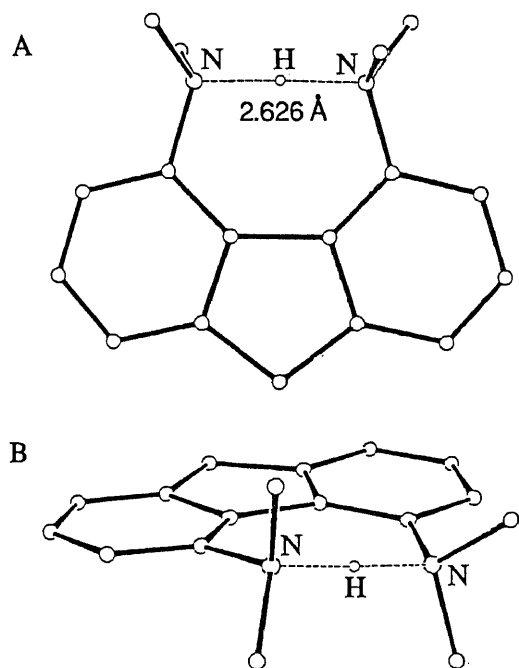


Table 1-1. Basicities of Some "Proton Sponges"; N-N Distances and N-H-N Angles in the Corresponding Monocations.

Compound	Skeleton	pKa	N-N (Å)	N-H-N (deg)
<b>4</b>	Naphthalene	12.1	2.60	141
<b>5</b>	Fluorene	12.8	2.626	178
<b>6</b>	Phenanthrene	11.5	2.544	168
<b>7</b>	Dibenzothiophene	11.9	2.587	175
<b>8</b>	Dibenzoselenophene	11.8	2.573	175

Apparently from these results 4,5-bis(dimethyl-amino)fluorene **5** has the strongest basicity in the series of changing the aromatic skeletons. A possible reason for the reduced basicity of **6** compared to **5** could be explained that as a result of the particularly large steric strain, the N-H-N hydrogen bridge in **6** is compressed beyond the energetically optimal N-N distance for a hydrogen bridge (Fig. 1-2,1-3,1-4). Also other plausible explanation is that the steric strain in **6**



is so stronger than in **4** and **5** that the protonation cannot release the steric strain of the N-N lone pair repulsion. This may also applied to the comparison of the molecular structures of **4** and **7** or **8**. Since the compounds **7** and **8** have the medium N-N distances of that of compounds **5** and **6**, the basicities of **7** and **8** lie between those of **5** and **6**.

Structures of 1,9-Bis(dimethylamino)dibenzothiophene (**7**) and Dibenzoselenophene (**8**)<sup>21</sup>

In the series of structurally similar compounds Staab et al. estimated a stepwise change in the strength of the interaction between the dimethylamino groups attached in the positions 1 and 9 of dibenzothiophene and dibenzoselenophene. On the basis of X-ray structural analyses, 1,9-bis(dimethylamino)dibenzo-  
thiophene (**7**) and 1,9-bis(dimethylamino)dibenzoselenophene (**8**) show that they have slightly torsioned forms due to repulsion between the two outer dimethylamino groups (Fig. 1-5,1-6).

The stronger interactions exist between the two dimethylamino groups, the larger the deviation appears from the planarity in the molecules. These steric forces are demonstrated by the torsional angle between the central C<sub>9a</sub>-C<sub>9b</sub> bond (21.3 °), which causes C<sub>1</sub> and C<sub>9</sub> to be displaced in opposite directions by 0.331 and 0.303 Å respectively from the plane of the five membered ring. The N<sub>1</sub> and N<sub>9</sub> atoms are also displaced 0.748 and 0.656 Å above and below from this plane, so that the N-N distance is 2.861 Å.

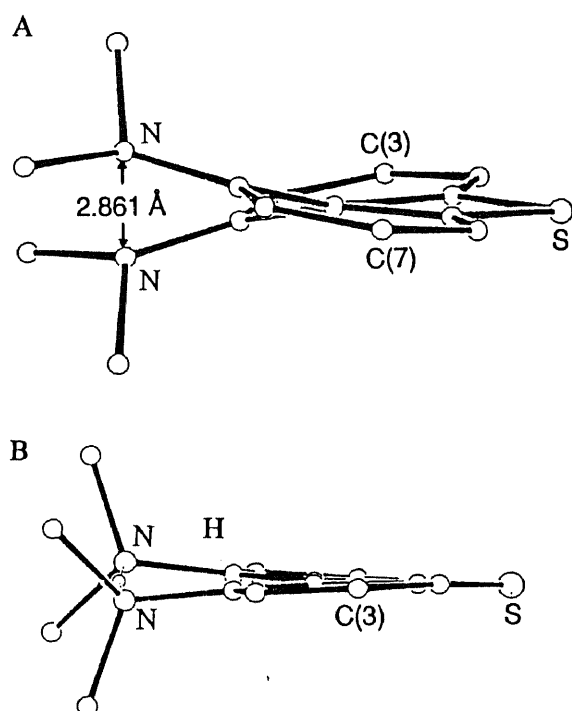


Fig. 1-5. Molecular Structure of **7** (A) and **7**-Tetrafluoroborate (B) looking from the Side along the C<sub>3</sub>-C<sub>7</sub> axis

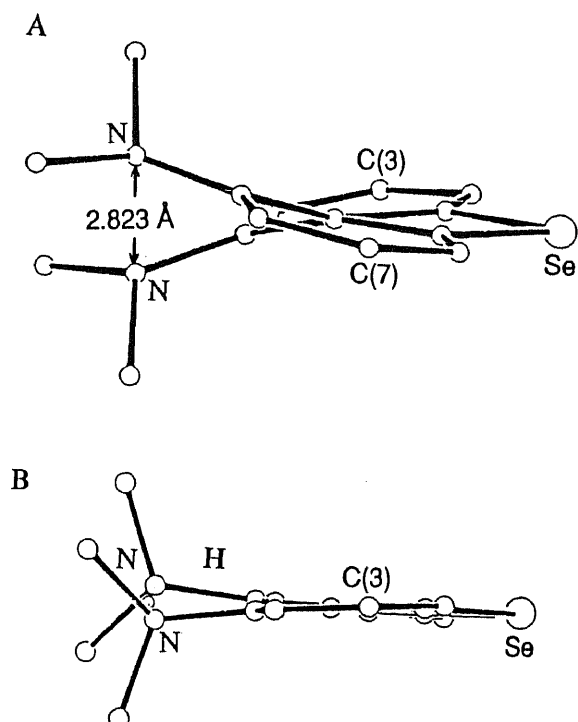


Fig. 1-6. Molecular Structure of **8** (A) and **8**-Tetrafluoroborate (B) seen from the Side along the C<sub>3</sub>-C<sub>7</sub> Axis.

A comparison of the molecular structures of **7** and the protonated **7a** (tetrafluoroborate) (Fig. 1-5) from the side view, looking the molecules along the C<sub>3</sub>-C<sub>7</sub> axis shows directly how much the protonation of **7** and the concomitant formation of a strong N-H-N hydrogen bridge leads to a relief of the steric strain: in **7a** the torsional angle around the central C-C bond is only 7.7 ° (instead of 21.3 ° in **7**) and the N-N distance is reduced by 0.274 to 2.587 Å. The N-H-N bridge is almost linear, the angle being 175 °.

The compound **8** also gives a mono tetrafluoroborate **8a**, in the <sup>1</sup>H-NMR the N-H-N proton absorbs at 19.28 ppm (DMSO-d<sub>6</sub>, 500 MHz). The structures of **8** and **8a** are analogous to those of the

sulfur compounds **7** and **7a**. A comparison of torsional angles between **8** and the monoprotonated cation **8a** (Fig. 1-6) shows clearly the reduction in the steric strain on protonation. The N-N distance is reduced from 2.823 to 2.573 Å, and the N-H-N bridge is here again almost linear (175 °).

#### Reaction of Cyclic and Rigid Compounds

As described above, sterically congested compounds containing nitrogens have interesting characters by forming a strong hydrogen bonding with respect to their nitrogen substituents. On the other hand, analogous phenomena using sulfur compounds have been rarely observed. A few known examples are shown below.

Hydrolysis of cyclic naphthalene-1,8-thiosulfinate and naphthalene-1,8-thiosulfonate was found to have different reaction rate as compared to the corresponding acyclic compounds (Fig. 1-7).<sup>22</sup>

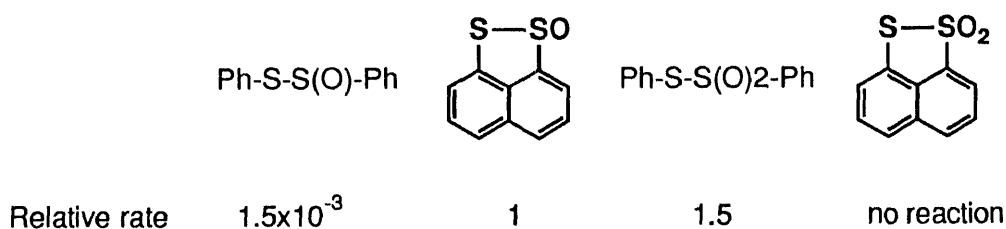
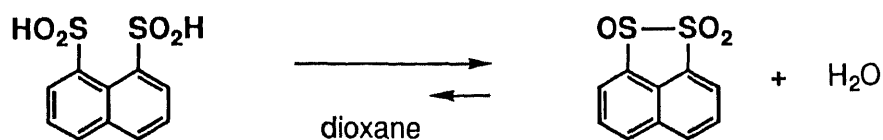
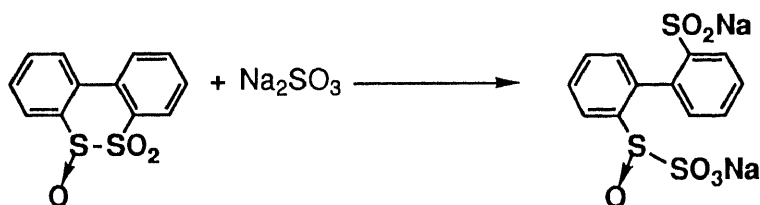


Fig. 1-7



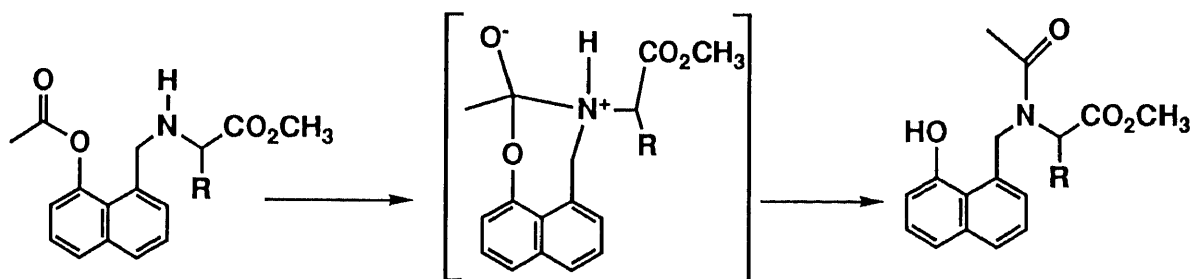
Scheme 1-10

The hydrolysis of acyclic sulfinylsulfones was performed in aqueous dioxane to give the sulfinic acids, but in the case of sterically congested cyclic compound, the rate of the hydrolysis of i.e. naphthalene-1,8-sulfinylsulfone proceeds slowly (Scheme 1-10).<sup>23</sup>



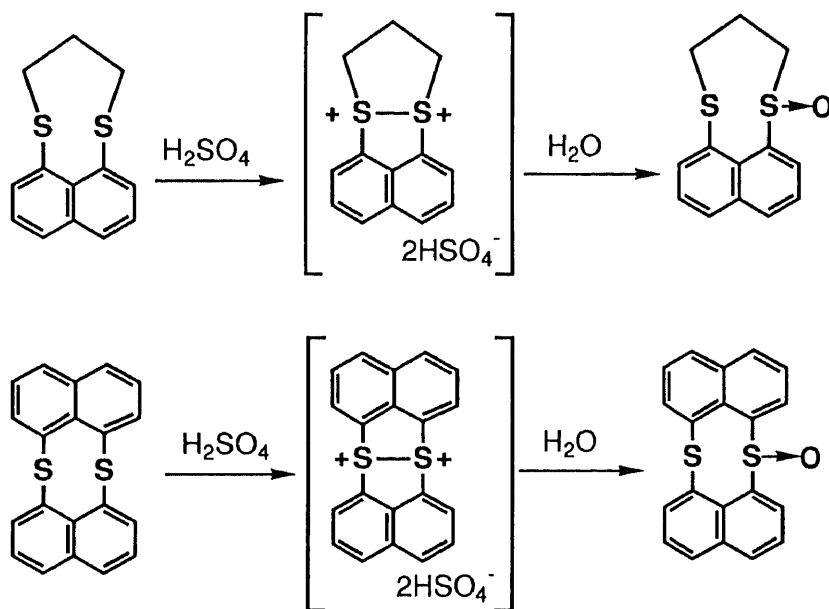
Scheme 1-11

On the other hand, the substitution reaction of biphenylene-2,2'-sulfinylsulfone with  $\text{Na}_2\text{SO}_3$  was found to undergo readily to give the ring opening product (Scheme 1-11).<sup>24</sup> These results reveal clearly that if cyclic compounds containing sulfur atoms constitute sterically congested rigid forms the nucleophilic substitution reactions using these substrates should proceed unexpectedly different manner comparing to non strained compounds.



Scheme 1-12

Kemp et al. have reported that the O,N-acyl transfer reaction using methyl N-[(8-acetoxy-1-naphthyl)methylene]-2-aminoacetate proceeds via a cyclic intermediate and the reaction rates are influenced by the steric strain of the corresponding cyclic intermediate (Scheme 1-12).<sup>25</sup>



Scheme 1-13

Recently, it has been reported that the cyclic 1,8-dithiosubstituted naphthalenes react with concentrated sulfuric acid to give the stable dithia dication intermediates on oxidation and then these dication intermediates were treated with water to give the corresponding monosulfoxides (Scheme 1-13).<sup>26,27</sup> These compounds have been known to have the very closely located two sulfur atoms at the peri positions and hence to possess the strong interaction between these sulfur atoms.

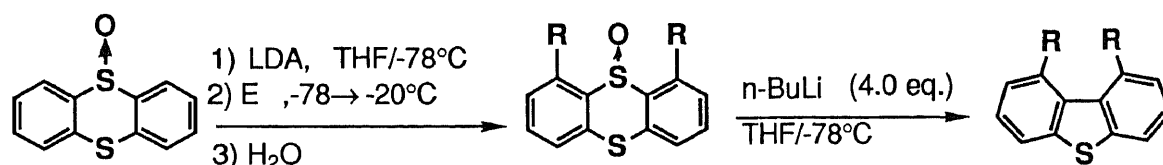
As described above, the compounds having sterically congested substituents in the molecule show quite often the strange reactivities as compared with that of the simply hindered compounds. Therefore, it is noteworthy to undergo the studies with respect to the nature of the sterically congested compounds and to reveal how steric strain creates unexpected influences on the normal reactions.

This thesis describes the following studies: i) a new methodology was invented for the synthesis of sterically congested 1,9-disubstituted dibenzothiophenes using ligand coupling reaction of 4,6-disubstituted thianthrene-5-oxides; ii) these dibenzothiophenes having strong interactions between the two outer sulfur atoms produced a new dithia dications; iii) photolysis and thermolysis of these sterically congested dibenzothiophene derivatives gave novel dibenzodithiopentalene, triphenylenothiophene and tribenzodithioazulene.

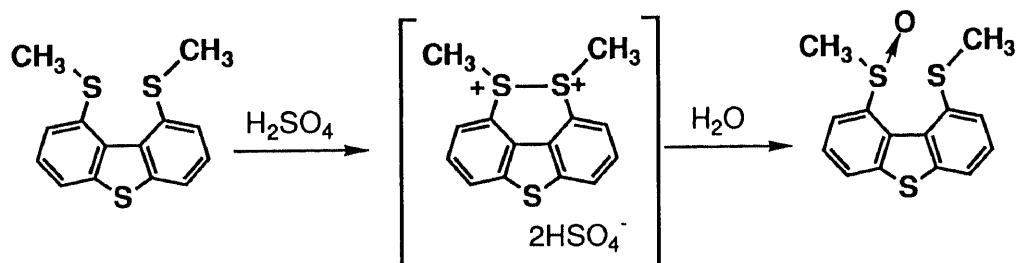
Each chapter is consisted of the following topics.

Chapter 2: Sterically congested 1,9-disubstituted dibenzothiophenes were synthesized by the ortho lithiation of thianthrene-5-oxide with lithiumdiisopropylamide (LDA), and subsequent ligand coupling reactions of 4,6-disubstituted thianthrene-5-oxides with *n*-butyllithium. The structure of 1,9-bis(phenylthio)dibenzothiophene was determined by X-ray crystallographic analysis.

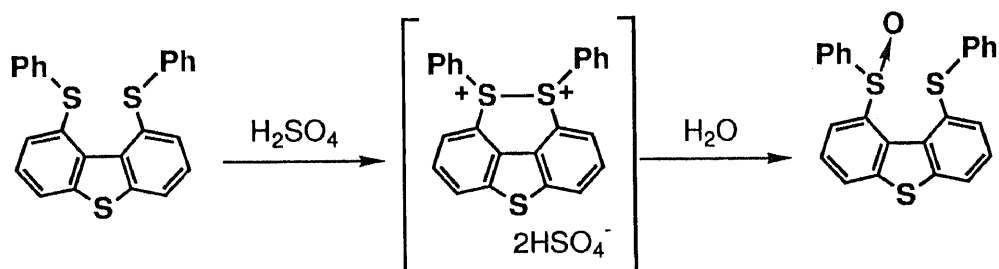




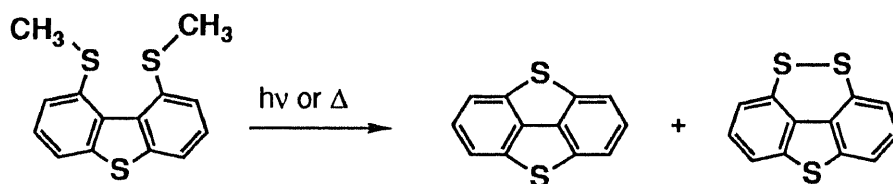
Chapter 3: 1,9-Bis(methylthio)dibenzothiophene and 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene reacted with concentrated sulfuric acid to give the corresponding dithia dications of which generation was identified by  $^1\text{H}$ -NMR spectroscopy and by isolation. Whereas the analogous compounds 2,8-bis(methylthio)dibenzothiophene and 1-(methylthio)dibenzothiophene decomposed in conc. sulfuric acid. These results suggest that the  $\sigma$ -bond is formed between the two sulfur atoms to stabilize the dication.



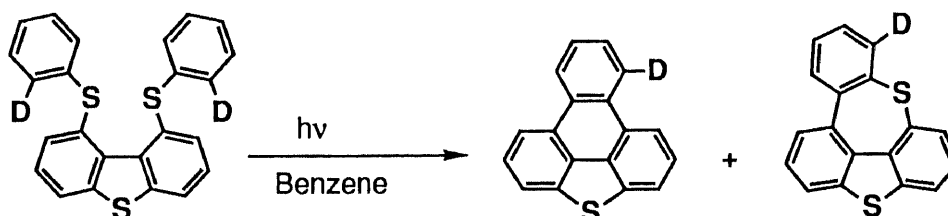
Chapter 4: The structure of 1-(phenylsulfinyl)-9-(phenylthio)-dibenzothiophene was determined by X-ray crystallographic analysis. Formation and detection of 1,9-bis(arylethio)dibenzothiophene dication were performed by the  $^1\text{H}$ -NMR and FAB MS in conc.  $\text{H}_2\text{SO}_4$ . The structure of dithia dication in the conc.  $\text{H}_2\text{SO}_4$  solution was estimated by variable temperature  $^1\text{H}$ -NMR.



Chapter 5: A novel dibenzo[*bc,fg*][1,4]dithiopentalene was obtained by photolysis and thermolysis of 1,9-bis(methylthio)-dibenzothiophene. Its structure was confirmed by the X-ray crystallographic analysis revealing that the compound has a completely planar form.



Chapter 6: The photolysis of 1,9-bis(arylthio)dibenzothiophenes was performed in benzene solution to give the cyclization products triphenylenothiophene and tribenzodithioazulene. Deuterium tracer experiment indicates that the cyclization reactions proceed intramolecularly.



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## CHAPTER 2

### A CONVENIENT PREPARATION OF STERICALLY CROWDED 1,9-DISUBSTITUTED DIBENZOTHIOPHENES AND 3,3'-DISUBSTITUTED DIARYL SULFIDES

#### Abstract

Thianthrene-5-oxide (1) reacted with 2.2 equivalents of lithium diisopropylamide (LDA) to give 4,6-dilithiated 1 which was treated with several electrophiles to produce 4-substituted thianthrene-5-oxides (2) and 4,6-disubstituted thianthrene-5-oxides (3). Compounds 3 were further treated with *n*-butyllithium to afford sterically crowded 1,9-disubstituted dibenzothiophenes (4) in moderate yields.

## Introduction

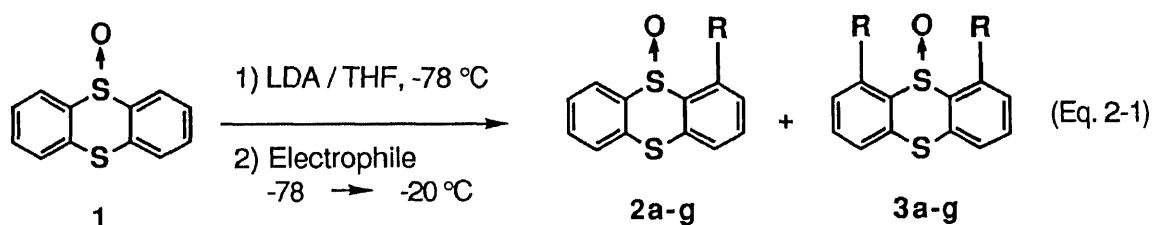
The regiospecific ortho metallation of aromatic compounds has been focused much attention in organic synthesis.<sup>1</sup> In 1955, Gilman reported that the lithiation of thianthrene-5-oxide (**1**) using *n*-butyllithium as a base afforded not only the *o*-lithiated **1** but also the ligand coupling (dibenzothiophene) and the reduction products simultaneously.<sup>2</sup> Recently, simple regiospecific *o*-lithiation of diaryl sulfoxides having phenyl or pyridyl substituents was performed using lithiumdiisopropylamide (LDA) instead of *n*-butyllithium.<sup>3,4</sup> On the other hand, thianthrene-5-oxide (**1**) was converted to 2,2'-disubstituted diaryl sulfides by treating initially with Grignard reagents and subsequently with aldehydes.<sup>5</sup>

In order to utilize *o*-lithiation reactions of diaryl sulfoxides for organic synthesis, the reactions of **1** with lithiumdiisopropylamide (LDA)<sup>3,4</sup> and subsequently with several electrophiles were examined. In this chapter, convenient preparations of sterically crowded 1,9-disubstituted dibenzothiophenes (**4**) and 3,3'-disubstituted diphenyl sulfides (**5**) are reported via the ligand coupling and ligand exchange reactions of 4,6-disubstituted thianthrene-5-oxides (**3**).<sup>6</sup>

## Results and Discussion

### Synthesis of 4,6-Disubstituted Thianthrene-5-oxides (3)

When thianthrene-5-oxide (**1**) was treated with LDA at  $-78^{\circ}\text{C}$  in THF, mono- and dilithiated **1** were produced. Then these lithiated **1** were treated with several electrophiles to give numerous 4- and 4,6-disubstituted thianthrene-5-oxides (**2,3**) (Eq. 2-1). The ratio of the compounds **2** and **3** changed enormously by changing the molar equivalent of LDA. These results are summarized in Table 2-1.

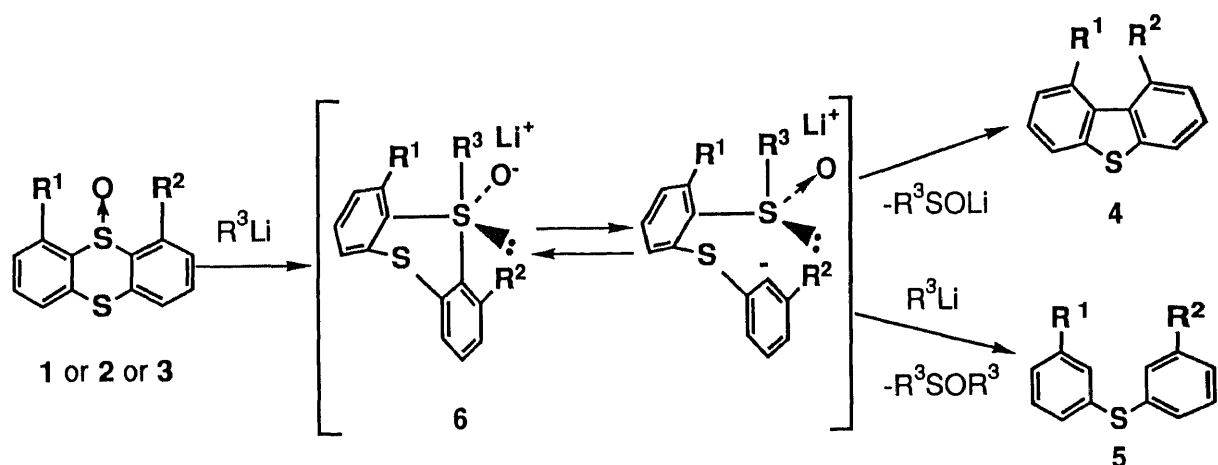
Table 2-1. Reaction of **1** with LDA and Electrophiles

LDA(eq.)	Electrophile	R	Yield(%)	
			2	3
1.1	( <i>p</i> -TolS) <sub>2</sub>	<i>p</i> -TolS	66 (2a)	21 (3a)
2.2	( <i>p</i> -TolS) <sub>2</sub>	<i>p</i> -TolS	26 (2a)	53 (3a)
1.1	(PhS) <sub>2</sub>	PhS	61 (2b)	19 (3b)
2.2	(PhS) <sub>2</sub>	PhS	25 (2b)	61 (3b)
1.1	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S	55 (2c)	26 (3c)
2.2	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S	29 (2c)	38 (3c)
2.2	S <sub>8</sub> + MeI	MeS	87 (2d)	trace (3d)
3.3	S <sub>8</sub> + MeI	MeS	trace (2d)	63 (3d)
2.2	(PhSe) <sub>2</sub>	PhSe	10 (2e)	63 (3e)
2.2	PhCHO	PhCHOH	77 (2f)	0 (3f)
2.2	Me <sub>3</sub> SiCl	Me <sub>3</sub> Si	4 (2g)	65 (3g)



### Ring Contraction of 4,6-Disubstituted Thianthrene-5-oxides (3)

It has been known that one can introduce the substituents to the 4,6-positions of dibenzothiophene but the introduction of the two substituents to the 1,9-positions of **4k** is very difficult, since dibenzothiophene has no reactive protons on the 1,9-positions. Recently it was found that when the reactions of **2** and **3** bearing sulfenyl moieties were carried out using *n*-butyllithium or phenyllithium, both the ring contraction and ring opening reactions took place simultaneously affording the corresponding dibenzothiophenes (**4**) and diphenyl sulfide derivatives (**5**) (Scheme 2-1). The results are shown in Table 2-2.



Scheme 2-1

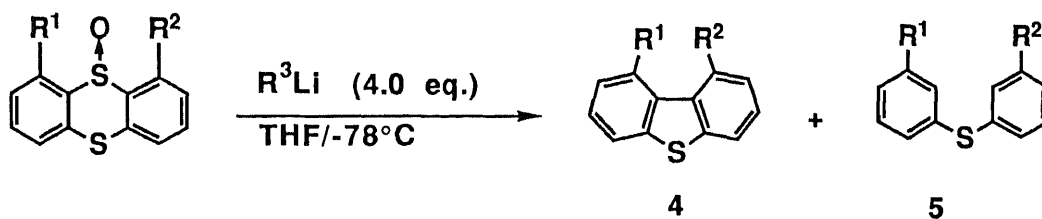


Table 2-2. Reactions of Substituted Thianthrene-5-oxides with Organolithium Reagents

Run	Substrate	R <sup>1</sup>	R <sup>2</sup>	Yield (%)	
				4	5
1 <sup>a</sup>	3c	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S	59 (4c)	30 (5c)
2 <sup>a</sup>	3b	PhS	PhS	65 (4b)	25 (5b)
3 <sup>b</sup>	3b	PhS	PhS	49 (4b)	17 (5b)
4 <sup>a</sup>	3a	<i>p</i> -TolS	<i>p</i> -TolS	46 (4a)	40 (5a)
5 <sup>a</sup>	3h	PhS	MeS	19 (4h)	35 (5h)
6 <sup>a</sup>	2b	PhS	H	10 (4j)	70 (5j)
7 <sup>b</sup>	2b	PhS	H	50 (4j)	45 (5j)
8 <sup>a</sup>	2a	<i>p</i> -TolS	H	10 (4i)	52 (5i)
9 <sup>a</sup>	3d	MeS	MeS	22 (4d)	65 (5d)
10 <sup>a</sup>	1	H	H	4 (4k)	42 (5k)
11 <sup>b</sup>	1	H	H	78 (4k)	trace (5k)

<sup>a</sup> R<sup>3</sup>Li: *n*-butyllithium, <sup>b</sup> R<sup>3</sup>Li: phenyllithium.

Diaryl sulfoxides have never been known affording biaryl derivatives by the reactions with organometallic reagents. These reactions of 4,6-disubstituted thianthrene-5-oxides (3) with organolithium reagents are attractive not only for investigating the mechanism of the coupling reactions of diaryl sulfoxides but also for providing a convenient preparation of various dibenzothiophene derivatives (4). The reactions should be initiated by the attack of organolithium on the sulfinyl sulfur atom to form the sulfurane (6) as an intermediate which

gives **4** and **5** via the intramolecular ligand coupling or ligand exchange process.<sup>6</sup> On the basis of X-ray crystallographic analysis, it is clear that 1,9-disubstituted dibenzothiophene **4** has a distorted form arising from steric repulsion between the two substituents. Therefore, it is suggested that the ligand exchange reaction (ipso substitution reaction) hardly takes place by this steric repulsion. Furthermore, the fact that the sulfoxides (**3a-c**) bearing arylthio substituents gave better yields of the coupling products than the methylthio derivative (**3d**) indicates that the ligand coupling reaction of **3a-c** undergoes favorably due to the electronic stabilization of the intermediate,  $\sigma$ -sulfurane (**6**) by the presence of two electron-withdrawing arylthio groups (Scheme 2-1).

The present investigation provides convenient and simple procedures for preparation of sterically congested 1,9-dithiasubstituted dibenzothiophenes (**4**) which are hardly prepared by the common methods.

#### **X-ray Crystallographic Analysis of 1,9-Bis(phenylthio)-dibenzothiophene (**4b**)**

The detailed structural analysis of **4b** was performed by X-ray crystallographic analysis. The ORTEP drawing of **4b** is depicted in Fig. 2-1. The molecular structure of **4b** indicates that the central thiophene ring is considerably distorted due to the steric repulsion between the two phenylthio groups attached at the C<sub>8</sub> and the C<sub>12</sub> atoms but the distance between the two sulfur atoms is 3.012Å which is within van der Waals contact

(3.70Å).<sup>7</sup> The two phenyl rings are located at anti orientation and are close to the dibenzothiophene ring.

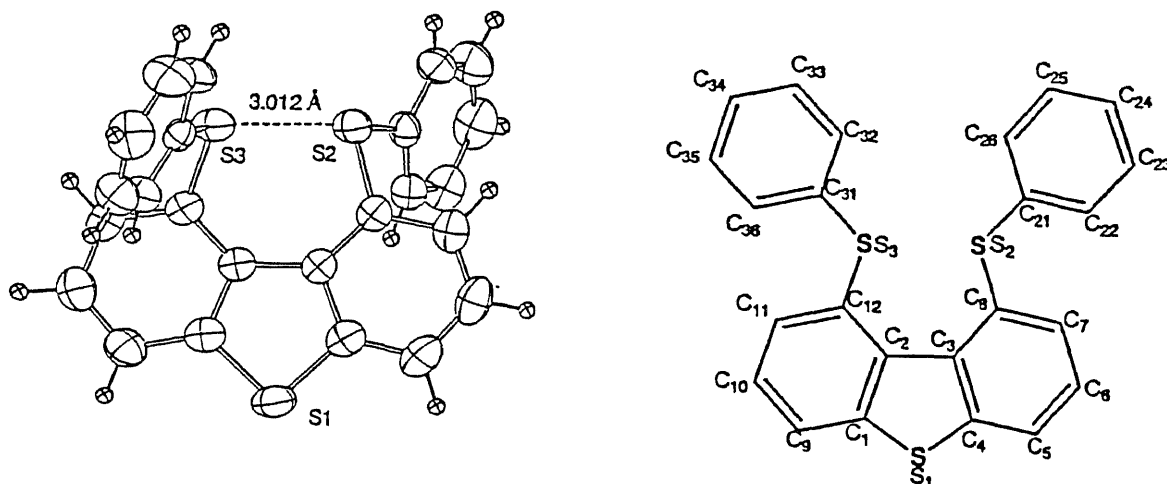


Fig. 2-1. X-Ray Crystallographic Analysis of **4b**

Table 2-3. Bond Distances of 1,9-Bis(phenylthio)dibenzothiophene (**4b**)

Atoms	distance (Å)	ESD	Atoms	distance (Å)	ESD
S <sub>1</sub> -C <sub>1</sub>	1.746	0.003	C <sub>9</sub> -C <sub>10</sub>	1.375	0.005
S <sub>1</sub> -C <sub>4</sub>	1.743	0.003	C <sub>10</sub> -C <sub>11</sub>	1.395	0.005
S <sub>2</sub> -C <sub>8</sub>	1.786	0.003	C <sub>11</sub> -C <sub>12</sub>	1.388	0.004
S <sub>2</sub> -C <sub>21</sub>	1.783	0.003	C <sub>21</sub> -C <sub>22</sub>	1.379	0.004
S <sub>3</sub> -C <sub>12</sub>	1.775	0.003	C <sub>21</sub> -C <sub>26</sub>	1.397	0.004
S <sub>3</sub> -C <sub>31</sub>	1.781	0.003	C <sub>22</sub> -C <sub>23</sub>	1.399	0.006
C <sub>1</sub> -C <sub>2</sub>	1.414	0.004	C <sub>23</sub> -C <sub>24</sub>	1.370	0.006
C <sub>1</sub> -C <sub>9</sub>	1.395	0.005	C <sub>24</sub> -C <sub>25</sub>	1.381	0.005
C <sub>2</sub> -C <sub>3</sub>	1.456	0.004	C <sub>25</sub> -C <sub>26</sub>	1.388	0.005
C <sub>2</sub> -C <sub>12</sub>	1.412	0.004	C <sub>31</sub> -C <sub>32</sub>	1.380	0.004
C <sub>3</sub> -C <sub>4</sub>	1.417	0.004	C <sub>31</sub> -C <sub>36</sub>	1.391	0.004
C <sub>3</sub> -C <sub>8</sub>	1.413	0.004	C <sub>32</sub> -C <sub>33</sub>	1.383	0.005
C <sub>4</sub> -C <sub>5</sub>	1.395	0.005	C <sub>33</sub> -C <sub>34</sub>	1.378	0.006
C <sub>5</sub> -C <sub>6</sub>	1.373	0.005	C <sub>34</sub> -C <sub>35</sub>	1.369	0.006
C <sub>6</sub> -C <sub>7</sub>	1.379	0.005	C <sub>35</sub> -C <sub>36</sub>	1.384	0.006
C <sub>7</sub> -C <sub>8</sub>	1.402	0.004			

Table 2-4. Bond Angles of 1,9-Bis(phenylthio)dibenzothiophene  
(4b)

Atoms	angle (deg.)	ESD	Atoms	angle (deg.)	ESD
C <sub>1</sub> -S <sub>1</sub> -C <sub>4</sub>	91.28	0.15	C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	119.78	0.34
C <sub>8</sub> -S <sub>2</sub> -C <sub>21</sub>	100.07	0.13	C <sub>10</sub> -C <sub>11</sub> -C <sub>12</sub>	121.81	0.31
C <sub>12</sub> -S <sub>3</sub> -C <sub>31</sub>	101.49	0.13	S <sub>3</sub> -C <sub>12</sub> -C <sub>2</sub>	121.67	0.21
S <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	112.64	0.22	S <sub>3</sub> -C <sub>12</sub> -C <sub>11</sub>	118.16	0.23
S <sub>1</sub> -C <sub>1</sub> -C <sub>9</sub>	124.54	0.25	C <sub>2</sub> -C <sub>12</sub> -C <sub>11</sub>	119.31	0.27
C <sub>2</sub> -C <sub>1</sub> -C <sub>9</sub>	122.73	0.28	S <sub>2</sub> -C <sub>21</sub> -C <sub>22</sub>	117.43	0.23
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	111.41	0.24	S <sub>2</sub> -C <sub>21</sub> -C <sub>26</sub>	122.42	0.22
C <sub>1</sub> -C <sub>2</sub> -C <sub>12</sub>	116.71	0.25	C <sub>22</sub> -C <sub>21</sub> -C <sub>26</sub>	119.94	0.27
C <sub>3</sub> -C <sub>2</sub> -C <sub>12</sub>	131.67	0.25	C <sub>21</sub> -C <sub>22</sub> -C <sub>23</sub>	119.59	0.32
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	111.23	0.24	C <sub>22</sub> -C <sub>23</sub> -C <sub>24</sub>	120.50	0.38
C <sub>2</sub> -C <sub>3</sub> -C <sub>8</sub>	132.24	0.25	C <sub>23</sub> -C <sub>24</sub> -C <sub>25</sub>	120.02	0.36
C <sub>4</sub> -C <sub>3</sub> -C <sub>8</sub>	116.30	0.25	C <sub>24</sub> -C <sub>25</sub> -C <sub>26</sub>	120.34	0.32
S <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	112.70	0.21	C <sub>21</sub> -C <sub>26</sub> -C <sub>25</sub>	119.57	0.28
S <sub>1</sub> -C <sub>4</sub> -C <sub>5</sub>	124.02	0.24	S <sub>3</sub> -C <sub>31</sub> -C <sub>32</sub>	126.01	0.22
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	123.13	0.28	S <sub>3</sub> -C <sub>31</sub> -C <sub>36</sub>	114.31	0.22
C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	117.98	0.31	C <sub>32</sub> -C <sub>31</sub> -C <sub>36</sub>	119.68	0.27
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	121.21	0.32	C <sub>31</sub> -C <sub>32</sub> -C <sub>33</sub>	119.84	0.30
C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	121.00	0.32	C <sub>32</sub> -C <sub>33</sub> -C <sub>34</sub>	120.68	0.36
S <sub>2</sub> -C <sub>8</sub> -C <sub>3</sub>	122.76	0.21	C <sub>33</sub> -C <sub>34</sub> -C <sub>35</sub>	119.36	0.38
S <sub>2</sub> -C <sub>8</sub> -C <sub>7</sub>	116.86	0.22	C <sub>34</sub> -C <sub>35</sub> -C <sub>36</sub>	120.94	0.38
C <sub>3</sub> -C <sub>8</sub> -C <sub>7</sub>	119.67	0.27	C <sub>31</sub> -C <sub>36</sub> -C <sub>35</sub>	119.47	0.33
C <sub>1</sub> -C <sub>9</sub> -C <sub>10</sub>	118.61	0.32			

The crystal data for **4b**; C<sub>24</sub>H<sub>16</sub>S<sub>3</sub>, monoclinic, space group P2<sub>1</sub>/n, a=17.862(2), b=8.050(2), c=13.594(2) Å, β=95.74(1)°, V=1938.4(5) Å<sup>3</sup>, z=4, D<sub>x</sub>=1.373 gcm<sup>-3</sup>, μ (Mo-Kα)=0.372 mm<sup>-1</sup>, R=0.0526 (wR=0.0744).

## Experimental Section

### General.

IR were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer.  $^1\text{H}$ -NMR spectra were measured on a Hitachi R-600 or a JEOL JNM-EX270 or a Bruker AM-500.  $^{13}\text{C}$ -NMR spectra were taken with a JEOL JNM-EX270 or a Bruker AM-500. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX SX102 mass spectrometer. Elemental analyses were carried out by Chemical Analysis Center at this University. X-ray crystallographic analysis was performed by Prof. Iwasaki at University of Electro-Communications.

### Materials.

All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Kanto Chemical Co., or Aldrich Chemical Co.. The reaction solvents were further purified by general methods.

### Synthesis

#### 4-(*p*-Tolylthio)thianthrene-5-oxide (2a) and 4,6-Bis(*p*-tolylthio)thianthrene-5-oxide (3a)

Thianthrene-5-oxide **1** (464 mg, 2 mmol) dissolved in THF (20 ml) was lithiated with 0.22 M lithiumdiisopropylamide (LDA) (10 ml, 2.2 mmol) at  $-78\text{ }^{\circ}\text{C}$ . To this solution was added *p*-tolyl disulfide (1.23 g, 5 mmol) in THF (10 ml). After usual work-up and purification by column chromatography (silica gel; eluent,  $\text{CH}_2\text{Cl}_2$ ) and then preparative liquid chromatography, 4-(*p*-tolylthio)thianthrene-5-oxide (**2a**) and 4,6-bis(*p*-tolyl-

thio)thianthrene-5-oxide (**3a**) were obtained in 66 and 21% yields respectively.

Similarly, thianthrene-5-oxide **1** (464 mg, 2 mmol) dissolved in THF (20 ml) was lithiated with 0.44 M LDA (10 ml, 4.4 mmol) at -78 °C and then was treated with *p*-tolyl disulfide (2.46 g, 10 mmol) in THF (10 ml) to give 4-(*p*-tolylthio)thianthrene-5-oxide (**2a**) and 4,6-bis(*p*-tolylthio)thianthrene-5-oxide (**3a**) in 26 and 53% yields respectively.

**2a**: mp 212-213.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.93-6.90 (m, 14H, Ar-H); IR (KBr) 1025 cm<sup>-1</sup>; MS (m/z) 354 (M<sup>+</sup>); Anal. Calcd for C<sub>19</sub>H<sub>14</sub>OS<sub>3</sub>: C, 64.37; H, 3.98. Found: C, 64.42; H, 4.01.

**3a** (Ar=*p*-Tol) mp. 272-275 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.0 Hz, 2H, Ar-H), 7.38 (d, J=7.8 Hz, 4H, Ar-H), 7.25 (t, J=7.8 Hz, 2H, Ar-H), 7.10 (d, J=7.8 Hz, 4H, Ar-H), 7.04 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.0 Hz, 2H, Ar-H), 2.37 (s, 6H, CH<sub>3</sub>); IR (KBr) 1046 cm<sup>-1</sup>; MS (m/z) 476 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>4</sub>: C, 65.51; H, 4.23. Found: C, 65.22; H, 4.15.

**4-(Phenylthio)thianthrene-5-oxide (2b) and 4,6-Bis-(phenylthio)thianthrene-5-oxide (3b)**

**2b**: mp 149-150 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.83-6.97 (m, 12H, Ar-H); IR (KBr) 1038 cm<sup>-1</sup>; MS (m/z) 340 (M<sup>+</sup>); Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>OS<sub>3</sub>: C, 63.50; H, 3.55. Found: C, 63.42; H, 3.49.

**3b**: mp 212.5-213.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.82-6.83 (m, 16H, Ar-H); IR (KBr) 1027 cm<sup>-1</sup>; MS (m/z) 432 (M<sup>+</sup>-16); Anal. Calcd for C<sub>24</sub>H<sub>16</sub>OS<sub>4</sub>: C, 64.25; H, 3.59. Found: C, 64.07; H, 3.62.

**4-(p-Chlorophenylthio)thianthrene-5-oxide (2c) and 4,6-Bis(p-chlorophenylthio)thianthrene-5-oxide (3c)**

**2c:** mp 195.5 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.83-7.13 (m, 11H, Ar-H); IR (KBr) 1015  $\text{cm}^{-1}$ ; MS (m/z) 374 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{ClOS}_3$ : C, 57.66; H, 2.96. Found: C, 57.54; H, 2.98.

**3c:** mp 259-261 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.90-7.03 (m, 14H, Ar-H); IR (KBr) 1015  $\text{cm}^{-1}$ ; MS (m/z) 516 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{OS}_4$ : C, 55.70; H, 2.73. Found: C, 55.61; H, 2.51.

**4-(Phenylseleno)thianthrene-5-oxide (2e) and 4,6-Bis(phenylseleno)thianthrene-5-oxide (3e)**

**2e:** mp 156 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.83-6.97 (m, 12H, Ar-H); IR (KBr) 1036  $\text{cm}^{-1}$ ; MS (m/z) 388 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{12}\text{OS}_2\text{Se}$ : C, 55.81; H, 3.12. Found: C, 55.69; H, 3.14.

**3e:** mp 202-203 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.82-6.83 (m, 16H, Ar-H); IR (KBr) 1035  $\text{cm}^{-1}$ ; MS (m/z) 544 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{24}\text{H}_{16}\text{OS}_2\text{Se}_2$ : C, 53.14; H, 2.97. Found: C, 52.89; H, 3.04.

**4-(1-Phenyl-1-hydroxymethyl)thianthrene-5-oxide (2f)**

**2f:** mp 157-158 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.79-7.03 (m, 12H, Ar-H), 6.68 (s, 0.3H, CH), 6.39 (s, 0.7H, CH), 3.97 (bs, 1H, OH); Anal. Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}_2$ : C, 67.43; H, 4.17. Found: C, 67.21; H, 4.29.

**4-(Trimethylsilyl)thianthrene-5-oxide (2g) and 4,6-Bis(trimethylsilyl)thianthrene-5-oxide (3g)**

**2g:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.98-7.12 (m, 7H, Ar-H), 0.52 (s, 9H,  $\text{CH}_3$ ); IR (KBr) 1020  $\text{cm}^{-1}$ ; MS (m/z) 304 ( $\text{M}^+$ ).

**3g:** mp 214.5-215 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.73-7.14 (m, 6H, Ar-H), 0.57 (s, 18H,  $\text{CH}_3$ ); IR (KBr) 1025  $\text{cm}^{-1}$ ; MS (m/z) 376 ( $\text{M}^+$ ); Anal.



Calcd for  $C_{18}H_{24}OS_2Si_2$ : C, 57.39; H, 6.42. Found: C, 57.31; H, 6.39.

**4-(Methylthio)thianthrene-5-oxide (2d) and 4,6-Bis-(methylthio)thianthrene-5-oxide (3d)**

Thianthrene-5-oxide **1** (232 mg, 1 mmol) dissolved in THF (5 ml) was lithiated with 0.44 M LDA (5 ml, 2.2 mmol) at  $-78\text{ }^{\circ}\text{C}$ . To this solution was added elemental sulfur (1.09 g, 5 mmol). After 12 h,

(10 ml, 100 mmol) was added with a syringe and the solution was stirred for 6 h. After work-up and purification by column chromatography (silica gel; eluent,  $\text{CH}_2\text{Cl}_2$ ) and then preparative liquid chromatography, 4-(methylthio)thianthrene-5-oxide (**2d**) was obtained in 87% yield together with a trace of 4,6-bis(methylthio)thianthrene-5-oxide (**3d**).

Similar treatment of thianthrene-5-oxide **1** (232 mg, 1 mmol) dissolved in THF (5 ml) with 0.66 M LDA (5 ml, 3.3 mmol) at  $-78\text{ }^{\circ}\text{C}$  then with elemental sulfur (1.09 g, 5 mmol) and

(10 ml, 100 mmol) gave 4,6-bis(methylthio)thianthrene-5-oxide (**3d**) in 63% yield together with a trace of 4-(methylthio)thianthrene-5-oxide (**2d**).

**2d**: mp  $128\text{ }^{\circ}\text{C}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.13–7.87 (m, 1H, Ar-H), 7.67–7.12 (m, 6H, Ar-H), 2.76 (s, 3H,  $\text{CH}_3$ ); Anal. Calcd for  $C_{13}H_{10}OS_3$ : C, 63.50; H, 3.55. Found: C, 63.42; H, 3.49.

**3d**: mp  $190.5\text{--}191.5\text{ }^{\circ}\text{C}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.69–7.06 (m, 16H, Ar-H), 2.59 (s, 1H,  $\text{CH}_3$ ); IR (KBr)  $1020\text{ cm}^{-1}$ ; MS ( $m/z$ ) 324 ( $M^+$ ); Anal. Calcd for  $C_{14}H_{12}OS_4$ : C, 51.82; H, 3.73. Found: C, 51.96; H, 3.75.

**Preparation of 1,9-Disubstituted Dibenzothiophenes (4) by Ring Contraction of 4,6-Disubstituted Thianthrene-5-oxides (3) with *n*-Butyllithium.**

**1,9-Bis(phenylthio)dibenzothiophene (4b) and 3,3'-Bis(phenylthio)diphenyl Sulfide (5b)**

4,6-Bis(phenylthio)thianthrene-5-oxide (**3b**) (896 mg, 2 mmol) dissolved in THF (20 ml) was treated with *n*-butyllithium (10 ml, 2.2 mmol) at -78 °C. After usual work-up procedures and purification by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub>) and then preparative liquid chromatography, 1,9-bis(phenylthio)dibenzothiophene (**4b**) and 3,3'-bis(phenylthio)diphenyl sulfide (**5b**) in 65 and 25% yields respectively.

4,6-Bis(phenylthio)thianthrene-5-oxide (**3b**) (464 mg, 2 mmol) dissolved in THF (20 ml) was treated with phenyllithium (10 ml, 2.2 mmol) at -78 °C to give 1,9-bis(phenylthio)dibenzothiophene (**4b**) and 3,3'-bis(phenylthio)diphenyl sulfide (**5b**) were obtained in 49 and 17% yields respectively.

**4b:** (R<sup>1</sup>=R<sup>2</sup>=PhS), mp 212.5-213.5 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, J<sub>1</sub>=7.9 Hz, J<sub>2</sub>=0.8 Hz, 2H, Ar-H), 7.89 (dd, J<sub>1</sub>=7.9 Hz, J<sub>2</sub>=0.8 Hz, 2H, Ar-H), 7.61 (t, J=7.9 Hz, 2H, Ar-H), 7.50-7.45 (m, 4H, Ar-H), 7.38-7.31 (m, 6H, Ar-H); MS (m/z) 400 (M<sup>+</sup>); Anal. Calcd for C<sub>24</sub>H<sub>16</sub>S<sub>3</sub>: C, 71.96; H, 4.03. Found: C, 72.06; H, 4.04.

**5b:** (R<sup>1</sup>=R<sup>2</sup>=PhS), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.33-6.98 (m, 18H, Ar-H); Found: m/z 402.0583. Calcd for C<sub>24</sub>H<sub>18</sub>S<sub>3</sub>: M, 402.0571.

**1,9-Bis(p-tolylthio)dibenzothiophene (4a) and 3,3'-Bis-(p-tolylthio)diphenyl Sulfide (5a)**

**4a:** ( $R^1=R^2=p\text{-TolS}$ ) mp 177 °C;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.52 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.34 (t,  $J=7.8$  Hz, 2H, Ar-H), 6.96 (s, 8H, Ar-H), 2.24 (s, 6H,  $\text{CH}_3$ ); IR (KBr) 1437, 1388, 1166, 810, 799, 762, 700  $\text{cm}^{-1}$ ; MS ( $m/z$ ) 428 ( $M^+$ ); Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{S}_3$ : C, 72.86; H, 4.70. Found: C, 72.99; H, 4.74.

**5a:** ( $R^1=R^2=p\text{-TolS}$ ),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.47-6.93 (m, 16H, Ar-H), 2.34 (s, 6H,  $\text{CH}_3$ ); Found:  $m/z$  430.0841. Calcd for  $\text{C}_{26}\text{H}_{22}\text{S}_3$ : 430.884.

**1,9-Bis(p-chlorophenylthio)dibenzothiophene (4c) and 3,3'-Bis(p-chlorophenylthio)diphenyl Sulfide (5c)**

**4c:** ( $R^1=R^2=p\text{-ClC}_6\text{H}_4\text{S}$ ), mp 158 °C;  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (dd,  $J_1=7.6$  Hz,  $J_2=1.4$  Hz, 2H, Ar-H), 7.50 (dd,  $J_1=7.6$  Hz,  $J_2=1.4$  Hz, 2H, Ar-H), 7.41 (s,  $J=7.6$  Hz, 2H, Ar-H), 7.10 (dd,  $J_1=6.5$  Hz,  $J_2=1.9$  Hz, 4H, Ar-H), 6.89 (dd,  $J_1=6.5$  Hz,  $J_2=1.9$  Hz, 4H, Ar-H); MS ( $m/z$ ) 400 ( $M^+$ ); Anal. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{S}_3$ : C, 61.40; H, 3.01. Found: C, 61.23; H, 3.01.

**5c:** ( $R^1=R^2=p\text{-ClC}_6\text{H}_4\text{S}$ ),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.26 (s, 8H, Ar-H), 7.17 (s, 8H, Ar-H); Found:  $m/z$  469.9791. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{S}_3$ : M, 469.9791.

**1,9-Bis(methylthio)dibenzothiophene (4d) and 3,3'-Bis-(methylthio)diphenyl Sulfide (5d)**

**4d:** ( $R^1=R^2=\text{CH}_3\text{S}$ ) mp 147.5-148 °C;  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J=7.6$  Hz, 2H, Ar-H), 7.59 (d,  $J=7.6$  Hz, 2H, Ar-H), 7.45 (t,  $J=7.6$  Hz, 2H, Ar-H), 2.41 (s, 6H,  $\text{CH}_3$ ); MS ( $m/z$ ) 276 ( $M^+$ );

Anal. Calcd for  $C_{14}H_{12}S_3$ : C, 60.83; H, 4.38. Found; C, 60.83; H, 4.37.

**5d**: ( $R^1=R^2=CH_3S$ )  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.37-6.93 (m, 8H, Ar-H), 2.44 (s, 6H,  $CH_3$ ); Found: m/z 278.0273. Calcd for  $C_{14}H_{14}S_3$ : M, 278.0258

**1-(Phenylthio)-9-(methylthio)dibenzothiophene (4h) and 3-(Phenylthio)-3'-(methylthio)diphenyl Sulfide (5h)**

**4h**: ( $R^1=PhS$ ,  $R^2=CH_3S$ ), mp 212.5-213.5 °C;  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.86-6.76 (m, 16H, Ar-H); MS (m/z) 400 ( $M^+$ ).

**5h**: ( $R^1=Ph$ ,  $R^2=CH_3S$ )  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.53-6.83 (m, 13H, Ar-H), 2.50-2.33 (m, 3H,  $CH_3$ ); Found: m/z 340.041. Calcd for  $C_{19}H_{20}S_3$ : M, 340.414.

**1-(p-Tolylthio)dibenzothiophene (4i) and 3-(p-Tolylthio)diphenyl Sulfide (5i)**

**4i**: ( $R^1=p-TolS$ ,  $R^2=H$ ), mp 106 °C;  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  9.12-9.05 (m, 1H, Ar-H), 7.88-7.84 (m, 1H, Ar-H), 7.78-7.74 (m, 1H, Ar-H), 7.48-7.43 (m, 2H, Ar-H), 7.35-7.23 (m, 4H, Ar-H), 7.17-7.10 (m, 2H, Ar-H), 2.33 (s, 3H,  $CH_3$ ); MS (m/z) 400 ( $M^+$ ); Anal. Calcd for  $C_{19}H_{14}S_2$ : C, 74.47; H, 4.58. Found: C, 74.15; H, 4.58.

**5i**: ( $R^1=p-TolS$ ,  $R^2=H$ )  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.47-6.80 (m, 13H, Ar-H), 2.33 (s, 3H,  $CH_3$ ); Found: m/z 308.0686. Calcd for  $C_{19}H_{16}S_2$ : M, 308.0693.

**1-(Phenylthio)dibenzothiophene (4j) and 3-(Phenylthio)-diphenyl Sulfide (5j)**

**4j**: ( $R^1=PhS$ ,  $R^2=H$ ), mp 212.5-213.5 °C;  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.86-6.76 (m, 16H, Ar-H); Found: 292.0936. Calcd for  $C_{18}H_{12}S_2$ : M, 292.0380.

**5j**: (R<sup>1</sup>=PhS, R<sup>2</sup>=H) <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.40-6.97 (m, 16H, Ar-H);

Found: 294.0540. Calcd for C<sub>18</sub>H<sub>14</sub>S<sub>2</sub>: M, 294.0537.

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## CHAPTER 3

### GENERATION OF NEW DITHIA DICATIONS FROM STERICALLY CONGESTED 1,9-BIS(METHYLTIO)DIBENZOTHIOPHENE AND THEIR MONOOXIDES IN CONCENTRATED SULFURIC ACID

#### Abstract

Sterically congested 1,9-bis(methylthio)dibenzothiophene **2** was prepared by ring contraction of 4,6-bis(methylthio)-thianthrene-5-oxide (**1**) with *n*-butyllithium. In the compound **2** the two sulfur atoms are located near by each other, and the strong interaction may take place between them. The compound **2** and its monooxide **3** upon dissolution in concentrated sulfuric acid indicated the formation of the corresponding dithia dications which was identified by tracer experiments using trideuterated and <sup>18</sup>O-labeled **3** with conc. sulfuric acid. Electrochemical oxidation of **2** suggests also the strong interaction between the two 1,9-sulfenyl sulfur atoms.

## Introduction

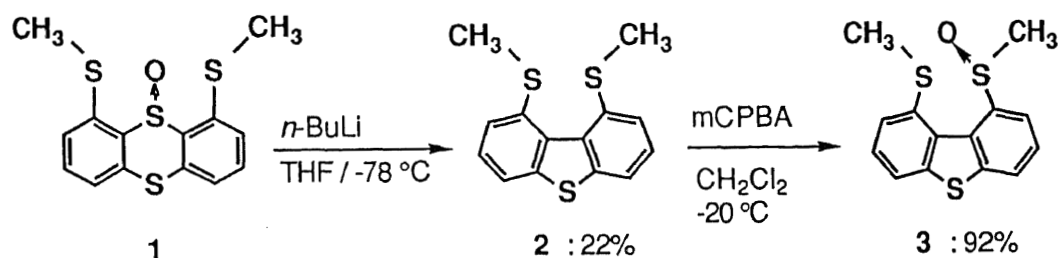
Two or more heteroatoms which are arranged appropriately in space are able to interact intramolecularly with each other.<sup>1</sup> Recently, transannular interactions of several heteroatoms such as N-N,<sup>2</sup> S-S<sup>3,4</sup> and S-S-S<sup>5,6</sup> types have been reported. Their dication salts were isolated and their structures were determined by X-ray crystallographic analysis.<sup>1,4a</sup>

On the other hand, sterically congested two or more substituents are found to have exceptionally strong interaction between them.<sup>7</sup> The two important factors which govern this transannular effect are; i) the existence of strong steric strain in these systems and the effect of the overlap of the lone electron pairs, ii) the formation of bond between heteroatoms on one or two electron oxidation leading to a considerable relaxation of the steric strain. This chapter reports the formation of new dithia dications by oxidation of 1,9-bis(methylthio)dibenzothiophene (**2**) and its monooxide **3** in conc. H<sub>2</sub>SO<sub>4</sub>, together with electrochemical oxidation and mass spectrometry.



## Results and Discussion

1,9-Bis(methylthio)dibenzothiophene (**2**) was prepared by the reactions of 4,6-bis(methylthio)thianthrene-5-oxide (**1**) with *n*-butyllithium in THF at  $-78^{\circ}\text{C}$ , in 22% yield (Scheme 3-1). Then, **2** was oxidized with an equimolar of *m*-chloroperbenzoic acid (mCPBA) to afford the corresponding monosulfoxide **3** in 92% yield.



Scheme 3-1

These 1,9-disubstituted dibenzothiophenes **2** and **3** have two closely located sulfur substituents which are expected to possess the strong interaction between each sulfur atoms and to produce the dithia dicationic species. The formation of dication from **2** and **3** was confirmed by the following experiments. When the sulfoxide **3** was dissolved in conc.  $\text{D}_2\text{SO}_4$  and its  $^1\text{H}$ -NMR was measured, the two methyl protons of **3** appeared at 2.79 (SOCH<sub>3</sub>), 2.33 (SCH<sub>3</sub>) ppm in  $\text{CDCl}_3$  shifted to down field and coalesced to a singlet at 3.04 ppm (Fig. 3-1).

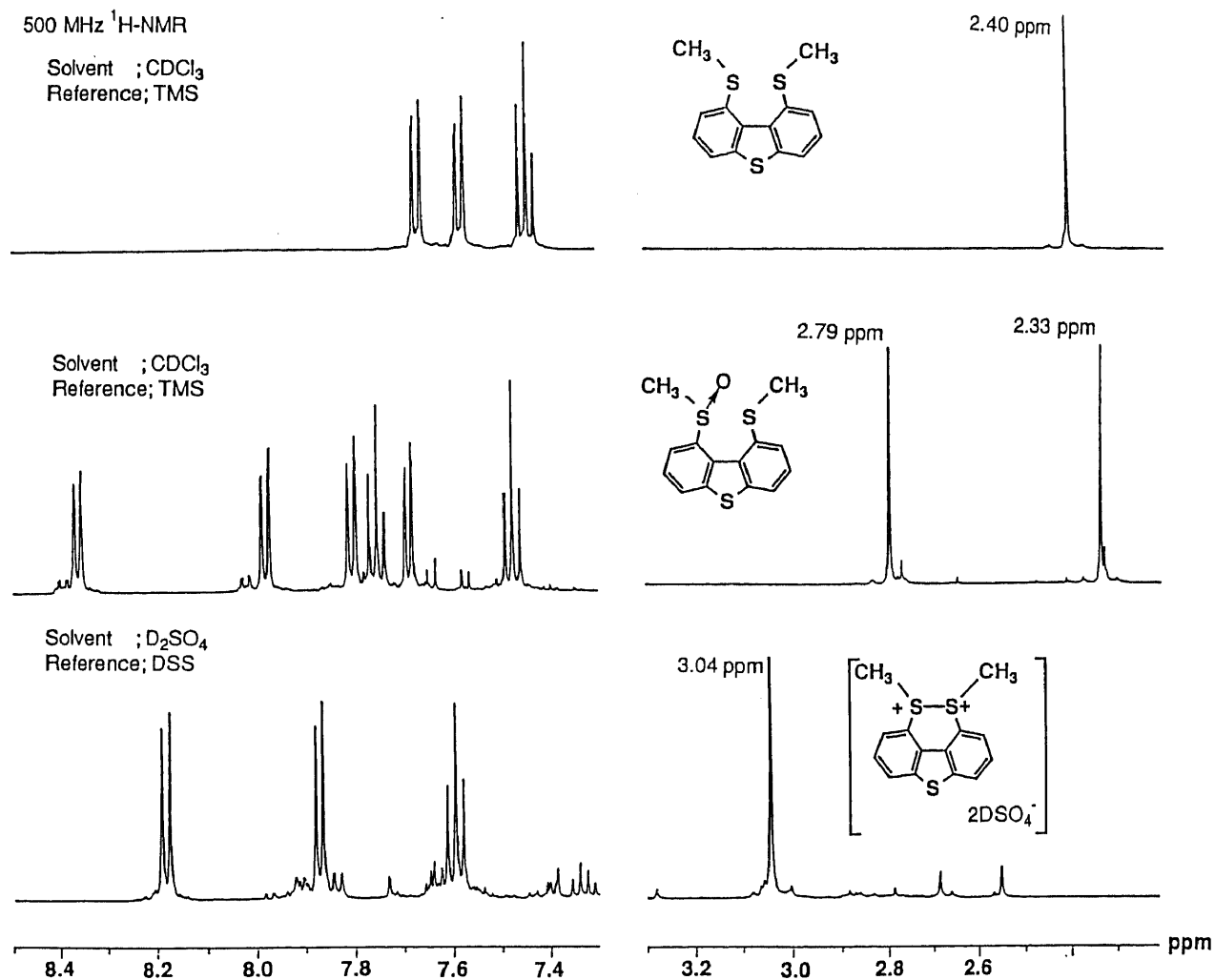
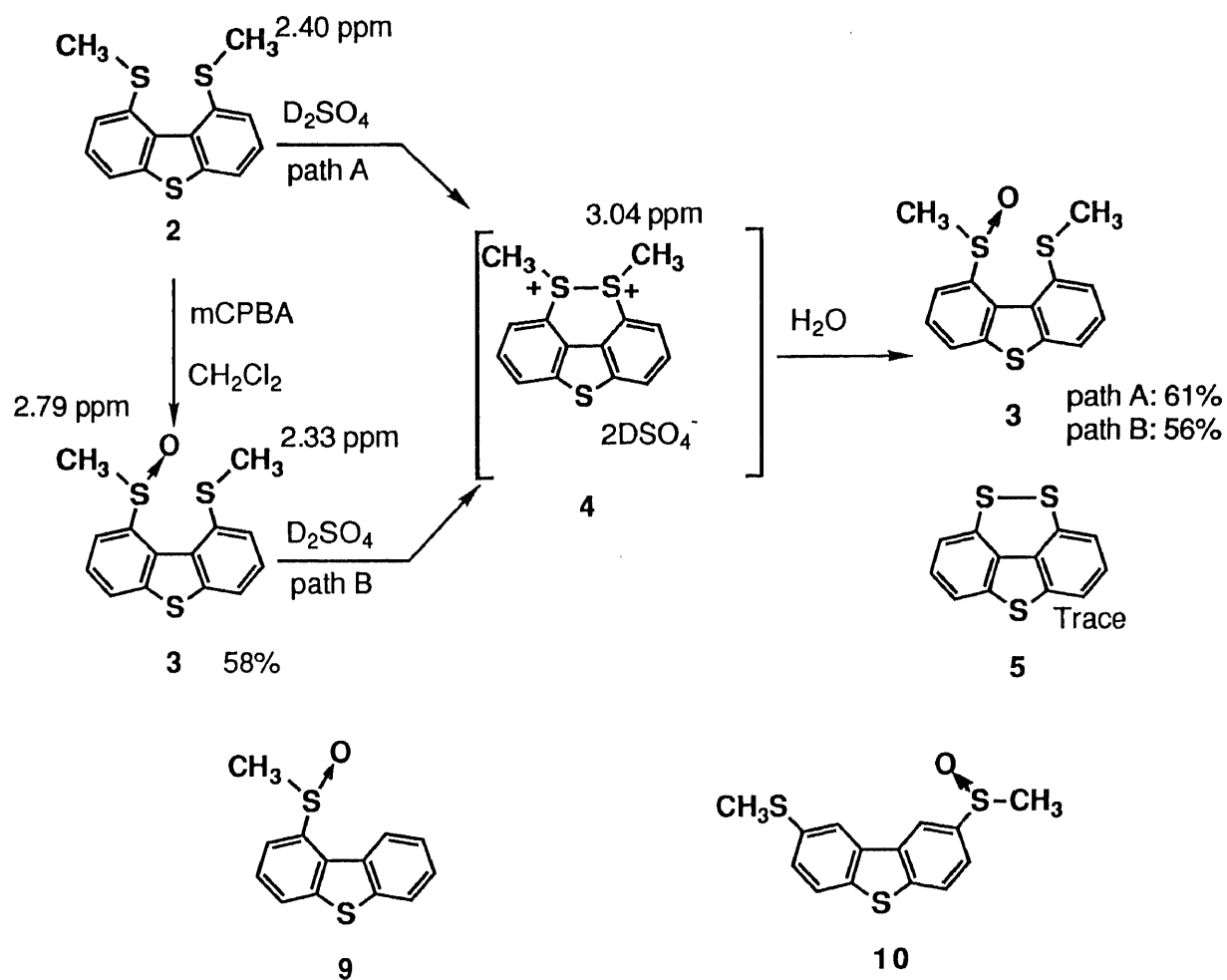


Fig. 3-1. 500 MHz  $^1\text{H}$ -NMR Spectra of Compounds **2**, **3** and Dication **4**

The sulfide **2** was also oxidized in conc. sulfuric acid to give the corresponding dithia dication **4**. The  $^1\text{H}$ -NMR spectrum of **2** in conc.  $\text{D}_2\text{SO}_4$  displayed nearly the same with that of the sulfoxide **3**. These results suggest again that the dication **4** is formed from the oxidation of the sulfide **2**.

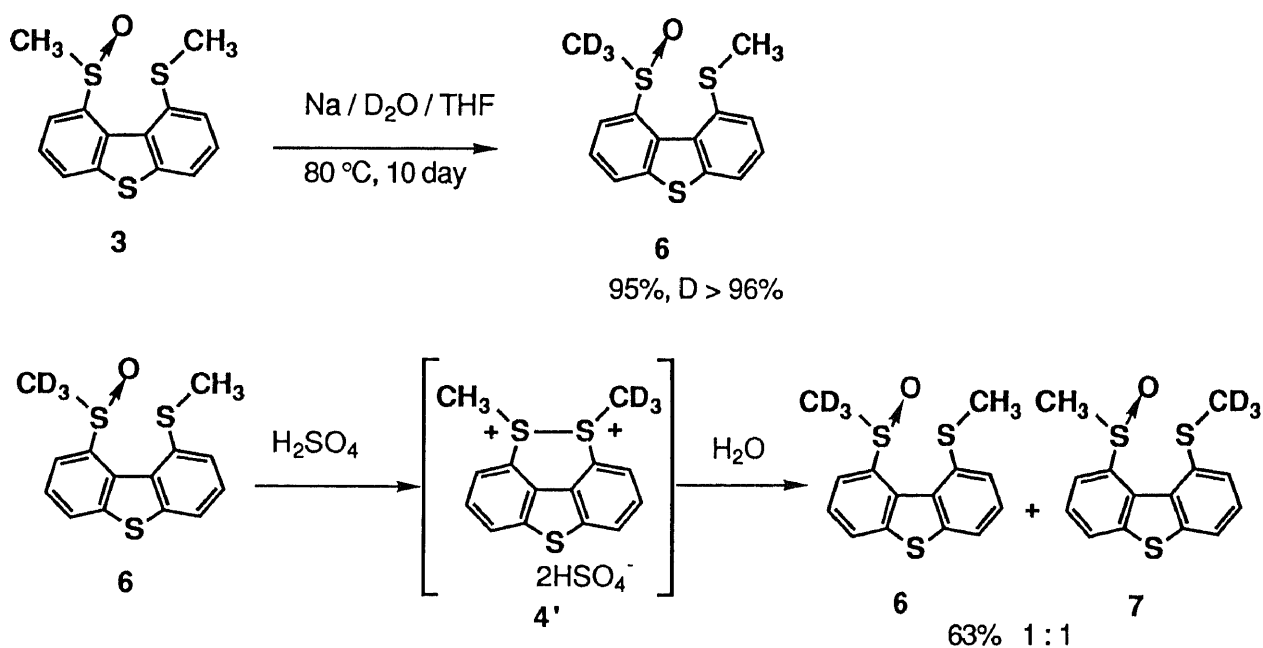


Scheme 3-2

Then the solution was treated with ice water to give again the sulfoxide **3** in 56% (from **3**) and 61% (from **2**) yields together with the demethylated disulfide **5** in a trace yield (Scheme 3-2).

Furthermore, to prove the formation of dithia dication in conc.  $H_2SO_4$ , deuterium and  $^{18}O$  tracer experiments were carried out. Actually, when the deuterated sulfoxide (1- $CD_3SO$ -9- $CH_3S$ ) **6** (D-content >96%) prepared by H-D exchange reaction of **3** with

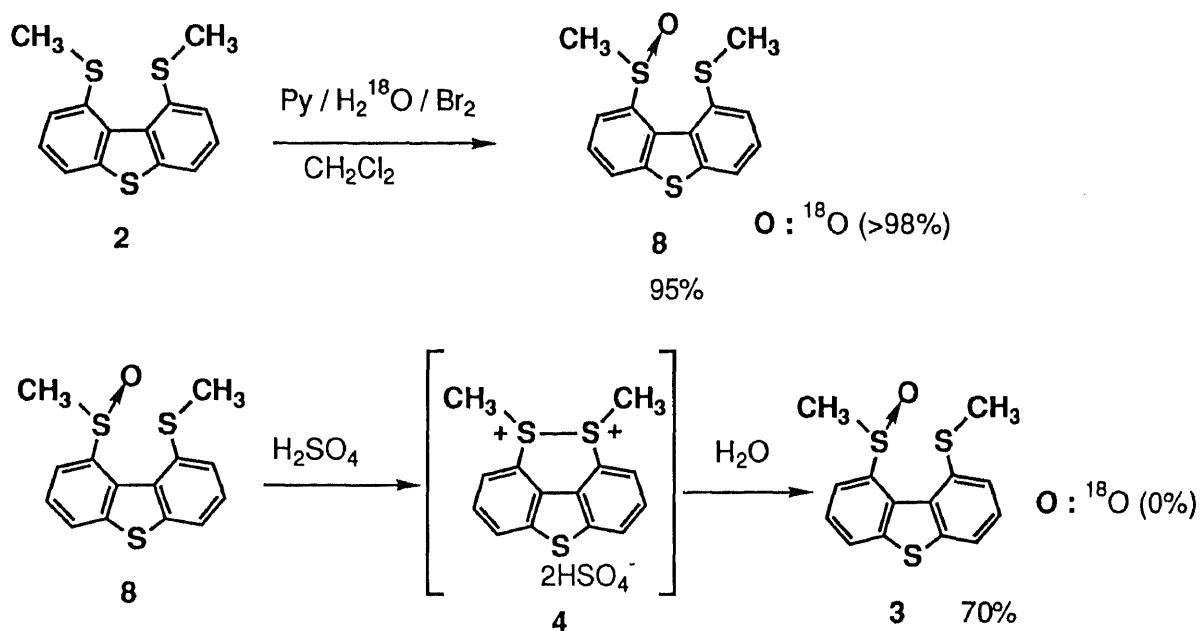
D<sub>2</sub>O-THF and NaOD in 95% yield, was treated similarly in conc. H<sub>2</sub>SO<sub>4</sub> and after decomposition of the solution with H<sub>2</sub>O, a 1:1 mixture of (1-CD<sub>3</sub>SO-9-CH<sub>3</sub>S) **6** and (1-CH<sub>3</sub>SO-9-CD<sub>3</sub>S) **7** was obtained in 63% yield (Scheme 3-3).



Scheme 3-3

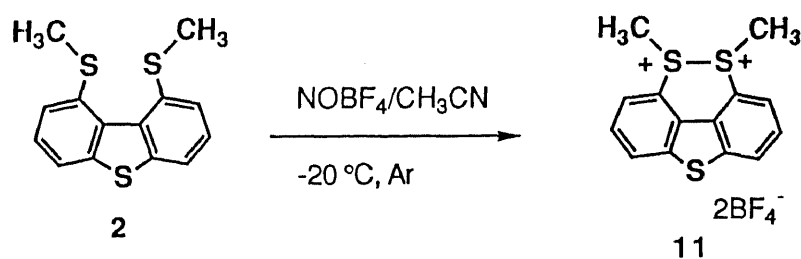
Similarly <sup>18</sup>O-labeled sulfoxide **8** was prepared from **2** in 95% yield (<sup>18</sup>O content > 98%)<sup>8</sup> and was treated with conc. H<sub>2</sub>SO<sub>4</sub> and then excess H<sub>2</sub>O to give non labeled sulfoxide **3** in 70% yield (Scheme 3-4).

The present results demonstrate clearly that a new dithia dication **4** and **4'** are formed as an intermediate in the deoxygenation reaction by the neighboring group participation of the sulfenyl sulfur atom. On the other hand, 1-(methylsulfinyl)dibenzothiophene (**9**) and 2-(methylsulfinyl)-8-(methylthio)dibenzothiophene (**10**) were unstable in conc. H<sub>2</sub>SO<sub>4</sub>,



Scheme 3-4

and their  $^1\text{H}$ -NMR could not be measured in conc.  $\text{D}_2\text{SO}_4$ . These results seem to support that the formation of dithia dication (4) requires the two nearly located sulfur atoms in space.



Scheme 3-5

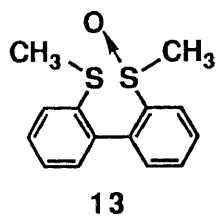
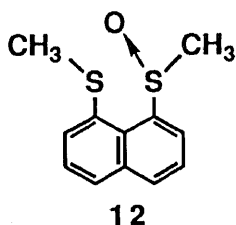
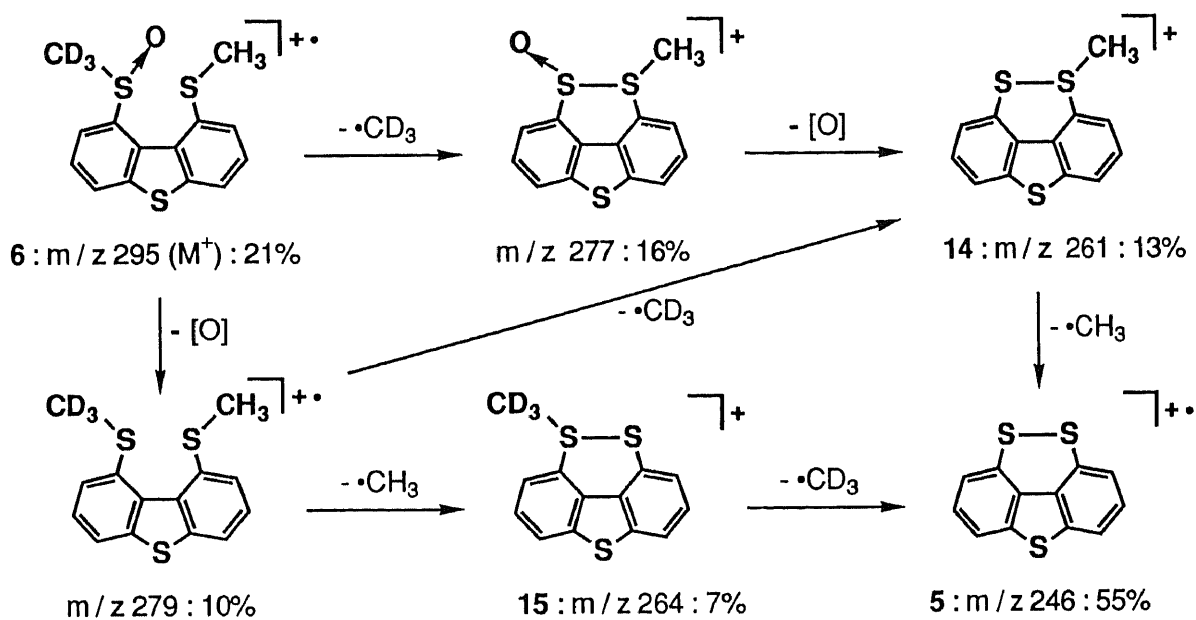
On the other hand, when 2 was treated with  $\text{NOBF}_4$ , its dicationic salt 11 was actually isolated as white powder (Scheme 3-5). The  $^1\text{H}$ -NMR measured in acetonitrile- $d_3$  was similar to

that of compound **3** in  $D_2SO_4$ . This result also supports that the formation of dithia dication is actually performed using the compounds **2** and **3** in conc  $H_2SO_4$ . This white powder like compound **11** is very moisture sensitive and slightly decomposes in the air.

#### **Mass Fragmentation of 3 and Related Compounds.**

EI mass spectra of 1,9-bis(methylthio)dibenzothiophene (**2**) show a base peak corresponding to the  $M^+ - 2 \times CH_3$  fragment from which the following mechanism for mass fragmentation is proposed: transannular interaction between the two sulfur atoms, intramolecular cyclization with ejection of one methyl group, and aromatization involving a loss of  $CD_3 \cdot$  group and leading to methylthiosulfonium cation and then stable radical cation of **5**. The fragmentation of 1-(trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (**6**) is shown in Scheme 3-6.

The fragment peak of **6** was observed at  $(m/z)$  246 ( $M^+ - 49$ ) corresponding to the disulfide **5**, while the parent peak **6**:  $(m/z)$  295  $M^+$  was observed clearly. In the spectra, both the demethylation and deoxygenation processes from the methyl sulfinyl group take place initially to give the fragments at  $(m/z)$  277 and 279 respectively, followed by the deoxygenation from the fragment **14** or the demethylation from the fragment **15** to give the fragment of the thiosulfonium species  $(m/z)$  261 and 264 from which the demethylation results in the formation of fragment **5**. In the general mass fragmentation of sulfoxides is the sulfinyl oxygen atom used to be removed on electron impact



Scheme 3-6

and hence the present mass pattern of **6** is quite different from that of ordinary sulfoxides. This result seems to indicate the initial formation of the S-S bond from **6** via transannular interaction.<sup>9</sup> However, in the analogous compounds **12**<sup>10,11</sup> and **13**<sup>12</sup> this fragmentation pattern was not observed at all. These results suggest that in 1,9-dithiosubstituted dibenzothiophenes, the two outer sulfur atoms should have a strong interaction to form the  $\sigma$ -bond formation on electron impact.

## Electrochemical Oxidation of 1,9-Disubstituted Dibenzothiophenes and Related Compounds

It has been known that several cyclic compounds bearing closely located two heteroatoms have unusually low oxidation potentials due to transannular bond formation between the two atoms.<sup>5</sup> Accordingly, to investigate the nature of the transannular interaction of the compound **2** and the related compounds, the oxidation potential of **2** was measured with cyclic voltammetry, and the value was compared with that of 1-(methylthio)dibenzothiophene, 2,8-bis(methylthio)dibenzothiophene, dibenzothiophene and thioanisole; using Pt electrode and Ag/(0.01 M)AgNO<sub>3</sub> as a reference electrode (scan rate: 200 mV/s) at 25 °C in acetonitrile. Interestingly, the first peak potential of **2** is relatively low, namely **2** (0.76 V) in comparison with 1-(methylthio)dibenzothiophene (1.02 V), 2,8-bis(methylthio)-dibenzothiophene (0.96 V), dibenzothiophene (1.31 V) and thioanisole (1.21 V). But the electrochemical oxidations of these compounds gave irreversible cyclic voltammograms. On the basis of comparison to other dibenzothiophene derivatives, the observed low peak potential of **2** gives the supporting evidence for the transannular interaction between the two outer sulfur atoms on electrochemical oxidation.<sup>5</sup>



## Experimental Section

### General.

IR spectra were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer.  $^1\text{H}$ -NMR spectra were measured on a Hitachi R-600 or a JEOL JNM-EX270 or a Bruker AM-500.  $^{13}\text{C}$ -NMR spectra were taken with a JEOL JNM-EX270 or a Bruker AM-500. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX SX102 mass spectrometer. For cyclic voltammetry measurements, a Hokuto Denko Co. Model HB-104 apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder. Elemental analyses were carried out by Chemical Analysis Center at this University.

### Materials.

All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co., Kanto Chemical Co., or Aldrich Chemical Co.. The reaction solvents were further purified by general methods.

### Synthesis

#### Preparation of 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (3)

To a solution of 1,9-bis(methylthio)dibenzothiophene (2) (321 mg, 1.16 mmol) prepared as described in a previous chapter in 50 ml  $\text{CH}_2\text{Cl}_2$ , *m*-chloroperbenzoic acid (mCPBA) (286 mg, 1.16 mmol) dissolved in 50 ml  $\text{CH}_2\text{Cl}_2$  was added at  $-20\text{ }^\circ\text{C}$ . The solution was stirred for 12 h, and then ammonia gas was bubbled for a few minutes at  $25\text{ }^\circ\text{C}$ . A white solid was filtered off and the solvent was evaporated. The reaction mixture was purified by

column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub> and ethylacetate), and 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (**3**) was obtained in 92% yield.

**3**: mp 158-160 °C; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 8.36 (dd, J<sub>1</sub>=7.6 Hz, J<sub>2</sub>=1.1 Hz, 1 H, Ar-H), 7.99 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.4 Hz, 1H, Ar-H), 7.82 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.4 Hz, 1H, Ar-H), 7.76 (t, J=7.8 Hz, 1H, Ar-H), 7.70 (dd, J<sub>1</sub>=7.6 Hz, J<sub>2</sub>=1.1 Hz, 1H, Ar-H), 7.47 (t, J=7.6 Hz, 1H, Ar-H), 2.79 (s, 3H, SOCH<sub>3</sub>), 2.33 (s, 3H, SCH<sub>3</sub>); IR (KBr) 1021 cm<sup>-1</sup>; MS (m/z) 292 (M<sup>+</sup>); Anal. Calcd for C<sub>14</sub>H<sub>12</sub>OS<sub>3</sub>: C, 57.50; H, 4.14. Found: C, 57.65; H, 4.11.

#### **Preparation of 1-(Methylsulfinyl)dibenzothiophene (9)**

To a solution of 1-(methylthio)dibenzothiophene (100 mg, 0.43 mmol) in 20 ml CH<sub>2</sub>Cl<sub>2</sub>, mCPBA (106 mg, 0.43 mmol) dissolved in 20 ml CH<sub>2</sub>Cl<sub>2</sub> was added at -20 °C. After similar treatment as described above, 1-(methylsulfinyl)dibenzothiophene (**9**) was obtained in 99% yield.

**9**: mp 78.5-79 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 8.32-7.28 (m, 7H, Ar-H), 2.85 (s, 3H, CH<sub>3</sub>); IR (KBr) 1050 cm<sup>-1</sup>; MS (m/z) 230 (M<sup>+</sup>); Anal. Calcd for C<sub>13</sub>H<sub>10</sub>OS<sub>2</sub>: C, 67.78; H, 4.38. Found: C, 67.53; H, 4.42.

#### **Preparation of 2,8-Bis(methylthio)dibenzothiophene**

To a solution of 2,8-dibromodibenzothiophene<sup>13</sup> (684 mg, 2 mmol) in 30 ml THF, *n*-butyllithium (1.55 M) (3.2 ml, 5 mmol) was added at -78 °C. The solution was stirred for 1 h, and then dimethyl disulfide (0.9 ml, 10 mmol) was added with a syringe. After usual work up and purification by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub>), 2,8-bis(methylthio)dibenzothiophene was obtained in 81% yield.

mp 142.5;  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J=2.4$  Hz, 2H, Ar-H), 7.75 (d,  $J=8.4$  Hz, 2H, Ar-H), 7.39 (dd,  $J_1=8.4$  Hz,  $J_2=2.4$  Hz, 2H, Ar-H), 2.59 (s, 6H,  $\text{CH}_3$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{S}_3$ : C, 60.83; H, 4.38. Found: C, 60.70; H, 4.37.

**Preparation of 2-(Methylsulfinyl)-8-(methylthio)dibenzothiophene (10)**

To a solution of 2,8-bis(methylthio)dibenzothiophene (276 mg, 1 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$ , mCPBA (247 mg, 1 mmol) dissolved in 50 ml  $\text{CH}_2\text{Cl}_2$  was added at  $-20^\circ\text{C}$ . The solution was stirred for 12 h, and then ammonia gas was bubbled for a few minutes at  $25^\circ\text{C}$ . A white solid was filtered off and the solvent was evaporated. The reaction mixture was purified by column chromatography (silica gel; eluent,  $\text{CH}_2\text{Cl}_2$  and ethylacetate), and 2-(methylsulfinyl)-8-(methylthio)dibenzothiophene (10) was obtained in 44% yield.

10: mp  $105\text{--}105.5^\circ\text{C}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.53–7.20 (m, 6H, Ar-H), 2.83 (s, 3H,  $\text{SOCH}_3$ ), 2.61 (s, 3H,  $\text{SCH}_3$ ); IR (KBr)  $1046\text{ cm}^{-1}$ ; MS ( $m/z$ ) 292 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{OS}_3$ : C, 57.50; H, 4.14. Found: C, 57.73; H, 4.11.

**Preparation of 1-(Trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (6)**

To a 29% solution of sodium deuterioxide in 5 ml heavy water, a solution of 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (3) (150 mg, 0.51 mmol) in 2 ml THF was added at  $0^\circ\text{C}$ . The solution was stirred for 10 days at  $80^\circ\text{C}$ , and THF (2 ml x 4) was added every 48 hours. Then the solution was cooled to room temperature and 5 N hydrochloric acid (20 ml) was added. After

usual work up and purification by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub> and ethylacetate), 1-(trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (6) was obtained in 95% yield (D content > 96%).

The deuterium content was determined by 270 MHz <sup>1</sup>H-NMR.

**Preparation of <sup>18</sup>O-Labeled 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (8)**

To a solution of 1,9-bis(methylthio)dibenzothiophene (2) (138 mg, 0.47 mmol), pyridine (0.5 ml), and <sup>18</sup>O-labeled water (<sup>18</sup>O content > 99%) (0.1 ml, 5.5 mmol) in 1.5 ml CH<sub>2</sub>Cl<sub>2</sub>, Br<sub>2</sub> (0.03 ml, 0.58 mmol) in 1 ml CH<sub>2</sub>Cl<sub>2</sub> was added at 25 °C under argon atmosphere. The solution was stirred for 1 h, and sodium thiosulfate (248 mg, 1 mmol) was added. After usual work up and purification by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub> and ethylacetate), <sup>18</sup>O-labeled 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (8) was obtained in 95% yield (<sup>18</sup>O content > 98%).

The <sup>18</sup>O content was determined with mass spectrometry.

**Reaction of 1,9-Bis(methylthio)dibenzothiophene (2) with conc. H<sub>2</sub>SO<sub>4</sub>**

1,9-Bis(methylthio)dibenzothiophene (2) was dissolved in conc. H<sub>2</sub>SO<sub>4</sub>, and the solution was stirred for 5 min. This solution was poured into ice water and the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. After evaporation and column chromatography, 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (3) was obtained in 61% yield together with a trace of compound 5.

**5**: mp 132.5–133 °C;  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J=7.9$  Hz, 2H, Ar-H), 7.40 (d,  $J=7.9$  Hz, 2H, Ar-H), 7.25 (t,  $J=7.9$  Hz, 2H, Ar-H); 67 MHz  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  140.4, 131.8, 128.2, 128.1, 121.9, 121.7; MS ( $m/z$ ) 246 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{S}_3$ : C, 58.50; H, 2.45. Found: C, 58.40; H, 4.48.

**Reaction of 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (3) with conc.  $\text{H}_2\text{SO}_4$**

1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (**3**) was dissolved in conc.  $\text{H}_2\text{SO}_4$ , and after usual work up, (**3**) was obtained in 56% yield together with a trace of compound **5**.

**Reaction of 1-(Trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (6) with conc.  $\text{H}_2\text{SO}_4$**

1-(Trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (**6**) was dissolved in conc.  $\text{H}_2\text{SO}_4$ , and after usual work up, a 1:1 mixture of 1-(trideuterated methylsulfinyl)-9-(methylthio)-dibenzothiophene (**6**) and 1-(methylsulfinyl)-9-(trideuterated methylthio)dibenzothiophene (**7**) was obtained in 63% yield.

The deuterium content was determined by 270 MHz  $^1\text{H}$ -NMR.

A 1:1 mixture of compound **6** and **7**:  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (dd,  $J_1=7.6$  Hz,  $J_2=1.1$  Hz, 1 H, Ar-H), 7.99 (dd,  $J_1=7.8$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.82 (dd,  $J_1=7.8$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.76 (t,  $J=7.8$  Hz, 1H, Ar-H), 7.70 (dd,  $J_1=7.6$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.47 (t,  $J=7.6$  Hz, 1H, Ar-H), 2.79 (s, 1.5H,  $\text{SOCH}_3$ ), 2.33 (s, 1.5H,  $\text{SCH}_3$ )

**Reaction of  $^{18}\text{O}$ -Labeled 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (8) with conc.  $\text{H}_2\text{SO}_4$**

$^{18}\text{O}$ -Labeled 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (8) was dissolved in conc.  $\text{H}_2\text{SO}_4$ , and after usual work up 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (3) was obtained in 70% yield.

The  $^{18}\text{O}$  content was determined with mass spectrometry.

**Reaction of 1,9-Bis(methylthio)dibenzothiophene (2) with  $\text{NOBF}_4$**

To 2 and  $\text{NOBF}_4$  in a reactor,  $\text{CH}_3\text{CN}$  (10 ml) was added and the solution was stirred at  $-20\text{ }^\circ\text{C}$  for 1 h under argon. To this solution cooled dry diethyl ether (50 ml) was added and white precipitates appeared. After filtration, the solid was washed with dry ether. The white solid (dication 11) was collected and analyzed.

11: mp  $113\text{ }^\circ\text{C}$ ;  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.50 (d,  $J=7.9\text{ Hz}$ , 2H, Ar-H), 8.38 (d,  $J=7.9\text{ Hz}$ , 2H, Ar-H), 8.40 (t,  $J=7.9\text{ Hz}$ , 2H, Ar-H), 3.37 (s, 6H,  $\text{CH}_3$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{S}_3\text{B}_2\text{F}_8$ : C, 37.36; H, 2.69. Found: C, 38.25; H, 3.91.

**Preparation of 4,8-Bis(methylthio)naphthalene**

1,8-Naphthalenedithiole (190 mg, 1 mmol)<sup>10</sup> in THF (15 ml) and ethanol (15 ml) was treated with sodium borohydride (76 mg, 2 mmol) and the solution was stirred for 15 min at room temperature. To this solution was added 1 ml water and then iodomethane (0.3 ml, 5 mmol). After usual work up procedures and purification by column chromatography (silica gel; eluent,

$\text{CCl}_4$ ), 1,8-bis(methylthio)naphthalene was obtained in 81% yields.

mp 85.5–86 °C (lit. 84 °C);  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J_1=8.1$  Hz,  $J_2=1.4$  Hz, 2H, Ar-H), 7.49 (dd,  $J_1=8.1$  Hz,  $J_2=1.4$  Hz, 2H, Ar-H), 7.38 (t,  $J=8.1$  Hz, 2H, Ar-H), 2.54 (s, 6H,  $\text{CH}_3$ ); MS (m/z) 220 ( $\text{M}^+$ )

#### **Preparation of 2,2'-Bis(methylthio)biphenyl**

2,2'-Biphenylenedithiin (90 mg, 0.42 mmol)<sup>12</sup> in THF (10 ml) and ethanol (10 ml) was treated with sodium borohydride (38 mg, 1 mmol) and the solution was stirred for 15 min at room temperature. To this solution was added 1 ml water and then iodomethane (0.13 ml, 2 mmol). After usual work up procedures and purification by column chromatography (silica gel; eluent,  $\text{CCl}_4$ ), 2,2'-bis(methylthio)biphenyl was obtained in 99% yield.

mp 160.5–161.5 °C (lit. 155 °C);  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.35 (m, 2H, Ar-H), 7.32–7.27 (m, 2H, Ar-H), 7.25–7.14 (m, 4H, Ar-H), 2.38 (s, 6H,  $\text{CH}_3$ ); MS (m/z) 246 ( $\text{M}^+$ )

#### **Preparation of 4-(Methylsulfinyl)-8-(methylthio)-naphthalene (12)**

To a solution of 1,8-bis(methylthio)naphthalene (179 mg, 0.8 mmol) in 40 ml  $\text{CH}_2\text{Cl}_2$  was added mCPBA (197 mg, 0.8 mmol) in 40 ml  $\text{CH}_2\text{Cl}_2$  at -20 °C. The solution was stirred for 12 h, and then ammonia gas was bubbled for a few minutes at 25 °C. A white solid was filtered off and the solvent was evaporated. The reaction mixture was purified by column chromatography (silica gel; eluent,  $\text{CH}_2\text{Cl}_2$  and ethylacetate), and 4-

(methylsulfinyl)-8-(methylthio)naphthalene (**12**) was obtained in 34% yield.

**12**: mp 92-93 °C  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (dd,  $J_1=7.3$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.99 (dd,  $J_1=8.1$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.92 (dd,  $J_1=8.1$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.85 (dd,  $J_1=7.3$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.72 (t,  $J=8.1$  Hz, 1H, Ar-H), 7.49 (t,  $J=7.3$  Hz, 1H, Ar-H), 2.90 (s, 3H,  $\text{SOCH}_3$ ), 2.43 (s, 3H,  $\text{SCH}_3$ ); IR (KBr)  $1038\text{ cm}^{-1}$ ; MS ( $m/z$ ) 236 ( $\text{M}^+$ ).

**Preparation of 2-(Methylsulfinyl)-2'-(methylthio)-biphenyl (13)**

2,2'-Bis(methylthio)biphenyl was oxidized with mCPBA similarly as described above and 2-(methylsulfinyl)-2'-(methylthio)-biphenyl (**13**) was obtained in 66% yield.

**13** (isomeric mixture): mp 81.5-83.5 °C;  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17-8.11 (m, 1H, Ar-H), 7.70-7.48 (m, 2H, Ar-H), 7.45-7.37 (m, 1H, Ar-H), 7.34-7.29 (m, 1H, Ar-H), 7.28-7.17 (m, 2.5H, Ar-H), 7.08-7.03 (m, 0.5H, Ar-H), 2.51 (s, 1.5H,  $\text{SOCH}_3$ ), 2.46 (s, 1.5H,  $\text{SOCH}_3$ ), 2.40 (s, 1.5H,  $\text{SCH}_3$ ), 2.39 (s, 1.5H,  $\text{SCH}_3$ ); IR (KBr)  $1035\text{ cm}^{-1}$ ; MS ( $m/z$ ) 262 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{OS}_2$ : C, 64.08; H, 5.38. Found: C, 63.85; H, 5.27.



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## CHAPTER 4

### PREPARATION AND STRUCTURES OF 1,9-BIS(ARYLTHIO)DIBENZO- THIOPHENE DICATIONS IN CONCENTRATED SULFURIC ACID

#### Abstract

1,9-Bis(arylthio)dibenzothiophenes (**2**) and their monooxides (**3**) were prepared from the corresponding thianthrene-5-oxides (**1**) and the structure of **3a** was determined by X-ray crystallographic analysis. 1,9-Bis(arylthio)dibenzothiophene dications (**4**) were generated on dissolution of **2** and **3** in conc. sulfuric acid and their structures were characterized by  $^1\text{H}$ -NMR spectroscopy, fast atom bombardment mass spectrometry (FAB MS). In order to prove the existence of transannular interaction between the two sulfur atoms at the 1,9-positions, their oxidation potentials of the compound **2a** and the related compounds were measured.

## Introduction

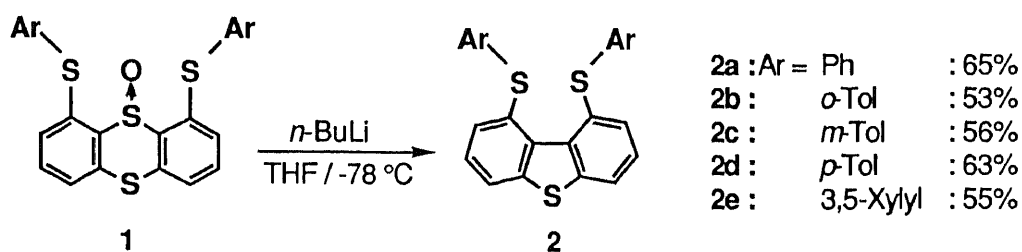
Dithia dications are of considerable interests because of their unusual bonding modes and reactivities as electron-acceptors.<sup>1,2,3</sup> In the previous chapter, the author described a convenient preparation of sterically congested 1,9-disubstituted dibenzothiophenes and the formation of the dithia dications of 1,9-bis(methylthio)dibenzothiophene. However, since its dithia dication was found to be unstable, its characteristic property and the structure could not be investigated in detail. Therefore, in order to know the more information on the structure of dithia dication in conc. H<sub>2</sub>SO<sub>4</sub>, 1,9-bis-(arylthio)dibenzothiophene (**2**) which produces the corresponding stable dithia dications **4** was used and treated with conc. sulfuric acid. This chapter reports the formation of stable dithia dications **4a-e** generated from the reaction of **2a-e** with conc. H<sub>2</sub>SO<sub>4</sub> and their detection with <sup>1</sup>H-NMR in conc. D<sub>2</sub>SO<sub>4</sub> and FAB MS.

## Results and Discussion

### Preparation of 1,9-Bis(arylthio)dibenzothiophene (**2**) and 1-(arylsulfinyl)-9-(arylthio)dibenzothiophene (**3**)

1,9-Bis(arylthio)dibenzothiophenes (**2**) were prepared by the intramolecular ring contraction of the corresponding thianthrene-5-oxides with *n*-butyllithium (Scheme 4-1) and then **2a** was

oxidized with an equimolar amount of *m*-chloroperbenzoic acid (mCPBA) to afford the monooxides (**3a**) in 78% yields.



Scheme 4-1

#### X-Ray Crystallographic Analysis of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**3a**)

The detailed structural analysis of **3a** was carried out by X-ray crystallographic analysis. The ORTEP drawing of **3a** is depicted in Fig. 4-1. The structure of sulfoxide (**3a**) indicates that the S-S distance between two sulfur atoms is 3.016 Å which is within van der Waals contact of S-S (3.70 Å) and the O-S<sub>2</sub>-S<sub>3</sub> angle is 158.8°,<sup>5</sup> suggesting that both the sulfenyl and the sulfinyl sulfur atoms interact transannularly.

Crystal data for **3a** is as follows: C<sub>24</sub>H<sub>16</sub>S<sub>3</sub>O, monoclinic, space group P2<sub>1</sub>/n, a=9.972(4), b=8.835(4), c=21.915(9) Å, β=92.21(4)°, V=1929.4(1) Å<sup>3</sup>, z=4, Dx=1.434 gcm<sup>-3</sup>, μ (Cu-kα)=3.546 mm<sup>-1</sup>, R=0.028 (wR=0.027).

Other detailed data of bond distances and angles of **3a** are summarized in Table 4-1 and 4-2.

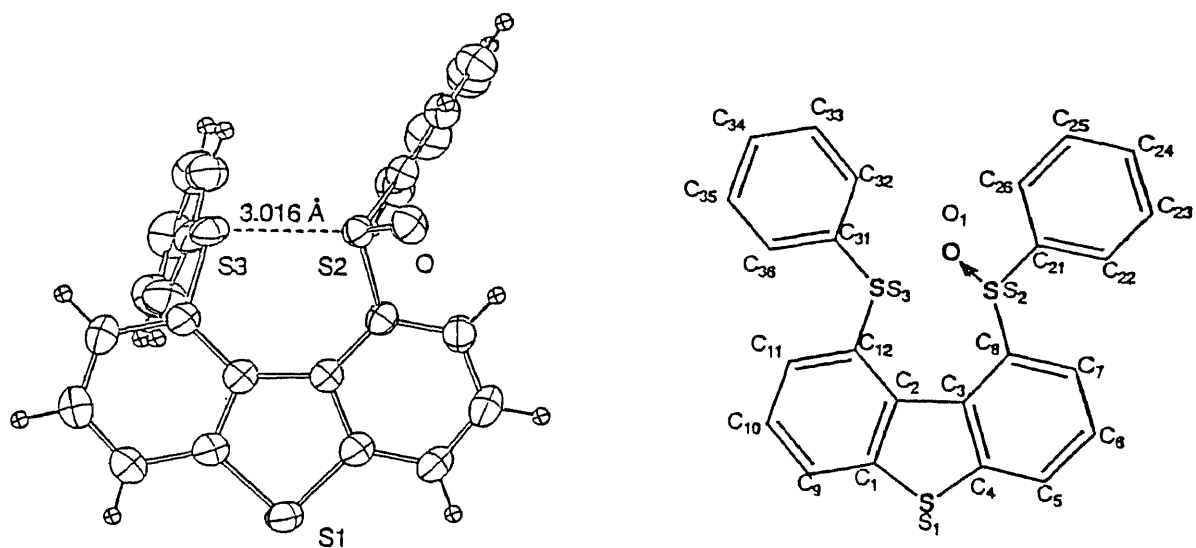


Fig. 4-1. X-Ray Crystallographic Analysis of **3a**

Table 4-1. Bond Distances of 1-(Phenylsulfinyl)-9-(phenylthio)-dibenzothiophene (**3a**)

Atoms	distance (Å)	ESD	Atoms	distance (Å)	ESD
S <sub>1</sub> -C <sub>1</sub>	1.742	0.002	C <sub>7</sub> -C <sub>8</sub>	1.379	0.003
S <sub>1</sub> -C <sub>4</sub>	1.744	0.002	C <sub>9</sub> -C <sub>10</sub>	1.370	0.003
S <sub>2</sub> -O <sub>1</sub>	1.496	0.001	C <sub>10</sub> -C <sub>11</sub>	1.388	0.003
S <sub>2</sub> -S <sub>8</sub>	1.810	0.002	C <sub>11</sub> -C <sub>12</sub>	1.386	0.003
S <sub>2</sub> -C <sub>21</sub>	1.812	0.002	C <sub>21</sub> -C <sub>22</sub>	1.384	0.003
S <sub>3</sub> -C <sub>12</sub>	1.776	0.002	C <sub>21</sub> -C <sub>26</sub>	1.382	0.003
S <sub>3</sub> -C <sub>31</sub>	1.778	0.002	C <sub>22</sub> -C <sub>23</sub>	1.387	0.003
C <sub>1</sub> -C <sub>2</sub>	1.401	0.002	C <sub>23</sub> -C <sub>24</sub>	1.365	0.004
C <sub>1</sub> -C <sub>9</sub>	1.394	0.003	C <sub>24</sub> -C <sub>25</sub>	1.377	0.004
C <sub>2</sub> -C <sub>3</sub>	1.461	0.002	C <sub>25</sub> -C <sub>26</sub>	1.373	0.004
C <sub>2</sub> -C <sub>12</sub>	1.412	0.002	C <sub>31</sub> -C <sub>32</sub>	1.375	0.003
C <sub>3</sub> -C <sub>4</sub>	1.415	0.002	C <sub>31</sub> -C <sub>36</sub>	1.385	0.003
C <sub>3</sub> -C <sub>8</sub>	1.411	0.002	C <sub>32</sub> -C <sub>33</sub>	1.381	0.003
C <sub>4</sub> -C <sub>5</sub>	1.386	0.003	C <sub>33</sub> -C <sub>34</sub>	1.358	0.003
C <sub>5</sub> -C <sub>6</sub>	1.368	0.003	C <sub>34</sub> -C <sub>35</sub>	1.374	0.003
C <sub>6</sub> -C <sub>7</sub>	1.386	0.003	C <sub>35</sub> -C <sub>36</sub>	1.376	0.003

Table 4-2. Bond Angles of 1-(Phenylsulfinyl)-9-(phenylthio)-dibenzothiophene (**3a**)

Atoms	angle (deg.)	ESD	Atoms	angle (deg)	ESD
C <sub>1</sub> -S <sub>1</sub> -C <sub>4</sub>	90.73	0.08	C <sub>1</sub> -C <sub>9</sub> -C <sub>10</sub>	118.31	0.18
O <sub>1</sub> -S <sub>2</sub> -C <sub>21</sub>	105.45	0.08	C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	120.22	0.19
O <sub>1</sub> -S <sub>2</sub> -C <sub>21</sub>	104.91	0.08	C <sub>10</sub> -C <sub>11</sub> -C <sub>12</sub>	121.50	0.18
C <sub>8</sub> -S <sub>2</sub> -C <sub>21</sub>	98.09	0.08	S <sub>3</sub> -C <sub>12</sub> -C <sub>2</sub>	122.58	0.13
C <sub>12</sub> -S <sub>3</sub> -C <sub>31</sub>	102.66	0.08	S <sub>3</sub> -C <sub>12</sub> -C <sub>11</sub>	117.32	0.13
S <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	113.52	0.13	C <sub>2</sub> -C <sub>12</sub> -C <sub>11</sub>	119.62	0.16
S <sub>1</sub> -C <sub>1</sub> -C <sub>9</sub>	123.29	0.14	S <sub>2</sub> -C <sub>21</sub> -C <sub>22</sub>	122.70	0.15
C <sub>2</sub> -C <sub>1</sub> -C <sub>9</sub>	123.14	0.17	S <sub>2</sub> -C <sub>21</sub> -C <sub>26</sub>	116.50	0.15
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	111.16	0.15	C <sub>22</sub> -C <sub>21</sub> -C <sub>26</sub>	120.74	0.19
C <sub>1</sub> -C <sub>2</sub> -C <sub>12</sub>	116.58	0.16	C <sub>21</sub> -C <sub>22</sub> -C <sub>23</sub>	118.62	0.21
C <sub>3</sub> -C <sub>2</sub> -C <sub>12</sub>	132.14	0.16	C <sub>22</sub> -C <sub>23</sub> -C <sub>24</sub>	120.65	0.24
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	110.98	0.15	C <sub>23</sub> -C <sub>24</sub> -C <sub>25</sub>	120.29	0.26
C <sub>2</sub> -C <sub>3</sub> -C <sub>8</sub>	132.62	0.16	C <sub>24</sub> -C <sub>25</sub> -C <sub>26</sub>	120.14	0.25
C <sub>4</sub> -C <sub>3</sub> -C <sub>8</sub>	116.08	0.15	C <sub>21</sub> -C <sub>26</sub> -C <sub>25</sub>	119.54	0.22
S <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	113.05	0.13	S <sub>3</sub> -C <sub>31</sub> -C <sub>32</sub>	125.44	0.14
S <sub>1</sub> -C <sub>4</sub> -C <sub>5</sub>	124.33	0.14	S <sub>3</sub> -C <sub>31</sub> -C <sub>36</sub>	115.29	0.14
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	122.52	0.16	C <sub>32</sub> -C <sub>31</sub> -C <sub>36</sub>	119.24	0.17
C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	119.11	0.18	C <sub>31</sub> -C <sub>32</sub> -C <sub>33</sub>	119.70	0.19
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	120.04	0.19	C <sub>32</sub> -C <sub>33</sub> -C <sub>34</sub>	121.07	0.22
C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	121.18	0.18	C <sub>33</sub> -C <sub>34</sub> -C <sub>35</sub>	119.66	0.22
S <sub>2</sub> -C <sub>8</sub> -C <sub>3</sub>	123.07	0.13	C <sub>34</sub> -C <sub>35</sub> -C <sub>36</sub>	120.08	0.21
S <sub>2</sub> -C <sub>8</sub> -C <sub>7</sub>	114.82	0.14	C <sub>31</sub> -C <sub>36</sub> -C <sub>35</sub>	120.25	0.19
C <sub>3</sub> -C <sub>8</sub> -C <sub>7</sub>	120.41	0.16			

**Preparation and Detection of 1,9-Bis(arylthio)-dibenzothiophene Dications in Conc. Sulfuric Acid.**

The <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>) of the S-phenyl rings of **2a** and **3a** appear at δ 7.0 (o-H) and 7.1-7.2 (m, p-H) (**2a**); 6.7 (o-H), 7.1, 7.4 (m, p-H) (**3a**). Other derivatives of **2** and **3** also have the identical chemical shifts to **2a** and **3a**.

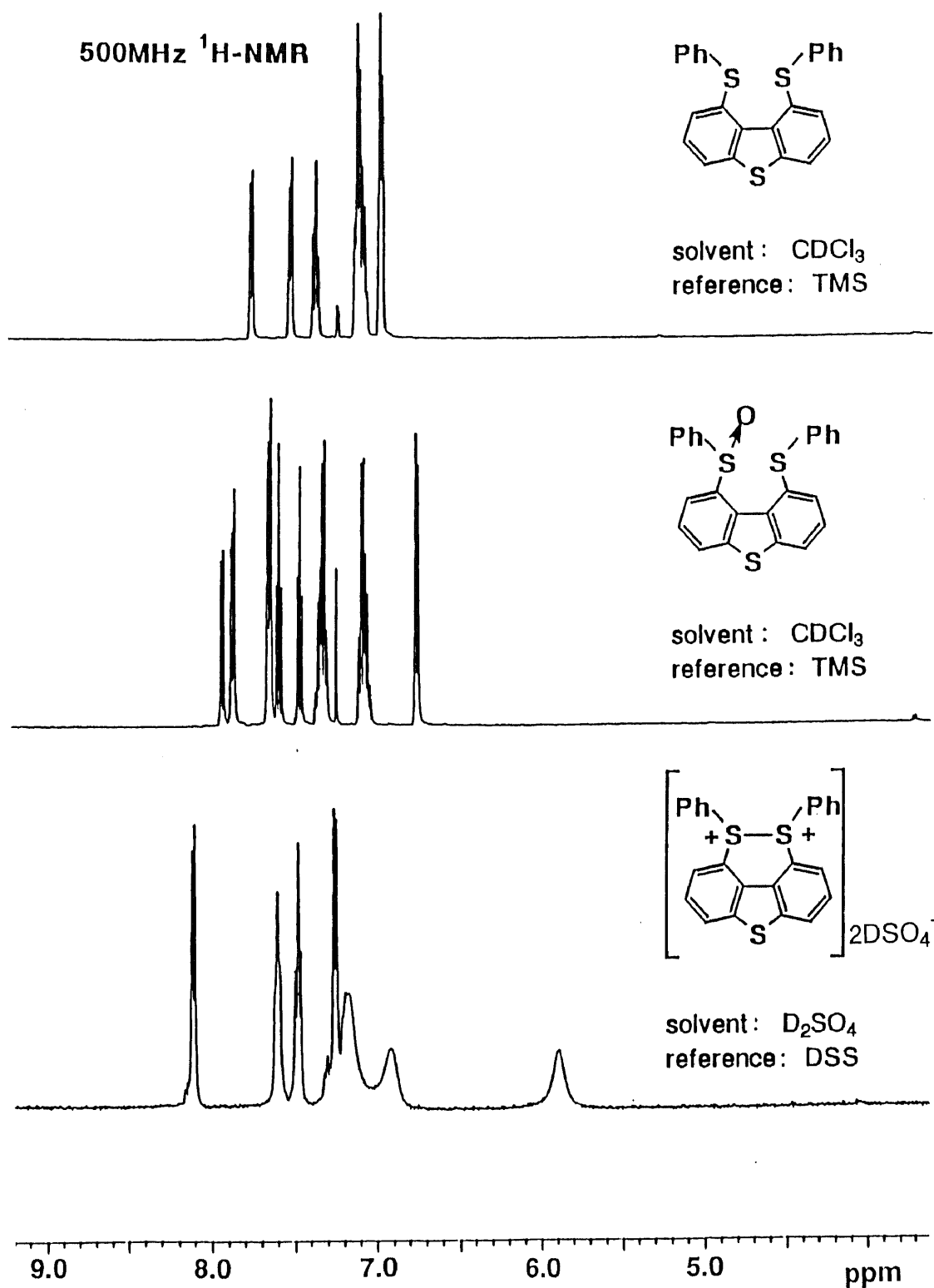
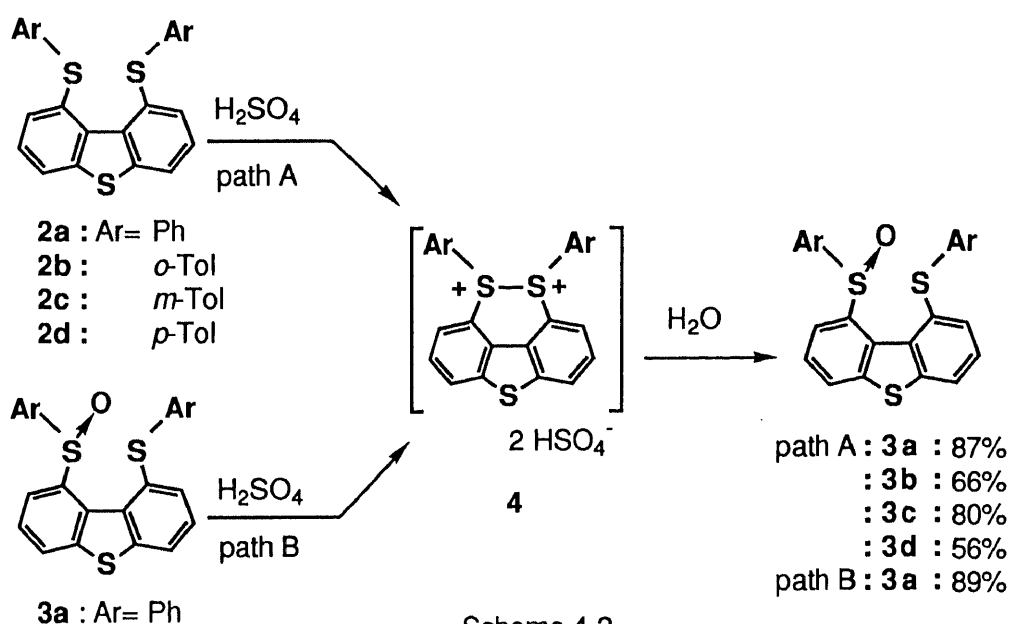


Fig. 4-2. 500 MHz  $^1\text{H}$ -NMR Spectra of Compounds **2a**, **3a** and Dication **4a**



In order to generate the dithia dications (**4**) the sulfides (**1**) and the sulfoxides (**2**) were dissolved in conc.  $\text{D}_2\text{SO}_4$  and took their  $^1\text{H}$ -NMR spectra according to the procedures employed for formation of dithia dications (Fig. 4-2).<sup>1</sup> The identical  $^1\text{H}$ -NMR spectra were observed by dissolving either **2** and **3** in conc.  $\text{D}_2\text{SO}_4$ . Both the compounds **2** and **3** in  $\text{H}_2\text{SO}_4$  solution gave the corresponding sulfoxides (**3**) in good yields after hydrolysis of the  $\text{H}_2\text{SO}_4$  solution demonstrating that the dication **4** should be formed. (Scheme 4-2).



Scheme 4-2

The  $^1\text{H}$ -NMR spectra of the dication (**4a**) in conc.  $\text{D}_2\text{SO}_4$ , unexpectedly, broadening of the phenyl protons attached to  $\text{PhS}$  groups was observed and the two protons shift to the upfield at 5.90 ppm (2H) as a broad singlet together with 6.94 (2H), 7.20

500 MHz  $^1\text{H}$ -NMR

solvent:  $\text{D}_2\text{SO}_4$

reference: DSS

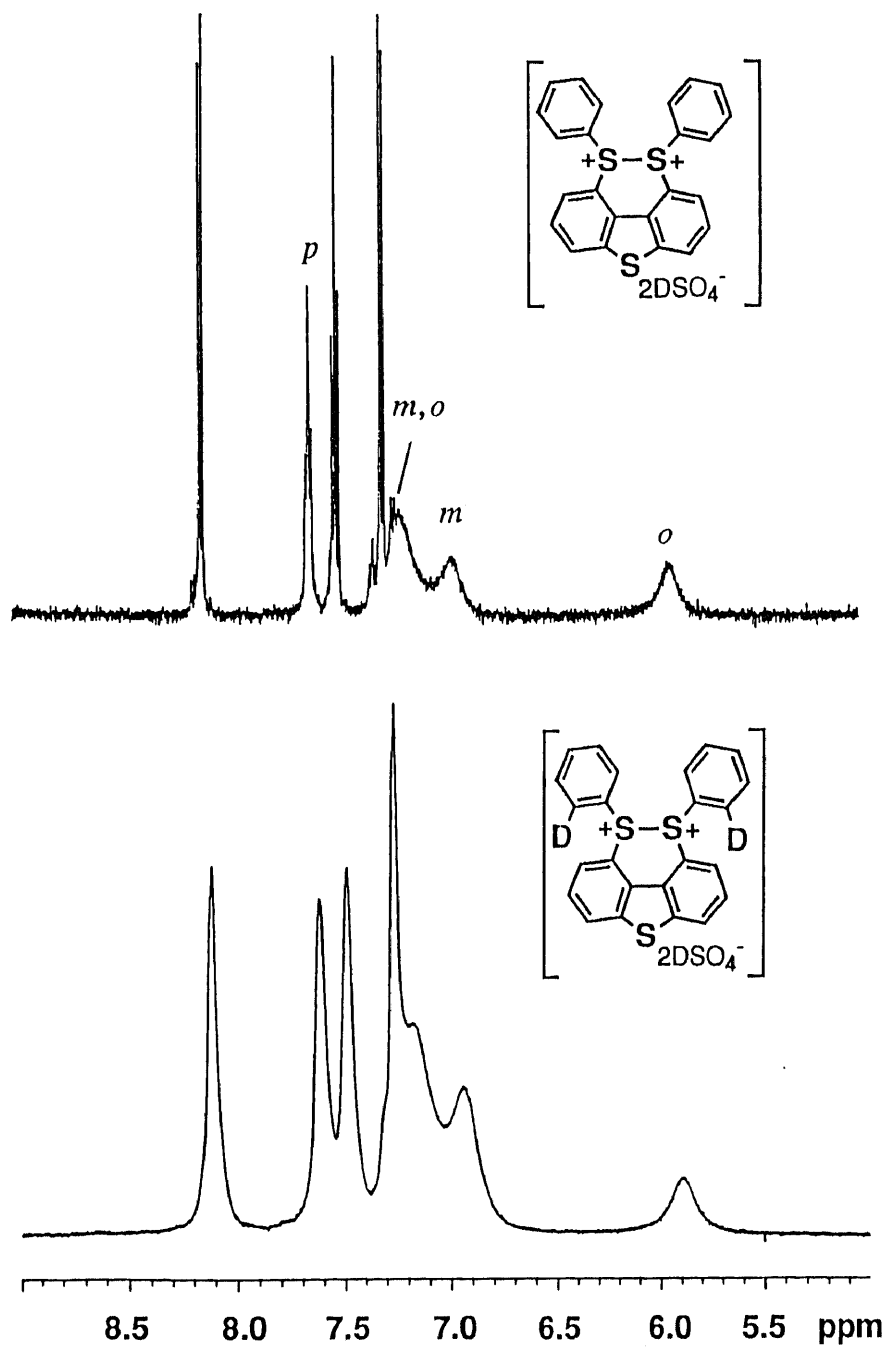


Fig. 4-3. 500 MHz  $^1\text{H}$ -NMR Spectra of Dications **4a** and **4a-d<sub>2</sub>**

(4H) and 7.61 (2H) ppm respectively. The highest signal at  $\delta$  5.90 is attributed to the two *o*-protons at the phenylthio group since in the signals of **2d** (Ar=*m*-Tol) and **2e** (Ar=2,5-Xylyl) in D<sub>2</sub>SO<sub>4</sub> only the shifts at 5.90 and 7.20 ppm are remained unchanged. The signal at  $\delta$  7.61 (t, 2H) is determined to be the *p*-protons due to the disappearance of this signal from **2b** (Ar=*p*-Tol). Thus the remaining four protons at 7.20 and 6.94 ppm are assigned to be the *m*-protons. Furthermore, 1,9-bis(*o*-deuterated phenylthio)dibenzothiophene (**2a-d<sub>2</sub>**) was synthesized and was dissolved in conc. D<sub>2</sub>SO<sub>4</sub> for measurement of the <sup>1</sup>H-NMR (Fig. 4-3).<sup>6</sup> In the NMR spectrum, the peak areas corresponding to two protons decreased from 5.90 ppm and 7.20 ppm indicating that the assignment of the <sup>1</sup>H-NMR of the dication **4a** in D<sub>2</sub>SO<sub>4</sub> is reasonable.

#### Studies on Variable Temperature <sup>1</sup>H-NMR Spectra of 1,9-Bis(phenylthio)dibenzothiophene Dication in D<sub>2</sub>SO<sub>4</sub> Solution

The <sup>1</sup>H-NMR spectra of **2a** and **3a** indicate clearly that the two phenyl rings at the sulfur atoms tend to overhang to the dibenzothiophene ring and the protons at the ortho and meta-positions are magnetically non-equivalent in the dithia dication (**3a**). Other substituted 1,9-bis(arylthio)dibenzothiophenes **2** show the identical <sup>1</sup>H-NMR behaviors, particularly, in 3,5-xylyl derivative (**2d**) two sharp methyl singlets appeared in the spectrum. These results demonstrate that the free rotation of

S-C(phenyl) bond should be restricted or pyramidal inversion at the sulfonium sulfur atoms in **4** does not take place at 27°C.

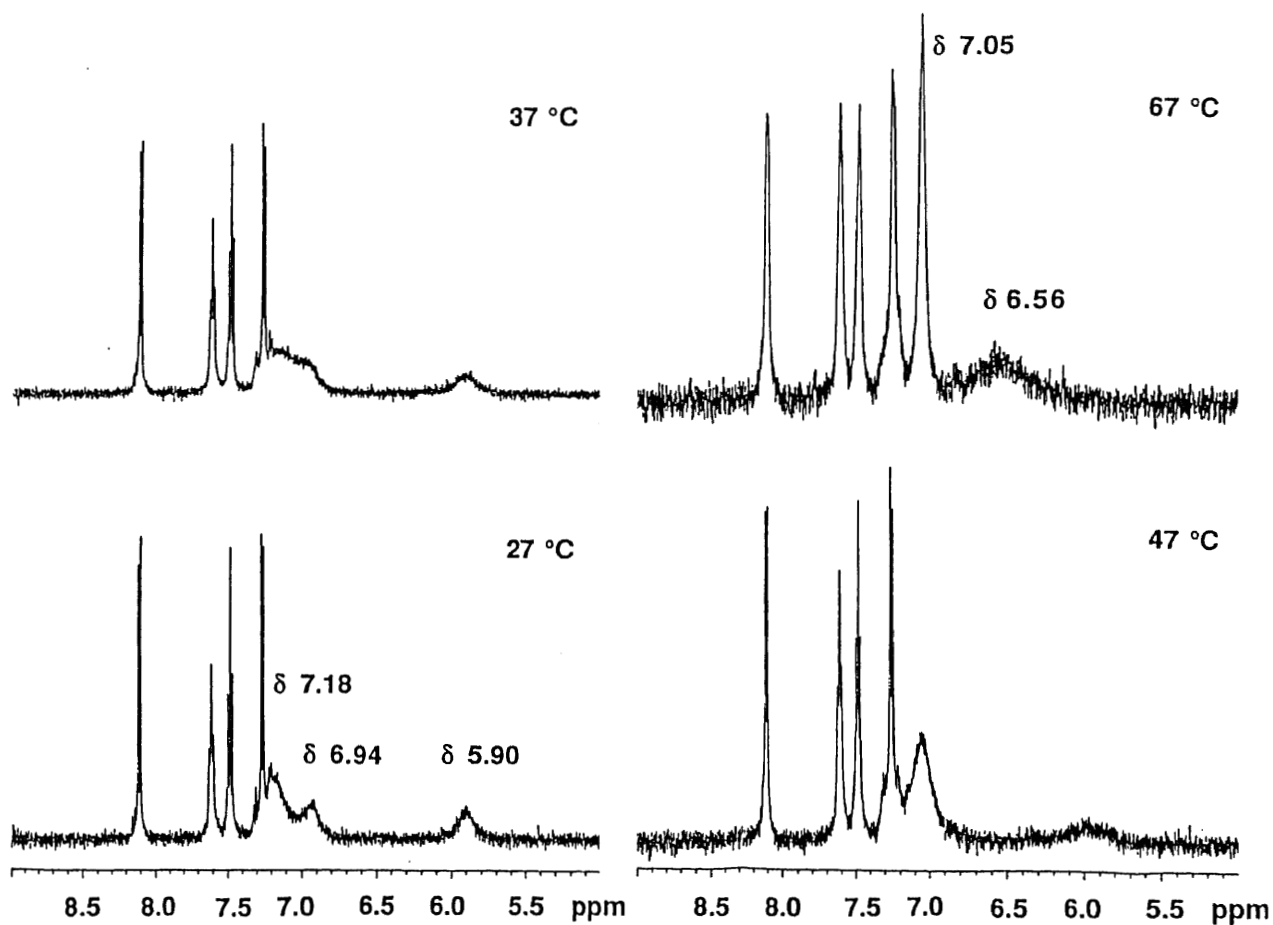


Fig. 4-4. Variable Temperature 500 MHz  $^1\text{H-NMR}$  Spectra of Dication **4a** in  $\text{D}_2\text{SO}_4$

The separation of the chemical shift and broadening for both the *o*- and *m*-protons in the phenyl rings in conc.  $\text{D}_2\text{SO}_4$  may be illustrated that the phenyl rings approach to the dibenzothiophene ring by the formation of S-S bond and change the positions by the slow ring rotation in the dithia dication. The broadening of the  $^1\text{H}$ -NMR by the presence of cation radical would be eliminated since the reaction of **3a** in  $\text{D}_2\text{SO}_4$  does not exhibit any ESR absorption (see infra). Dithia dication **4a** is unusually stable in conc.  $\text{H}_2\text{SO}_4$  even at  $70^\circ\text{C}$  for several hours. By elevating the temperature from  $27^\circ\text{C}$ , the two *o*-protons coalesced at  $67^\circ\text{C}$  into a broad singlet at 6.56 ppm (Fig. 4-4). The spectrum was recovered back to the original one by lowering the temperature to  $27^\circ\text{C}$ . Thus, the spectrum change by varying the temperature is attributed to the free rotation of the phenyl rings and the free energy of the rotation is calculated to be  $\Delta G^\ddagger = 63 \text{ KJ/mol}$  at  $67^\circ\text{C}$ .

#### ESR Spectra of 1,9-Disubstituted Dibenzothiophenes

In ESR spectrum of 1-(phenylsulfinyl)-9-(phenylthio)dibenzothiophene **3a**, very weak signal was obtained in conc.  $\text{H}_2\text{SO}_4$ . On the other hand, the ESR spectrum of **2a** was initially observed in conc.  $\text{H}_2\text{SO}_4$ , as composing one broad singlet with  $g=2.0058$  (Fig. 4-5), but this signal gradually and completely disappeared at  $25^\circ\text{C}$  after one week suggesting that one electron oxidation should take place to give the corresponding radical cation of **2b** which might be oxidized to the dication in conc.  $\text{H}_2\text{SO}_4$ .

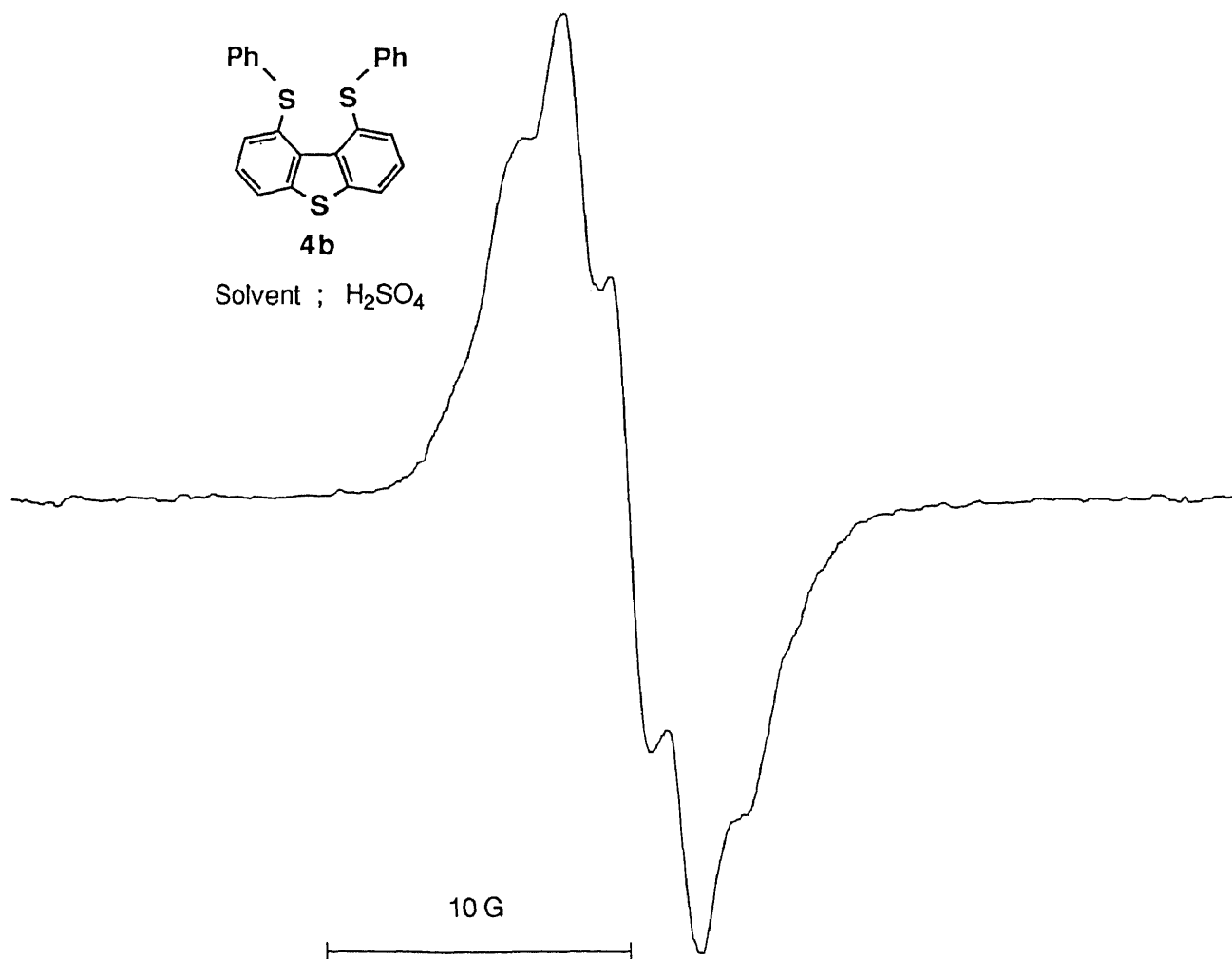


Fig. 4-5. ESR Spectra of Compound 2a

#### Fast Atom Bombardment Mass Spectrometry (FAB MS) of 1,9-Bis(phenylthio)dibenzothiophene Dication

To confirm the generation of dithia dications from **3a** in conc.  $\text{H}_2\text{SO}_4$ , first atom bombardment mass spectrometry (FAB MS) of 1,9-bis(phenylthio)dibenzothiophene dication (**4a**) was measured directly in the conc.  $\text{H}_2\text{SO}_4$  matrix. In the spectrum,  $m/z$  595 ( $\text{MH}^+$ ) and 497 ( $(\text{M}-\text{HSO}_4^-)^+$ ) were observed as the fragments of the salt of 1,9-bis(phenylthio)dibenzothiophene and  $2(\text{HSO}_4^-)$ .

These results directly support the formation of 1,9-dithia dication of 1,9-bis(phenylthio)dibenzothiophene in conc.  $\text{H}_2\text{SO}_4$ .

#### **Electrochemical Oxidation of 1,9-Disubstituted Dibenzothiophenes and Related Compounds**

The oxidation potential of **2a** was measured with cyclic voltammetry, and the value was compared with that of **4a**, dibenzothiophene and diphenyl sulfide using Pt electrode and  $\text{Ag}/(0.01 \text{ M})\text{AgNO}_3$  as a reference electrode (scan rate: 200 mV/s) at 25 °C in acetonitrile. Interestingly, the first peak potential of **2a** is very low, namely **2a** (0.86 V) in comparison with 1-(phenylthio)dibenzothiophene (1.12 V)<sup>7</sup>, dibenzothiophene (1.31 V) and diphenyl sulfide (1.21 V). But the electrochemical oxidations of these compounds were irreversible. The observed low peak potential of **2a** supports the transannular interaction between the two outer sulfur atoms on electrochemical oxidation.<sup>1</sup>

## Experimental Section

### General.

IR were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer.  $^1\text{H}$ -NMR spectra were measured on a Hitachi R-600 or a JEOL JNM-EX270 or a Bruker AM-500.  $^{13}\text{C}$ -NMR spectra were taken with a JEOL JNM-EX270 or Bruker AM-500. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX-SX102 mass spectrometer. For cyclic voltammetry measurements, a Hokuto Denko Co. Model HB-104 apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder. X-ray crystallographic analysis was performed by Prof. Iwasaki at University of Electro-Communications. Measurement of ESR spectrum was carried out by Dr. Morihashi and Dr. Yokoyama at the Department of Chemistry in this University. Elemental analyses were carried out by Chemical Analysis Center at this University.

### Materials.

All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co., Kanto Chemical Co., or Aldrich Chemical Co.. The reaction solvents were further purified by general methods.

### Synthesis

#### Preparation of 4,6-Disubstituted Thianthrene-5-oxides (1)

##### 4,6-Bis(o-tolylthio)thianthrene-5-oxide (1b)

Thianthrene-5-oxide (232 mg, 1 mmol) in THF (5 ml) was lithiated with 0.33 M LDA (10 ml, 3.3 mmol) at  $-78\text{ }^{\circ}\text{C}$ . To this solution was added o-tolyl disulfide (1.2 g, 5 mmol) in THF (10 ml) and



then stirred for 12 h at -20 °C. The solution was quenched with water, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (150 mlx3). The reaction mixture was purified by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub>). After purification by preparative liquid chromatography, 4,6-bis(*o*-tolylthio)thianthrene-5-oxide (**1b**) were obtained in 73% yield.

**1b:** (Ar=*o*-Tol) mp 221-222 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.64-6.67 (m, 14H, Ar-H) 2.44 (s, 6H, CH<sub>3</sub>); IR (KBr) 1054 cm<sup>-1</sup>; MS (m/z) 476 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>4</sub>: C, 65.51; H, 4.23. Found: C, 65.63; H, 4.25.

**4,6-Bis(*m*-Tolylthio)thianthrene-5-oxide (1c)**

**1c:** (Ar=*m*-Tol) mp 153 °C; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 7.60-7.20 (m, 14H, Ar-H), 2.31 (s, 6H, CH<sub>3</sub>); IR (KBr) 1031 cm<sup>-1</sup>; MS (m/z) 476 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>4</sub>: C, 65.51; H, 4.23. Found: C, 65.27; H, 4.07.

**4,6-Bis(3,5-xylylthio)thianthrene-5-oxide (1e)**

**1e:** (Ar=3,5-Xyl) 270 MHz <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.57 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.1 Hz, 2H, Ar-H), 7.29 (t, J=7.8 Hz, 2H, Ar-H) 7.14 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.1 Hz, 2H, Ar-H), 7.07 (s, 4H, *o*-Ph-H), 6.97 (s, 2H, *p*-Ph-H), 2.27 (s, 12H, CH<sub>3</sub>); MS (m/z) 504 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>24</sub>OS<sub>4</sub>: C, 66.63; H, 4.79. Found: C, 66.20; H, 4.74.

**Preparation of 1,9-Disubstituted Dibenzothiophenes (2) by Ring Contraction of 4,6-Disubstituted Thianthrene-5-oxides (1) with *n*-Butyllithium.**

**1,9-Bis(*o*-deuterated phenylthio)dibenzothiophene (2a-d<sub>2</sub>)**  
4,6-Bis(*o*-deuterated phenylthio)dibenzothiophene (1a-d<sub>2</sub>) was prepared by a similar method to the synthesis of 1a using 2,2'-bis(deuterated diphenyl)disulfide.<sup>6</sup>

4,6-Bis(*o*-deuterated phenylthio)thianthrene-5-oxide (1a-d<sub>2</sub>) (244 mg, 0.54 mmol) in THF (20 ml) was treated with *n*-butyllithium (1.64 M) (0.7 ml, 1.1 mmol) at -78 °C. After usual work-up procedures and purification by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub>) and then preparative liquid chromatography, 1,9-bis(*o*-deuterated phenylthio)dibenzothiophene (2a-d<sub>2</sub>) was obtained in 51% yield.

**1,9-Bis(*o*-tolylthio)dibenzothiophene (2b)**

**2b:** (Ar=*o*-Tol) mp 126 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.2 Hz, 2H, Ar-H), 7.37 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.2 Hz, 2H, Ar-H), 7.34 (t, J=7.8 Hz, 2H, Ar-H), 7.08-6.98 (m, 8H, Ar-H) 2.06 (s, 6H, CH<sub>3</sub>); IR (KBr) 1446, 1388, 741, 704 cm<sup>-1</sup>; MS (m/z) 428 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>S<sub>3</sub>: C, 72.86; H, 4.70. Found: C, 72.99; H, 4.74.

**1,9-Bis(*m*-tolylthio)dibenzothiophene (2c)**

**2c:** (Ar=*m*-Tol) mp 131-132 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, J=7.8 Hz, 2H, Ar-H), 7.52 (d, J=7.8 Hz, 2H, Ar-H), 7.37 (t, J=7.8 Hz, 2H, Ar-H), 6.91-6.90 (m, 4H, Ar-H), 6.74 (d, J=7.6 Hz, Ar-H) 2.20 (s, 6H, CH<sub>3</sub>); IR (KBr) 1591, 1386, 1179, 770, 706,

690,  $\text{cm}^{-1}$ ; MS ( $m/z$ ) 428 ( $M^+$ ); Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{S}_3$ : C, 72.86; H, 4.70. Found: C, 72.70; H, 4.67.

**1,9-Bis(*p*-tolylthio)dibenzothiophene (2d)**

**2d:** (Ar=*p*-Tol) mp 177 °C;  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.52 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.34 (t,  $J=7.8$  Hz, 2H, Ar-H), 6.96 (s, 8H, Ar-H), 2.24 (s, 6H,  $\text{CH}_3$ ); IR (KBr) 1437, 1388, 1166, 810, 799, 762, 700  $\text{cm}^{-1}$ ; MS ( $m/z$ ) 428 ( $M^+$ ); Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{S}_3$ : C, 72.86; H, 4.70. Found: C, 72.99; H, 4.74.

**1,9-Bis(3,5-xylylthio)dibenzothiophene (2e)**

**2e:** (Ar=3,5-Xyl) mp 184 °C;  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.51 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 2H, Ar-H), 7.36 (t,  $J=7.8$  Hz, 2H, Ar-H), 6.74 (s, 2H, *p*-Ph-H), 6.66 (s, 4H, *o*-Ph-H), 2.15 (s, 12H,  $\text{CH}_3$ ); IR (KBr) 1578, 1170, 835, 775, 685  $\text{cm}^{-1}$ ; MS ( $m/z$ ) 456 ( $M^+$ ); Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{S}_3$ : C, 73.64; H, 5.30. Found: C, 73.29; H, 5.34.

**Preparation of 1-(Phenylsulfinyl)-9-(phenylthio)-dibenzothiophene (3a)**

To a solution of 1,9-bis(phenylthio)dibenzothiophene (**2a**) (668 mg, 1.67 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$  was added *m*-chloroperbenzoic acid (mCPBA) (401 mg, 1.66 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$  at -20 °C. The solution was stirred for 8 h, and then ammonia gas was bubbled for a few minutes at 25 °C. A colorless precipitates were filtered off and the solvent was evaporated. The reaction mixture was purified by column chromatography (silica gel; eluent,  $\text{CH}_2\text{Cl}_2$  and ethylacetate), and 1,9-bis(phenylthio)-dibenzothiophene (**3a**) was obtained in 78% yield.

**3a**: mp 211-212 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, J=7.9 Hz, 1 H, Ar-H), 7.90 (d, J=7.9 Hz, 1H, Ar-H), 7.85 (d, J=7.8 Hz, 1H, Ar-H), 7.81 (d, J=7.8 Hz, 1H, Ar-H), 7.59 (t, J=7.9 Hz, 1H, Ar-H), 7.49 (d, J=7.0 Hz, 1 H, Ar-H), 7.42 (t, J=7.8 Hz, 1H, Ar-H), 7.28-7.19 (m, 2H, Ar-H), 7.10-7.05 (m, 2H, Ar-H), 7.00-6.94 (m, 2H, Ar-H), 6.84 (d, J=7.8 Hz, 1H, Ar-H); 125 MHz <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 146.0, 144.1, 141.3, 140.5, 138.7, 135.7, 133.8, 132.5, 130.5, 130.0, 128.8, 128.4, 128.3, 128.0, 127.8, 126.6, 126.1, 125.6, 125.2, 122.9; IR (KBr) 1031 cm<sup>-1</sup>; MS (m/z) 416 (M<sup>+</sup>); Anal. Calcd for C<sub>24</sub>H<sub>16</sub>OS<sub>3</sub>: C, 69.20; H, 3.87. Found: C, 69.16; H, 3.76.

**Reaction of 1,9-Bis(phenylthio)dibenzothiophene (2a) with conc. H<sub>2</sub>SO<sub>4</sub>.**

1,9-Bis(phenylthio)dibenzothiophene (**2a**) (198 mg, 0.495 mmol) was dissolved in 10 ml conc. H<sub>2</sub>SO<sub>4</sub>, and the solution was stirred for 24 h. To this solution was added ice water and 2 N NaOH solution. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mlx3). After evaporation of the solvent and purification of the product by column chromatography, 1,9-bis(phenylthio)dibenzothiophene (**2a**) and 1-(phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**3a**) were obtained in 6% and 87% yields respectively.

**Reaction of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzothiophene (3a) with conc. H<sub>2</sub>SO<sub>4</sub>.**

1-(Phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**3a**) (214 mg, 0.514 mmol) was dissolved in 10 ml conc. H<sub>2</sub>SO<sub>4</sub>, and the solution was stirred for 24 h. After similar treatment, 1,9-bis(phenylthio)dibenzothiophene (**2a**) and 1-(phenylsulfinyl)-9-

(phenylthio)dibenzothiophene (**3a**) were obtained in 5% and 89% yields respectively.

**Reaction of 1,9-Bis(o-tolylthio)dibenzothiophene (**2b**) with conc. H<sub>2</sub>SO<sub>4</sub>.**

**3b:** (Ar=o-Tol) mp 197 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, J=7.9 Hz, 1 H, Ar-H), 7.90 (d, J=7.9 Hz, 1H, Ar-H), 7.85 (d, J=7.8 Hz, 1H, Ar-H), 7.81 (d, J=7.8 Hz, 1H, Ar-H), 7.59 (t, J=7.9 Hz, 1H, Ar-H), 7.49 (d, J=7.0 Hz, 1 H, Ar-H), 7.42 (t, J=7.8 Hz, 1H, Ar-H), 7.28-7.19 (m, 2H, Ar-H), 7.10-7.05 (m, 2H, Ar-H), 7.00-6.94 (m, 2H, Ar-H), 6.84 (d, J=7.8 Hz, 1H, Ar-H), 2.07 (s, 3H, CH<sub>3</sub>), 1.83 (s, 3H, CH<sub>3</sub>); IR (KBr) 1021 cm<sup>-1</sup>; MS (m/z) 444 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>3</sub>: C, 70.23; H, 4.53. Found: C, 70.05; H, 4.45.

**Reaction of 1,9-Bis(m-tolylthio)dibenzothiophene (**2c**) with conc. H<sub>2</sub>SO<sub>4</sub>.**

**3c:** (Ar=m-Tol) mp 163.5-165 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, J=7.9 Hz, 1H, Ar-H), 7.90 (d, J=7.9 Hz, 1H, Ar-H), 7.86 (d, J=7.9 Hz, 1H, Ar-H), 7.67 (d, J=7.9 Hz, 1H, Ar-H), 7.62 (t, J=7.9 Hz, 1H, Ar-H), 7.55 (s, 1H, Tol-H), 7.49 (t, J=7.9 Hz, 1H, Ar-H), 7.47 (d, J=7.5 Hz, 1H, Tol-H), 7.23 (t, J=7.5 Hz, 1H, Tol-H), 7.19 (d, J=7.5 Hz, 1H, Ar-H), 6.98 (t, J=7.9 Hz, 1H, Tol-H), 6.88 (d, J=7.9 Hz, 1H, Tol-H), 6.62 (s, 1H, Tol-H), 6.46 (d, J=7.9 Hz, 1H, Tol-H), 2.25 (s, 3H, CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>); IR (KBr) 1035 cm<sup>-1</sup>; MS (m/z) 444 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>3</sub>: C, 70.23; H, 4.53. Found: C, 70.34; H, 4.48.

**Reaction of 1,9-Bis(*p*-tolylthio)dibenzothiophene (2d) with conc. H<sub>2</sub>SO<sub>4</sub>.**

**3d:** (Ar=*p*-Tol) mp. 218 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.94 (d, J=7.9 Hz, 1H, Ar-H), 7.88 (d, J=7.9 Hz, 1H, Ar-H), 7.84 (d, J=7.9 Hz, 1H, Ar-H), 7.61 (t, J=7.9 Hz, 1H, Ar-H), 7.60 (d, J=7.9 Hz, 1H, Ar-H), 7.56 (d, J=8.2 Hz, 2H, Tol-H), 7.44 (t, J=7.9 Hz, 1H, Ar-H), 7.14 (d, J=8.0 Hz, 2H, Ar-H), 6.94 (d, J=8.0 Hz, 2H, Ar-H), 6.77 (d, J=8.2 Hz, 2H, Ar-H), 2.34 (s, 3H, CH<sub>3</sub>), 2.23 (s, 3H, CH<sub>3</sub>); IR (KBr) 1031 cm<sup>-1</sup>; MS (m/z) 444 (M<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>20</sub>OS<sub>3</sub>: C, 70.23; H, 4.53. Found: C, 70.06; H, 4.57.

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5. The deuterium content for **2a-d<sub>2</sub>** was determined with MS spectrometry; 2,2'-bisdeuterated diphenyl disulfide was prepared with 2-deuterated thiophenol and hydrogen peroxide in 77% yield (deuterium content>99%); G. D. Figuly, C. K. Loop, J. C. Martin, *J. Am. Chem. Soc.*, **111**, 654 (1989).
6. See Chapter 1.

## CHAPTER 5

### FIRST PREPARATION OF NEW STABLE DIBENZO[*bc, fg*] - [1,4]DITHIOPENTALENE AND DETERMINATION OF THE STRUCTURE BY X-RAY ANALYSIS

#### Abstract

On photolysis and thermolysis of 1,9-bis(methylthio)dibenzo-  
thiophene, novel dibenzo[*bc, fg*][1,4]dithiopentalene (**1**) and  
thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene (**2**) were obtained  
substantially. X-ray crystallographic analysis revealed that  
the structure of the compound **1** was completely planar. The  
electrochemical oxidations of **1** and **2** were carried out by  
cyclic voltammetry.

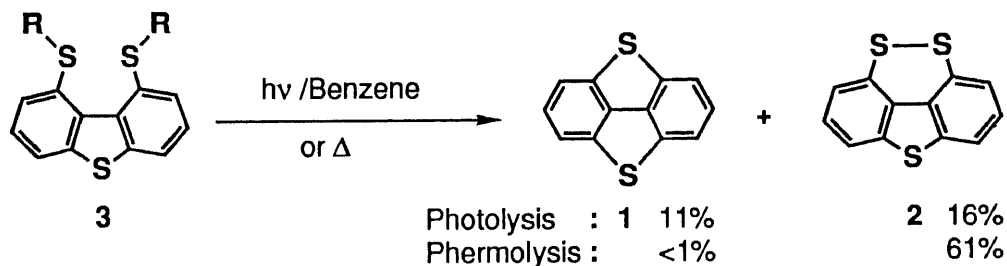


## Introduction

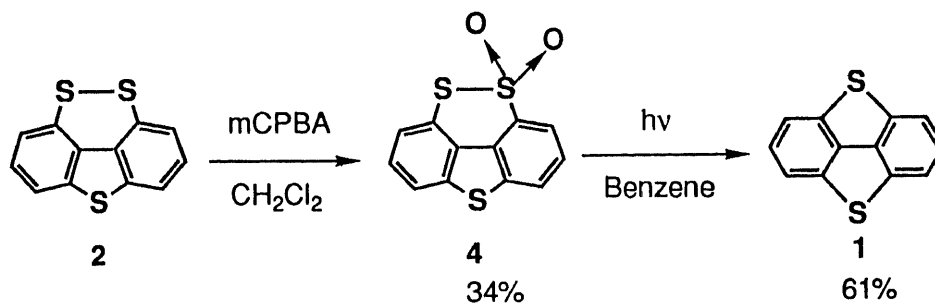
Recently, thiophene and its derivatives have been attracted much attention as important sources for new materials.<sup>1</sup> On the other hand, thienothiophenes having two fused thiophene rings have been investigated as one of the representatives of  $10\pi$  hetero aromatic compounds. There are four isomeric thienothiophenes among which thieno[3,4-*c*]thiophene, called nonclassical thiophene, is rather unstable since it must be used unusual bonding orbitals of the sulfur atoms to accommodate  $10\pi$  electrons for resonance stabilization.<sup>2</sup> Several stable thieno[3,4-*c*]thiophenes bearing four substituents such as tetraphenylthieno[3,4-*c*]thiophene and tetrakis(alkylthio)thieno[3,4-*c*]thiophene have been reported by Cava and Yoneda.<sup>3</sup> As a new stable thieno[3,4-*c*]thiophene, dibenzo[*bc,fg*][1,4]dithiopentalene (**1**), the dithio analogue of dibenzo[*cd,gh*]pentalene which was prepared by Trost and his co-workers,<sup>4</sup> was obtained serendipitously upon thermolysis or photolysis of 1,9-bis(methylthio)dibenzothiophene (**3**). As far as examined the literatures, dithiopentalene has never been reported except the hypothetical polymer of dibenzodithiopentalene by Kertesz.<sup>5</sup> This chapter reports the results of the first preparation of a new stable dithiopentalene (**1**) and determination of the structure by X-ray crystallographic analysis.

## Results and Discussion

Dibenzo[*bc, fg*][1,4]dithiopentalene (**1**) was found to be generated during the measurement of melting point of 1,9-bis(methylthio)dibenzothiophene **3**. Upon overheating (350–400 °C) the capillary tube containing **3**, both **1** and **2** were sublimed at the top of the tube from which was realized the formation of **1**. Typically, **3** was placed in a long pyrex tube and heated gently with a burner flame. The reaction mixture was separated and purified by column chromatography and preparative HPLC to afford the two products.



Scheme 5-1



Scheme 5-2

Surprisingly one minor product less than 1% yield was found to be the pentalene (**1**) together with thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene (**2**) in 61% yield. On the other hand, photolysis of **3** with a 400 W high pressure mercury lamp for 10 h gave **1** and **2** in 11% and 16% yields respectively (Scheme 5-1).

Meinwald reported the elegant preparation of naphtho[2,3,4-*ij*]thiete on photolysis of 1,8-dithionaphthalene-1,1-dioxide. It was expected that this ring contraction reaction could be applied to the photolysis of thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene-9,9-dioxide (**4**) for conversion to compound **1**. Actually, the photolysis of thiosulfonate **4** which was prepared by oxidation of **2** with *m*-chloroperbenzoic acid (mCPBA) proceeded cleanly under irradiation for 72 hr to afford **1** as a sole product in 61% yield together with the recovered **4** in 33% (Scheme 5-2).<sup>6</sup>

Table 5-1. UV Spectra

Compd.		$\lambda_{\max}$ nm ( $\epsilon$ )	
DT	233 (28000)	285 (5000)	323 (1400)
<b>1</b>	243 (32000)	270 (4300)	329 (1900)
<b>2</b>	224 (9200)	250 (9800)	357 (1400)

All compounds were measured in acetonitrile at 25 °C.

DT: Dibenzothiophene.

The UV spectrum of pentalene **1** lacks the visible band at around 530 nm observed in tetraphenylthieno[3,4-*c*]thiophene corresponding to the biradical structure (Table 5-1).<sup>2b,3a</sup> This

result suggests that the pentalene **1** should have neither a biradical nor a charged structure. Therefore, the detailed structural analysis of **1** was performed by X-ray crystallographic analysis shown in Fig. 5-1, 5-2 and the results are summarized in Tables 5-2 and 5-3.

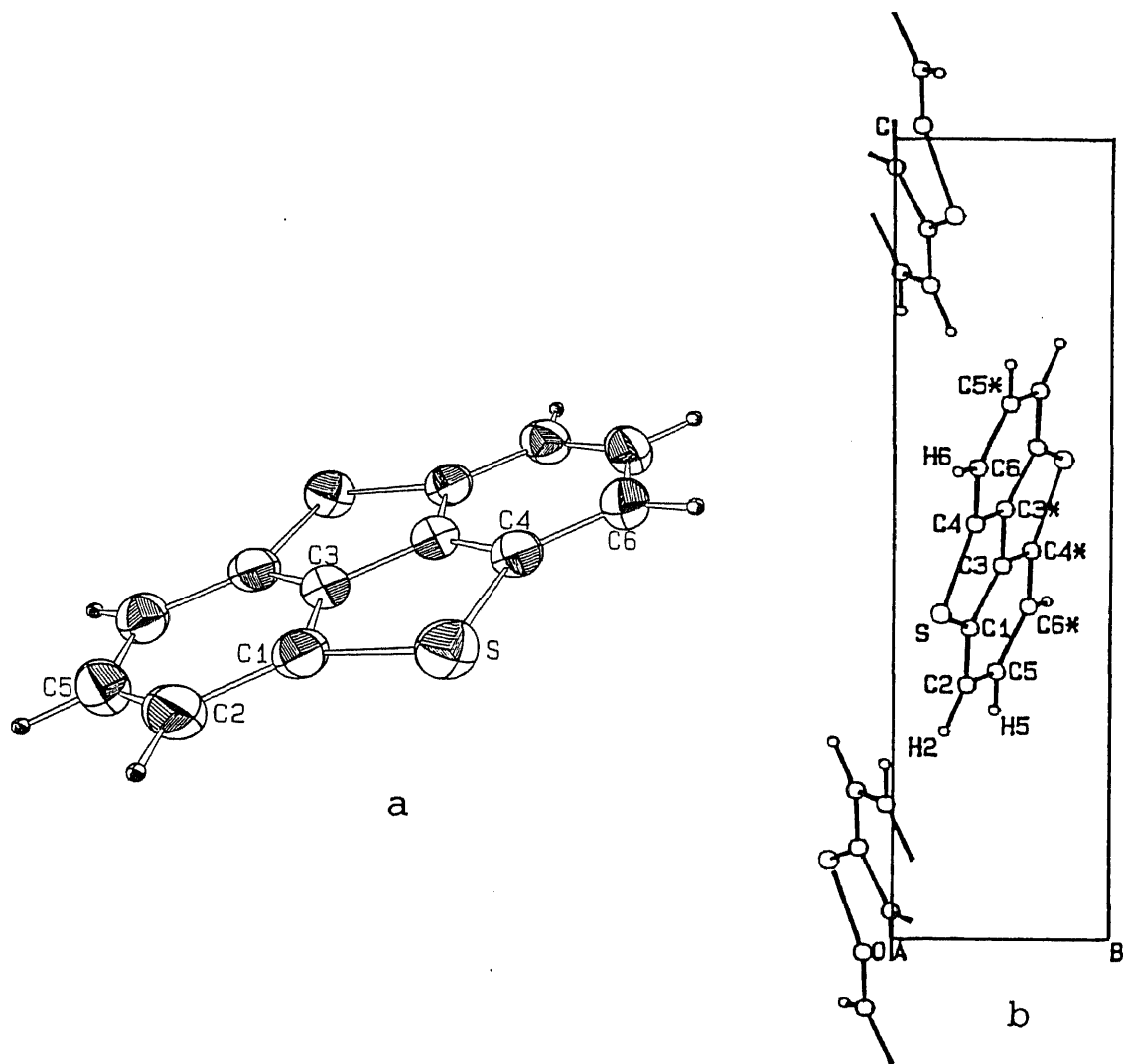


Fig. 5-1 X-Ray Crystallographic Analysis of Compound **1**; a) Molecular Structure; b) the Projection of the Crystal Structure Viewd along the A Axis.

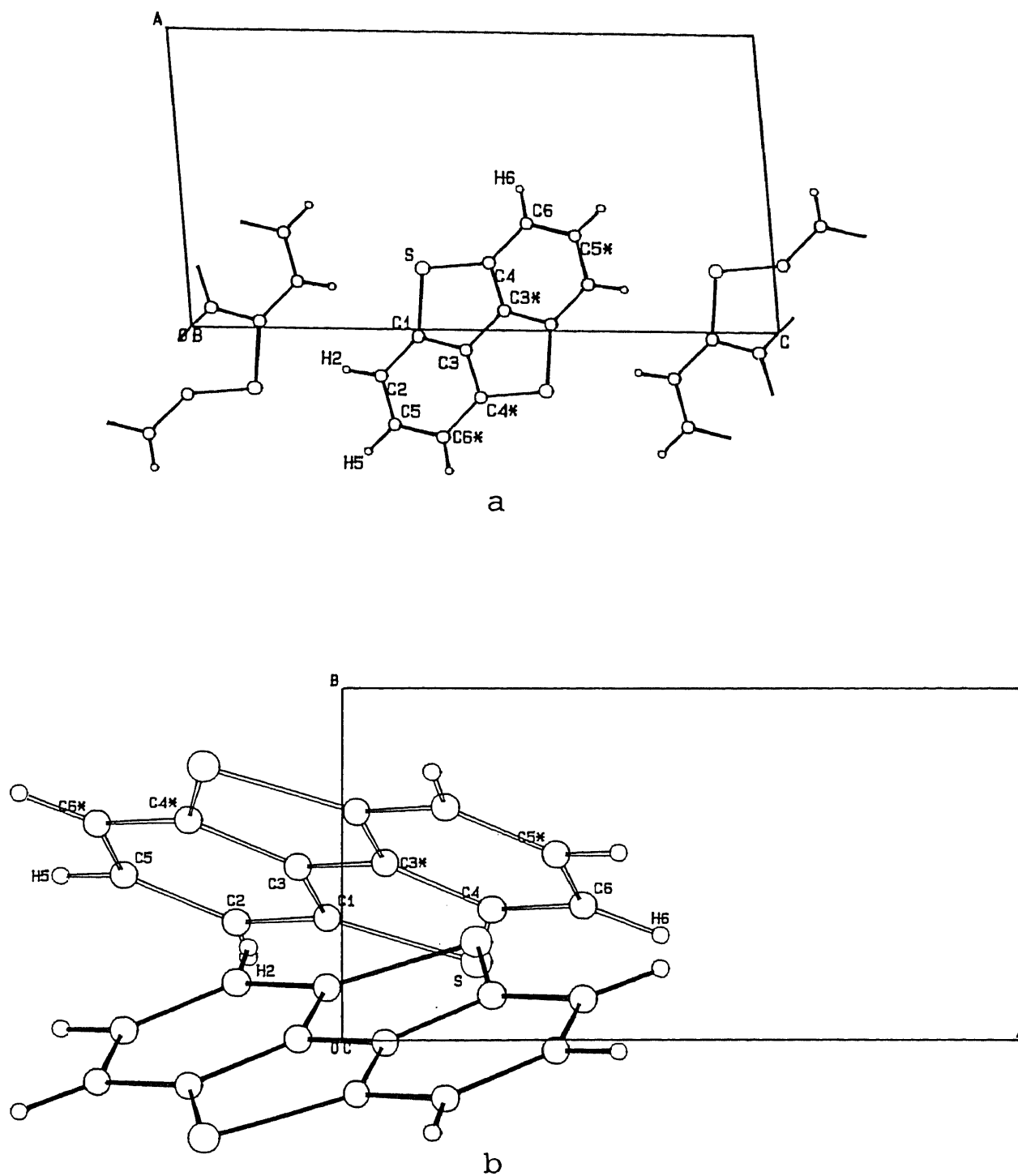


Fig. 5-2. The Projection of the Crystal Structure of **1**; a) Viewd along the *B* Axis; b) Viewd along the *C* Axis.

Table 5-2. Bond Angles of Dibenzo[*bc,fg*][1,4]dithiopentalene (**1**).

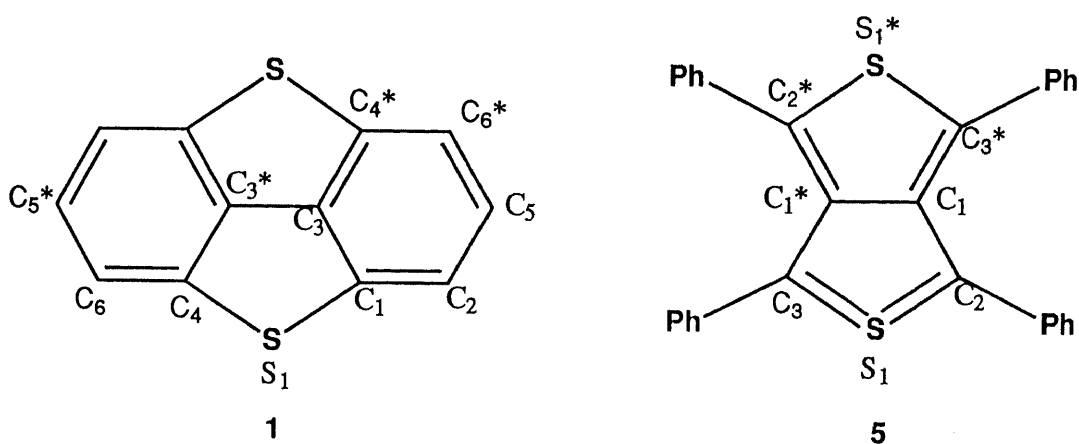
Atoms	angle (deg.)	ESD	Atoms	angle (deg.)	ESD
C <sub>1</sub> -S-C <sub>4</sub>	92.3	0.1	C <sub>2</sub> -C <sub>1</sub> -C <sub>3</sub>	116.1	0.2
S-C <sub>1</sub> -C <sub>3</sub>	108.2	0.2	C <sub>1</sub> -C <sub>2</sub> -C <sub>5</sub>	116.8	0.2
C <sub>1</sub> -C <sub>3</sub> -C <sub>3</sub> *	115.7	0.2	C <sub>2</sub> -C <sub>5</sub> -C <sub>6</sub> *	125.7	0.2
C <sub>3</sub> -C <sub>3</sub> *-C <sub>4</sub>	115.8	0.2	S-C <sub>4</sub> -C <sub>6</sub>	135.8	0.2
S-C <sub>4</sub> -C <sub>3</sub> *	108.1	0.2	C <sub>3</sub> *-C <sub>4</sub> -C <sub>6</sub>	116.1	0.2
S-C <sub>1</sub> -C <sub>2</sub>	135.8	0.2	C <sub>4</sub> -C <sub>6</sub> -C <sub>5</sub> *	116.8	0.2
C <sub>1</sub> -C <sub>3</sub> -C <sub>4</sub> *	128.5	0.2			

The Partial Torsional Angles (deg.) are as follows: C<sub>4</sub>-S-C<sub>1</sub>-C<sub>2</sub>, 179.94(0.29); C<sub>4</sub>-S-C<sub>1</sub>-C<sub>3</sub>, 0.26(0.20); C<sub>1</sub>-S-C<sub>4</sub>-C<sub>6</sub>, 179.81(0.28); S-C<sub>1</sub>-C<sub>2</sub>-C<sub>5</sub>, -179.79(0.22); C<sub>3</sub>-C<sub>1</sub>-C<sub>2</sub>-C<sub>5</sub>, -0.08(0.35).

This result indicates clearly that the pentalene **1** is a completely planar molecule having three C<sub>2</sub> axes bisecting the S-S\*, the C<sub>5</sub>-C<sub>5</sub>\* axes and the one perpendicular to the plane of the pentalene ring, belonging to the point group D<sub>2h</sub>. The C-S bonds of the thiophene rings are 1.791 and 1.790 Å which are considerably longer than that of tetraphenylthieno[3,4-*c*]thiophene (**5**) (1.705 and 1.707 Å)<sup>3b</sup> and the normal C-S bond length of thiophene (1.714 Å)<sup>7a</sup> and dibenzothiophene (1.740 Å)<sup>7b</sup>. Furthermore, the benzene rings of **1** are considerably distorted from that of normal hexagonal structure (Table 5-3). The bond length of C<sub>3</sub>-C<sub>3</sub>\* (1.386 Å) is shorter than that of thienothiophene (**5**) (1.452 Å) suggesting that the two benzene rings are stabilized by conjugation and the two sulfur atoms less participate to the essential  $\pi$ -conjugation than the thiophene ring.

The crystals have a following data: formula,  $C_{12}H_6S_2$ ; FW, 214.31;  $F(000)=220$ ; crystal dimensions, 0.30x0.20x0.40 mm; Mo  $K\alpha$  radiation ( $\lambda=0.70930$  Å); temperature= $23\pm 1$  °C; monoclinic space group,  $P2_1/c$ ;  $a=7.641(1)$  Å,  $b=4.000(0)$  Å,  $c=14.909(2)$  Å,  $\beta=95.23(6)$  °;  $v=453.8$  Å<sup>3</sup>;  $Z=2$ ;  $\rho=1.57$  g/cm<sup>3</sup>;  $\mu=5.1$  cm<sup>-1</sup>;  $R=0.029$  ( $R_w=0.033$ ).

Table 5-3. Comparison of Bond Lengths of X-Ray Crystallographic Analysis of Compound **1** with Structures of **1** Calculated by MNDO and X-ray Analysis of Tetraphenylthieno[3,4-*c*]thiophene (**5**)<sup>3b</sup>.



parameter	X-ray data of <b>1</b> (Å)	MNDO of <b>1</b> (Å)	Parameter	X-ray data of <b>5</b> (Å) <sup>3b</sup>
S-C <sub>1</sub>	1.791	1.738	S <sub>1</sub> *-C <sub>2</sub> *	1.707
S-C <sub>4</sub>	1.790		S <sub>1</sub> -C <sub>3</sub>	1.705
C <sub>1</sub> -C <sub>3</sub>	1.377	1.401	C <sub>1</sub> *-C <sub>2</sub> *	1.417
C <sub>4</sub> -C <sub>3</sub> *	1.375		C <sub>3</sub> -C <sub>1</sub> *	1.397
C <sub>3</sub> -C <sub>3</sub> *	1.386	1.422	C <sub>1</sub> -C <sub>1</sub> *	1.452
C <sub>1</sub> -C <sub>2</sub>	1.397	1.403		
C <sub>4</sub> -C <sub>6</sub>	1.395			
C <sub>2</sub> -C <sub>5</sub>	1.399	1.424		
C <sub>5</sub> -C <sub>6</sub> *	1.406			

To evaluate the theoretically most stable structure of **1**, MNDO calculation was carried out at the energetically most stable structure and the calculated bond lengths were compared with those obtained by the X-ray crystallographic analysis. These results are shown in Table 2 together with compound **5**. These results suggest that the structure of **1** determined by the X-ray crystallographic analysis is somewhat different from that obtained by the MNDO calculation.

On the other hand, Trost determined the structure of dibenzo[cd,gh]pentalene to have a completely planar structure and also to have a very large strain energy of 66 kcal/mol.<sup>4</sup> Similarly, it is natural to expect that dibenzodithiopentalene (**1**) should also possess a large strain energy.

#### **Measurement of Cyclic Voltammetry of Compounds 1 and 2**

It is predicted that the compound **1** has  $16\pi$  electrons and hence **1** is stabilized on aromatization by two electron oxidation. Since the electrochemical character of **1** would be attractive properties, the oxidation potentials of **1** and **2** were measured with cyclic voltammetry in acetonitrile at 20 °C, using a Pt electrode, Ag/0.01 M AgNO<sub>3</sub> as a reference electrode (scan rate: 200 mV/s).<sup>8</sup> The oxidation potentials of these compounds are listed as follows; **1** ( $E_p=1.16$  V, irreversible); **2** ( $E_{1/2}=0.91$  V, reversible); dibenzothiophene ( $E_p=1.31$  V, irreversible). However, the cyclic voltammogram of **1** after 20 times scanning at 200 mV/s reveals nearly the same behavior of polythiophene on electrolysis (Fig. 5-3).<sup>9</sup> Actually, the electrode was found to



be coated with a yellow polymer of which structure has not been determined.

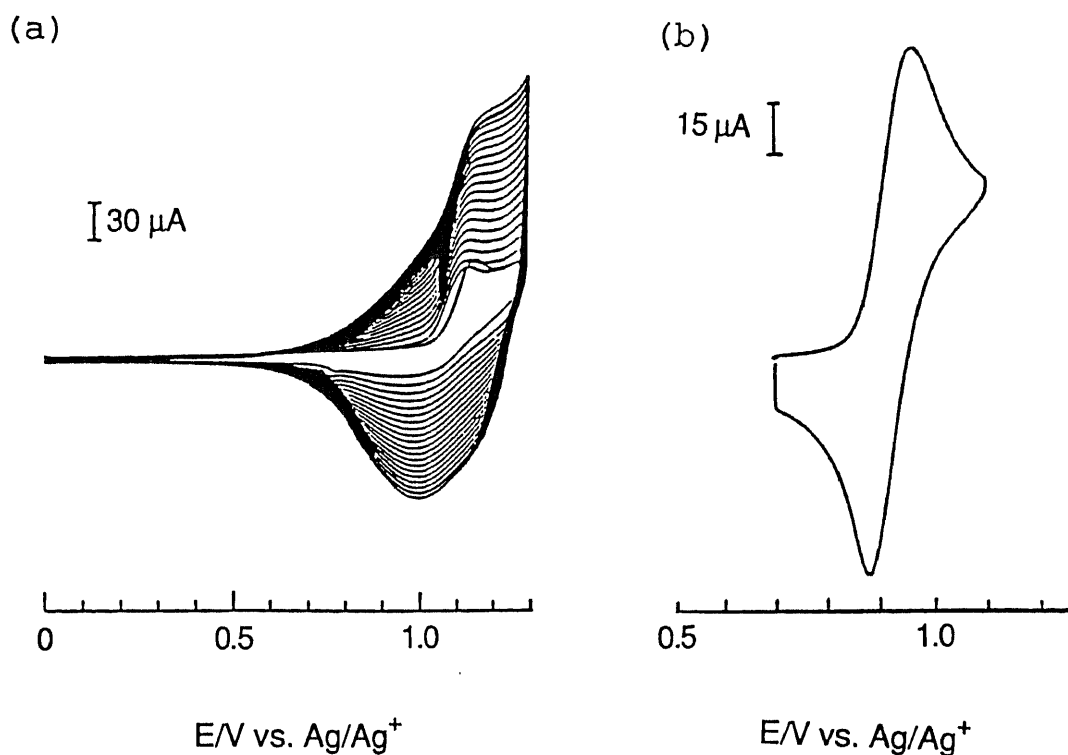


Fig. 5-3. (a) Cyclic Voltammogram of Compound **1** after 20 Times Scanning; (b) Cyclic Voltammogram of Compound **2** .

#### ESR Spectrum of Thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene (**2**)

Since the compound **2** has a reversible cyclic voltammogram as described above, the stable radical cation of **2** should be generated by oxidation. In fact in an ESR spectrum of thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene (**2**), a strong signal

was obtained in conc. sulfuric acid at 25 °C, as a broad signal with  $g=2.0106$  (Fig. 5-5). This result suggests that one electron oxidation takes place readily to give the corresponding radical cation of 2.

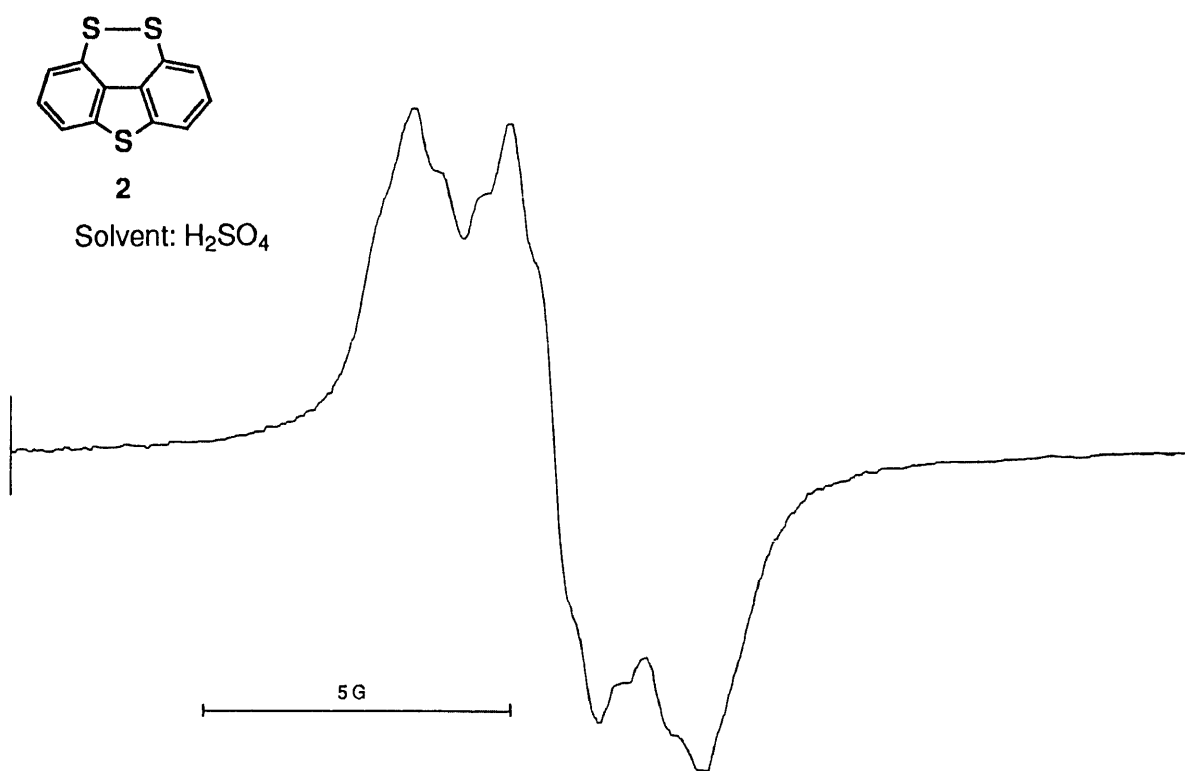


Fig. 5-5. ESR Spectrum of Compound 2 in Conc. H<sub>2</sub>SO<sub>4</sub>.

## Experimental Section

### General.

IR spectra were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer.  $^1\text{H}$ -NMR spectra were measured on a Hitachi R-600 or a JEOL JNM-EX270 or a Bruker AM-500.  $^{13}\text{C}$ -NMR spectra were taken with a JEOL JNM-EX270 or a Bruker AM-500. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX SX102 mass spectrometer. For cyclic voltammetry measurements, a Hokuto Denko Co. Model HB-104 apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder. X-ray crystallographic analysis and elemental analyses were carried out by Chemical Analysis Center at this University. MNDO calculation was performed by Prof. Kikuchi at Department of Chemistry in this University. Measurement of ESR spectrum was carried out by Dr. Morihashi at Department of Chemistry in this University.

### Materials.

All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co., Kanto Chemical Co., or Aldrich Chemical Co.. The reaction solvents were further purified by general methods.

### Synthesis

**Preparation of Dibenzo[bc,fg][1,4]dithiopentalene (1) and Thieno[2,3,4,5-lmn][9,10]dithiophenanthrene (2)**

### Thermolysis

1,9-Bis(methylthio)dibenzothiophene (3) (11 mg, 0.04 mmol) was placed in a pyrex tube and heated gradually with Bunzen burner

for a few minutes. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . After purification with column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ ) and preparative HPLC, the compounds **1** and **2** were obtained in <1% and 61% yields respectively.

### Photolysis

1,9-Bis(methylthio)dibenzothiophene (**3**) (100 mg, 0.36 mmol) was placed in a pyrex tube and dry benzene (5 ml) was added under argon atmosphere. The solution was irradiated with 400 W high pressure mercury lamp for 10 h at 20 °C. After distillation of the solvent, the reaction mixture was purified with column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ ). Further purification was carried out with preparative HPLC and the compounds **1** and **2** were obtained in 11% and 16% yields respectively.

**1**: mp 165 °C (sublimed);  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (t,  $J=7.7$  Hz, 4H, Ar-H), 7.60 (t,  $J=7.7$  Hz, 2H, Ar-H, 4,6-H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.6, 135.7, 128.3, 116.2; MS ( $m/z$ ) 214 ( $\text{M}^+$ ); UV  $\lambda_{\text{max}}$  ( $\epsilon$ ) 243 (32000), 270 (4300), 329 (1900); Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{S}_2$ : C, 67.25; H, 2.83. Found C, 67.34; H, 2.90.

**2**: mp 132.5-133°C.  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J=7.9$  Hz, 2H, Ar-H), 7.40 (t,  $J=7.9$  Hz, 2H, ArH) 7.25 (d,  $J=7.9$  Hz, 2H, Ar-H);  $^{13}\text{C}$ -NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 131.8, 128.2, 128.1, 121.9, 121.7. MS ( $m/z$ ) 246 ( $\text{M}^+$ ); UV  $\lambda_{\text{max}}$  ( $\epsilon$ ) 224 (9200), 250 (9800), 357 (1400); Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{S}_3$ : C, 58.50; H, 2.45. Found C, 58.40; H, 2.48.

**Oxidation of Thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene  
(2) with mCPBA**

To a solution of thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene (2) (132 mg, 0.54 mmol) in 30 ml CH<sub>2</sub>Cl<sub>2</sub>, mCPBA (370 mg, 1.5 mmol) in 30 ml CH<sub>2</sub>Cl<sub>2</sub> was added at 20 °C. The solution was stirred for 12 h, and then ammonia gas was bubbled for a few minutes at 20 °C. Coloreless solids were filtered off and the solvent was evaporated. The reaction mixture was purified by column chromatography (silica gel; eluent, CH<sub>2</sub>Cl<sub>2</sub> and ethylacetate) to give thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene-9,9-dioxide (4) in 34% yield.

**4:** mp 220-221 °C; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 8.17 (dd, J<sub>1</sub>=8.1 Hz, J<sub>2</sub>=0.5 Hz, 1H, Ar-H), 8.03 (dd, J<sub>1</sub>=7.6 Hz, J<sub>2</sub>=0.5 Hz, 1H, Ar-H), 7.94 (dd, J<sub>1</sub>=8.1 Hz, J<sub>2</sub>=0.5 Hz, 1H, Ar-H), 7.78 (t, J=8.1 Hz, 1H, Ar-H), 7.62 (t, J=7.6 Hz, 1H, Ar-H), 7.49 (dd, J<sub>1</sub>=7.6 Hz, J<sub>2</sub>=0.5 Hz, 1H Ar-H); <sup>13</sup>C-NMR (67 MHz, CDCl<sub>3</sub>) δ 141.3, 140.9, 137.2, 130.9, 128.4, 127.9, 127.7, 127.0, 126.8, 123.7, 122.3, 115.5. IR (KBr) 1317, 1149 (SO<sub>2</sub>) cm<sup>-1</sup>; MS (m/z) 278 (M<sup>+</sup>); Anal. Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>S<sub>3</sub>: C, 51.78; H, 2.17. Found C, 51.68; H, 2.22.

**Photolysis of Thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene-9,9-dioxide (4)**

Thieno[2,3,4,5-*lmn*][9,10]dithiophenanthrene-9,9-dioxide (4) (15 mg, 0.05 mmol) was placed in a pyrex tube and dry benzene (3 ml) was added after replacing air with Ar. The solution was irradiated with 400 W high pressure mercury lamp for 72 h. After distillation of the solvent, the reaction mixture was purified with column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>).

Further purification was carried out with preparative HPLC and the products **1** and **4** were obtained in 61% and 33% yields respectively.

## **X-Ray Crystallographic Analysis**

### **Data Collection**

A yellow needle crystal of  $C_{12}H_6S_2$  having approximate dimension of 0.30x0.20x0.40 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo  $K\alpha$  radiation ( $\lambda=0.70930$  Å) on Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflection in the range  $10^\circ < \theta < 14^\circ$ , measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are:  $a=7.641(1)$ ,  $b=4.000(0)$ ,  $c=14.909(2)$  Å,  $\beta=95.23(6)^\circ$ ,  $V=453.8$  Å<sup>3</sup>. For  $Z=2$  and F.W.=214.31 the calculated density is 1.57 g/cm<sup>3</sup>. From the systematic absences of :

$$h\ 0\ l\quad l=2n$$

$$0\ k\ 0\quad k=2n$$

and from subsequent least-squares refinement, the space group was determined to be  $P2_1/c$  (# 14).

The data were collected at a temperature of  $23\pm 1$  °C using the omega scan technique. The scan rate varied from 1 to 5 °/min (in omega). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is

used and assures good counting statistics for weak reflections where a slow scan ratio is used. Data were collected to a maximum  $2\theta$  of  $50.0^\circ$ . The scan range (in deg.) was determined as a function of  $\theta$  to correct for the separation of the  $k\alpha$  doublet;<sup>10</sup> the scan width was calculated as follows:

$$\omega \text{ scan width} = 0.5 + 0.350 \tan \theta$$

Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of  $\theta$ . The horizontal aperture width ranged from 1.8 to 2.3 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.80 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 13.8.

#### **Data Reduction**

A total of 765 reflections were collected. As a check on crystal and electronic stability 3 representative reflections were measured every 60 min. A linear decay correction was applied. The correction fraction on  $I$  ranged from 1.000 to 1.001 with an averaged value of 1.000.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $5.1 \text{ cm}^{-1}$  for Mo  $k\alpha$  radiation. No absorption correction was made. An extinction correction was not necessary. Intensities of equivalent reflections were averaged. The agreement factors for the

averaging of the 69 observed and accepted reflections was 0.9% based on intensity and 0.6% based on  $F_o$ .

### Structure Solution and Refinement

The structure was solved by direct methods. Using 184 reflections (minimum  $E$  of 1.20) and 2322 relationships, a total 16 phase sets were produced. A total of 6 atoms were located from an  $E$ -map prepared from the phase set with probability statistics: absolute figure of merit=1.19, residual=0.12, and  $\psi$  zero=1.122. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and their positions were refined in least-squares; their isotropic thermal parameters were held fixed at 4.0 Å. The structure was refined in full-matrix least-squares where the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight  $w$  is defined as 1.0 for all observed reflections.

Scattering factors were taken from Cromer and Waber.<sup>11</sup> Anomalous dispersion effects were included in  $F_c$ ;<sup>12</sup> the values for  $\Delta f'$  and  $\Delta f''$  were those of Cromer.<sup>13</sup> Only the 742 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 73 variable parameters and converged (largest parameter shift was 1.19 times its esd) with unweighted and weighted agreement factors of:

$$R_1 = \sum |F_o - F_c| / \sum |F_o| = 0.029$$

$$R_2 = \text{SQRT}(\sum w(F_o - F_c)^2 / \sum w F_o^2) = 0.033$$

The standard deviation of an observation of unit weight was 0.47. The highest peak in the final difference Fourier had a

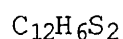


height of  $0.25 \text{ e}/\text{\AA}^3$  ; the minimum negative peak had a height of  $-0.19 \text{ e}/\text{\AA}^3$ .<sup>14</sup> Plots of  $\Sigma w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\lambda$ , and various classes of indices showed no unusual trends.

All calculations were performed on a VAX computer using SDP/VAX.<sup>15</sup>

## Tables of Experimental Details

### A. Crystal Data



F.W. 214.31                       $F(000) = 220$

crystal dimensions: 0.30x0.20x0.40 mm

Mo  $K\alpha$  radiation ( $\lambda=0.70930 \text{ \AA}$ )

temperature= $23 \pm 1$  °C

monoclinic space group  $P2_1/c$

$a=7.641(1) \text{ \AA}$     $b=4.000(0) \text{ \AA}$     $c=14.909(2) \text{ \AA}$

$\beta=95.23(6)^\circ$

$v = 453.8 \text{ \AA}^3$

$Z=2$     $\rho=1.57 \text{ g/cm}^3$

$\mu=5.1 \text{ cm}^{-1}$

## B. Intensity Measurements

Instruments: Enraf-Nonius CAD4 diffractometer

Monochromator: Graphite crystal, incident beam

Attenuator: Zr foil, factor 13.8

Detector aperture: 1.8 to 2.3 mm horizontal  
4.0 mm vertical

Crystal-detector dist.: 21 cm

Scan type:  $\omega$ - $2\theta$

Scan rate: 1-5 °/min (in omega)

Scan width, deg:  $0.5 + 0.35 \tan \theta$

Maximum  $2\theta$ :  $50.0^\circ$

No. of refl. measured: 765

Corrections: Lorentz-polarization  
Linear decay (from 1.000 to 1.001 on I)

### C. Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Refined with Biso = 4.0 Å
Refinement:	Full-Matrix least-squares
Minimization function:	$\sum w( F_o  -  F_c )^2$
Least-squares weights:	$4F_o^2/\sigma^2(F_o^2)$
Anomalous dispersion:	All non-hydrogen atoms
Reflection included:	742 with $F_o^2 > 3.0\sigma(I)$
Parameter refined:	73
Unweighted agreement factor:	0.029
Weighted agreement factor:	0.033
Esd of Obs. of unit weight:	0.47
Convergence, large shifts:	1.19σ
High peak in final diff. map:	0.25(4) e/Å <sup>3</sup>
Low peak in final diff. map:	-0.19(0) e/Å <sup>3</sup>
Computer hardware:	VAX
Computer software:	SDP/VAX (Enraf-Nonius & B. A. Frenz & Associates, Inc.)

#### D. Positional and Thermal Parameters

Table of Positional Parameters and Their Estimated  
Standard Deviations

Atom	x	y	z
S	0.20266(8)	0.2211(2)	0.40290(4)
C <sub>1</sub>	-0.0227(3)	0.3486(6)	0.3865(2)
C <sub>2</sub>	-0.1559(3)	0.3354(7)	0.3159(2)
C <sub>3</sub>	-0.0664(3)	0.4945(6)	0.4651(2)
C <sub>4</sub>	0.2250(3)	0.3718(6)	0.5164(2)
C <sub>5</sub>	-0.3188(3)	0.4705(7)	0.3326(2)
C <sub>6</sub>	0.3594(3)	0.3826(7)	0.5862(2)
H <sub>2</sub>	-0.138(4)	0.235(9)	0.257(2)
H <sub>5</sub>	-0.411(4)	0.467(9)	0.284(2)
H <sub>6</sub>	0.475(4)	0.293(9)	0.581(2)

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## CHAPTER 6

### NEW PHOTOCHEMICAL SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF TRIPHENYLENO[4,5-*bcd*]THIOPHENE DERIVATIVES

#### Abstract

Photolysis of sterically crowded 1,9-bis(phenylthio)-dibenzothiophene (**1a**) with high pressure mercury lamp in benzene afforded triphenyleno[4,5-*bcd*]thiophene (**2a**)<sup>1</sup> and tribenzo[*bc,e,hi*][2,7]dithioazulene (**3a**). When bis(*o*-deuterated phenylthio)dibenzothiophene (**1b**) was used, 5-deuterated triphenylenothiophene (**2b**) was obtained together with 6-deuterated tribenzodithioazulene (**3b**). These results suggest that this reaction proceeds via an intramolecular cyclization process. The electrochemical oxidation was performed with cyclic voltammetry for these triphenylenothiophene derivatives.



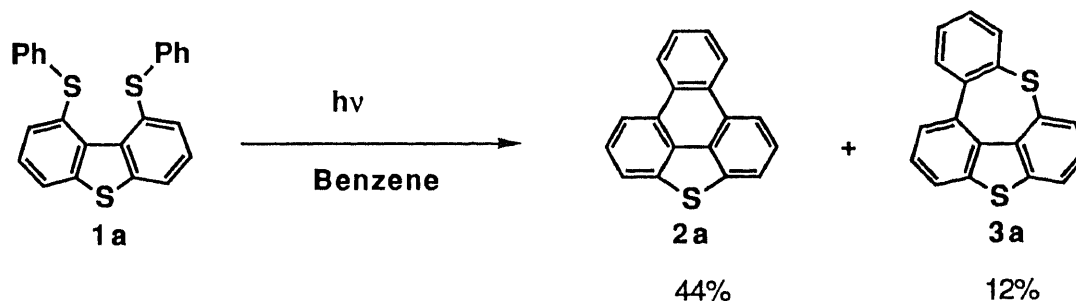
## Introduction

In the previous chapter, formation of a new type of dithiadications was described using sterically congested 1,9-disubstituted dibenzothiophenes and conc. sulfuric acid. On the other hand, it was also described that thermolysis of 1,9-bis(methylthio)dibenzothiophene produced dibenzo[*bc,fg*][1,4]-dithiopentalene and the structure was confirmed to be nearly planar by X-ray crystallographic analysis. In contrast to the thermolysis, in the photolysis of 1,9-bis(arylthio)dibenzothiophene a concomitant desulfurization and a ring contraction reaction were observed. A few photochemical reactions involving C-S bond cleavage of the diaryl sulfones and formation of C-C bond to produce biaryls have been reported.<sup>2</sup> This chapter reports that the photolysis of sterically congested 1,9-bis(arylthio)dibenzothiophenes (**1**) gives triphenylenothiophene derivatives (**2**) and tribenzodithioazulene derivatives (**3**) via intramolecular cyclization reaction. Their electrochemical oxidation was carried out with cyclic voltammetry.

## Results and Discussion

As a typical example, photolysis of 1,9-bis(phenylthio)dibenzothiophene (**2a**) was carried out using 400 W high pressure mercury lamp in dry benzene under argon atmosphere for 10 h. After usual work-up and purification with silica gel column chromatography and preparative HPLC, desulfurization and

cyclization products, triphenyleno[4,5-*bcd*]thiophene (**2a**) and hitherto unknown tribenzo[*bc,e,hi*][2,7]dithioazulene (**3a**) in 44% and 12% yields respectively (Scheme 6-1).

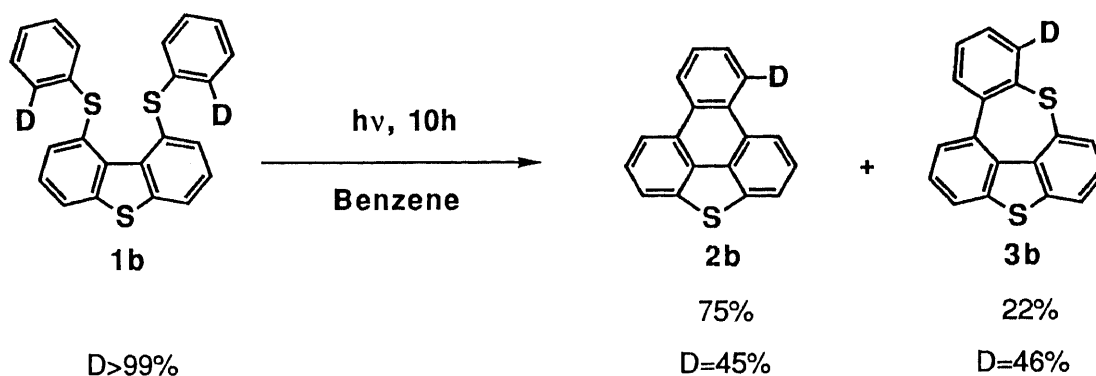


Scheme 6-1

In the reaction, the question is arisen whether the fused benzene ring to the 1,9-positions of dibenzothiophene skeleton came from the phenylthio substituents or solvent benzene. As an answer to the question, since *p*-xylene using as a reaction solvent was not incorporated in the product in this photolytic reaction, the photolytic cyclization of **1** should proceed intramolecular process.

As to further consideration of the reaction mechanism, tracer experiment was carried out using deuterated compound. 1,9-Bis(*o*-deuterated phenylthio)dibenzothiophene (**1b**) was prepared (deuterium content >99%)<sup>3</sup> and reacted in benzene solution as shown in Scheme 6-2. Interestingly, the products were confirmed to be 5-deuterated triphenylenothiophene (**2b**) (75%, D=45%) and 6-deuterated tribenzodithioazulene (**3b**) (22%, D=46%). The position and the content of deuterium were determined with the 500 MHz <sup>1</sup>H-NMR and Mass spectrometry of **2b**.

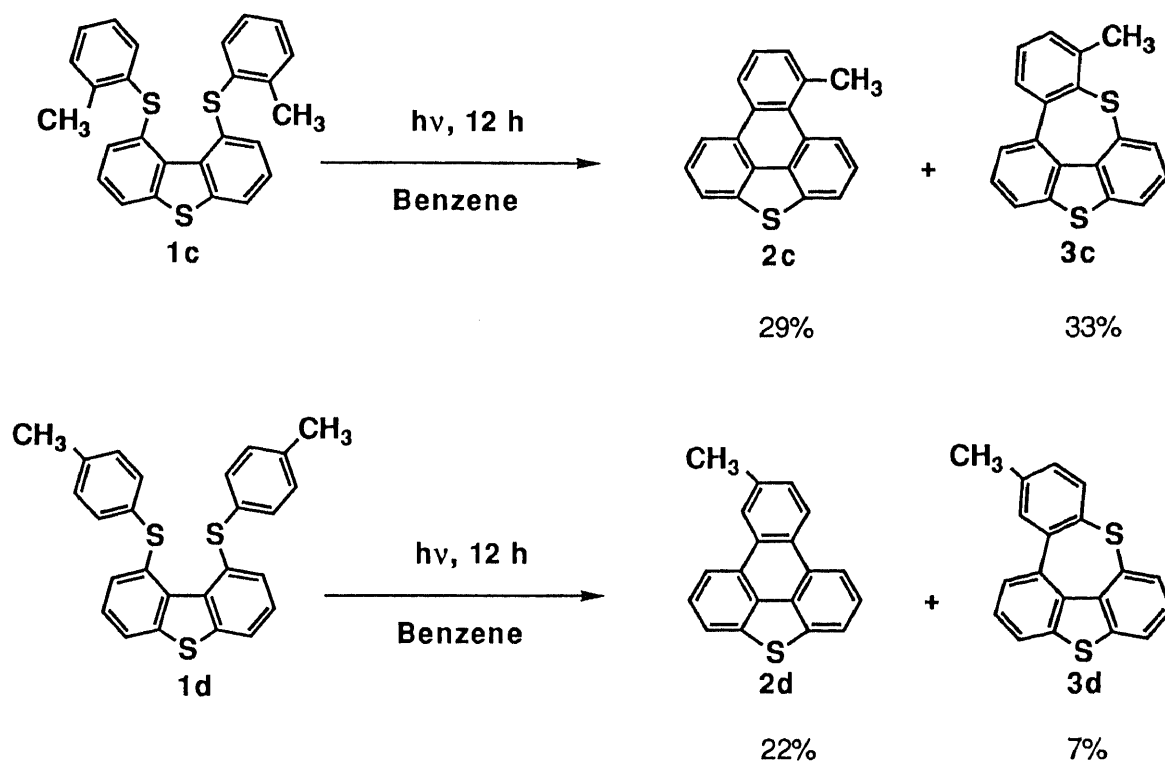
and **3b**. On the basis of these spectroscopic studies, it is clear that the isomerization of the deuterium atom did not occur during the cyclization process. These results demonstrate that these photolytic cyclization reactions proceed via an initial removal of one arylthio group as a radical to leave dibenzothiophene radical bearing one 9-phenylthio group which attacks intramolecularly at the ortho position of the phenylthio group.



Scheme 6-2

Meanwhile, although tribenzodithioazulene (**3**) which is presumed to be the intermediate in the formation of **2**, was irradiated with high pressure mercury lamp, the desulfurization reaction was not observed at all and triphenylenothiophene was not obtained. Furthermore, 4,6-bis(phenylthio)thianthrene and 1-(phenylthio)dibenzothiophene did not react at all under similar photolysis condition. These facts suggest that the cyclization reactions were initiated between the two sterically congested substituents which would be required essentially in these photolytic reactions. Thus it is predicted that one

electron transfer reaction occurs initially to exclude steric strain between the two encumbered sulfur atoms.



Scheme 6-3

Since no isomerization of deuterium in 1,9-bis(o-deuterated phenylthio)dibenzothiophene has been observed in the reaction, it is expected that these reactions become very useful for synthesis of the heterocyclic compounds fused triphenylenothiophene ring and that these reactions can be applied to the regiospecific introduction of the several substituents at the triphenylenothiophene ring. Actually, 1,9-bis(o-tolylthio)dibenzothiophene (**1c**) and 1,9-bis(p-tolylthio)dibenzothiophene (**1d**) were prepared and reacted under these photolytic conditions

(Scheme 6-3). The photolysis of *o*-tolylthio derivative **1c** proceeded similarly to give 5-methyltriphenylenothiophene (**2c**) and 6-methyltribenzodithioazulene (**3c**) in 29% and 33% yields respectively while in the photolysis of *p*-tolylthio derivative **1d** 6-methyltriphenylenothiophene (**2d**) and 7-methyltribenzodithioazulene (**3d**) were obtained in 22% and 7% yields respectively.

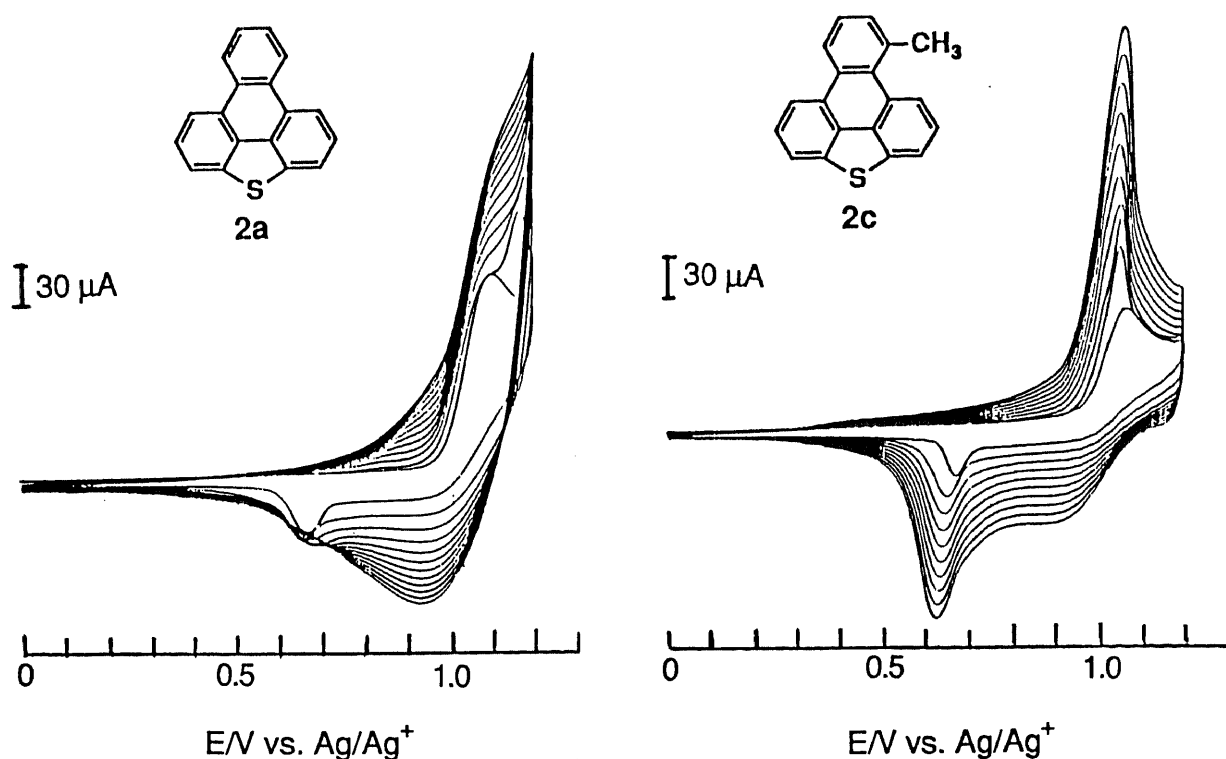


Fig. 6-1. Cyclic Voltammograms of Compounds **2a** and **2c** with Repeated Scan; **2a**: 12 Times, **2c**: 10 Times

It is well known that thiophene derivatives produce electroconductive and electrochromic polythiophenes by oxidation,<sup>4</sup> and therefore it is important to know the properties

of the present thiophene derivatives by electrochemical methods. To evaluate the electrochemical properties of triphenylenothiophene derivatives **2a,c,d** and tribenzodithioazulene (**3a**), the oxidation potentials were measured with cyclic voltammetry in acetonitrile at 20 °C. The voltammograms of compounds **2** and **3** were irreversible, and their peak potentials ( $E_p$  vs Ag/0.01 M AgNO<sub>3</sub>; scan rate: 200 mV/s) were as follows: **2a** (1.11 V), **2c** (1.08 V), **2d** (1.09 V) and **3a** (1.11 V).

Interestingly, when the cyclic voltammetries for **2a** and **2c** were measured with repeated scanings between 0 to 1.20 V; **2a**: 12 times and **2c**: 10 times, their peak intensities of electric current increased gradually in both voltammograms (Fig.6-1). However in the tribenzodithioazulene (**3a**) and dibenzothiophene these phenomena were not observed by repeated scanings. These results suggest that the electroconductive poly(triphenylenothiophene) derivatives were produced on the electrode surface in the compounds **2**.<sup>4</sup> In fact, light yellow materials appeared on the electrode surface after measuring cyclic voltammetry of compounds **2a** and **2c**.

## Experimental Section

### General.

IR spectra were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer.  $^1\text{H}$ -NMR spectra were measured on a Hitachi R-600 or a JEOL JNM-EX270 or a Bruker AM-500.  $^{13}\text{C}$ -NMR spectra were taken with a JEOL JNM-EX270 or a Bruker AM-500. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX SX102 mass spectrometer. For cyclic voltammetry measurements, a Hokuto Denko Co. Model HB-104 apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder. The deuterium contents of all compounds were determined with MS (JEOL JMX-SX102) and deuterated positions were confirmed by 270 or 500 MHz  $^1\text{H}$ -NMR spectrometry. The measurement of the oxidation potentials for all compounds was carried out using Pt electrode and Ag/(0.01 M)  $\text{AgNO}_3$  as a reference electrode (scan rate: 200 mV/s) at 20 °C in acetonitrile. Elemental analyses were carried out by Chemical Analysis Center at this University.

### Materials.

All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Kanto Chemical Co., or Aldrich Chemical Co.. The reaction solvents were further purified by general methods.

## Synthesis

### Triphenyleno[4,5-*bcd*]thiophene (2a) and Tribenzo-[*bc, e, hi*][2,7]dithioazulene (3a)

1,9-Bis(phenylthio)dibenzothiophene (1a) (40 mg, 0.1 mmol) was placed in a pyrex tube and dry benzene (5 ml) was added. The solution was irradiated with a 400 W high pressure mercury lamp for 10 h at 20 °C. After irradiation the solvent was evaporated and the residual mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and purified with column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>). After purification with preparative HPLC, the compounds 2a and 3a were obtained in 44% and 12% yields respectively.

**2a:** mp 196.5-197 °C (lit. 190-191)<sup>1a</sup>; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 8.79-8.71 (m, 2H, Ar-H), 8.49 (d, J=7.8 Hz, 2H, Ar-H), 8.08 (d, J=7.8 Hz, 2H, Ar-H), 7.88 (t, J=7.8 Hz, 2H, Ar-H), 7.80-7.72 (m, 2H, Ar-H); <sup>13</sup>C-NMR (67 MHz, CDCl<sub>3</sub>) δ 140.0, 130.9, 130.6, 128.8, 127.6, 127.1, 124.3, 120.1, 117.1; MS (m/z) 258 (M<sup>+</sup>).

**3a:** <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 7.90 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.1 Hz, 1H, Ar-H), 7.79-7.74 (m, 2H, Ar-H), 7.72-7.67 (m, 1H, Ar-H), 7.61 (t, J=7.8 Hz, 1H, Ar-H), 7.50 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.35 Hz, 1H, Ar-H), 7.42 (t, J=7.8 Hz, 1H, Ar-H), 7.41-7.32 (m, 3H, Ar-H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 143.0, 140.4, 139.7, 139.3, 134.0, 133.8, 133.2, 133.0, 129.0, 127.7, 127.5, 127.1, 126.8, 126.0, 125.7, 122.0, 121.8; Found: m/z 290.0216. Calcd for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: M, 290.0224



**5-Deuterated Triphenyleno[4,5-*bcd*]thiophene (2b) and 6-Deuterated Tribenzo[*bc,e,hi*][2,7]dithioazulene (3b)**

**2b:**  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79–8.71 (m, 1.5H, Ar-H), 8.49 (d,  $J=7.8$  Hz, 2H, Ar-H), 8.08 (d,  $J=7.8$  Hz, 2H, Ar-H), 7.88 (t,  $J=7.8$  Hz, 2H, Ar-H), 7.80–7.72 (m, 2H, Ar-H); MS ( $m/z$ ) 259 ( $\text{M}^+$ ),  $D=45\%$ .

**3b:**  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (dd,  $J_1=8.0$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.79–7.74 (m, 1.5H, Ar-H), 7.72–7.67 (m, 1H, Ar-H), 7.61 (t,  $J=7.8$  Hz, 1H, Ar-H), 7.50 (dd,  $J_1=7.8$  Hz,  $J_2=1.35$  Hz, 1H, Ar-H), 7.42 (t,  $J=7.8$  Hz, 1H, Ar-H), 7.40–7.34 (m, 3H, Ar-H); MS ( $m/z$ ) 291 ( $\text{M}^+$ ), 46%.

**5-Methyltriphenyleno[4,5-*bcd*]thiophene (2c) and 6-Methyltribenzo[*bc,e,hi*][2,7]dithioazulene (3c)**

**2c:** mp 169 °C;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J=7.9$  Hz, 1H, Ar-H), 8.68 (d,  $J=7.7$  Hz, 1H, Ar-H), 8.44 (d,  $J=7.9$  Hz, 1H, Ar-H), 8.06 (d,  $J=7.7$  Hz, 1H, Ar-H), 8.03 (d,  $J=7.7$  Hz, 1H, Ar-H), 7.83 (t,  $J=7.9$  Hz, 2H, Ar-H), 7.61 (t,  $J=7.7$  Hz, 1H, Ar-H), 7.56 (d,  $J=7.7$  Hz, 1H, Ar-H), 3.20 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 138.1, 137.8, 132.2(3), 132.1(6), 131.6, 131.1, 130.3, 130.2, 129.4, 127.0, 126.6, 126.4, 122.7, 122.5, 119.8, 119.8, 117.2, 27.3; MS ( $m/z$ ) 262 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{19}\text{H}_{12}\text{S}$ : C, 83.79; H, 4.44. Found: C, 83.56; H, 4.58

**3c:**  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.77 (dd,  $J_1=7.8$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.75 (dd,  $J_1=7.6$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.60 (t,  $J=7.8$  Hz, 1H, Ar-H), 7.55 (dd,  $J_1=7.6$  Hz,  $J_2=1.1$  Hz, 1H, Ar-H), 7.43 (t,  $J=7.6$  Hz, 1H, Ar-H), 7.33 (dd,  $J_1=7.8$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 7.25 (t,

$J=7.8$  Hz, 1H, Ar-H), 7.14 (dd,  $J_1=7.8$  Hz,  $J_2=1.4$  Hz, 1H, Ar-H), 2.75 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  144.0, 141.1, 140.2(3), 140.1(6), 139.5, 139.2, 133.5, 132.5, 131.5, 130.7, 128.6, 127.7, 126.8, 126.5, 126.2, 121.9, 121.7, 22.3; Found:  $m/z$  304.0384. Calcd for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: M, 304.0380.

**6-Methyltriphenyleno[4,5-*bcd*]thiophene (2d) and 7-Methyltribenzo[*bc,e,hi*][2,7]dithioazulene (3d)**

**2d:** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.62 (d,  $J=8.2$  Hz, 1H, Ar-H), 8.53 (s, 1H, Ar-H), 8.47 (d,  $J=7.8$  Hz, 1H, Ar-H), 8.44 (d,  $J=7.8$  Hz, 1H, Ar-H), 8.06 (d,  $J=7.8$  Hz, 1H, Ar-H), 8.04 (d,  $J=7.8$  Hz, 1H, Ar-H), 7.86(4) (t,  $J=7.8$  Hz, 1H, Ar-H), 7.85(9) (t,  $J=7.8$  Hz, 1H, Ar-H), 7.58 (d,  $J=8.2$  Hz, 1H, Ar-H), 2.67 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.9, 138.8, 137.4, 130.9, 130.5(4), 130.5(2), 128.9, 128.8, 128.6, 128.1, 127.0, 126.9, 124.2, 124.0, 119.9, 119.6, 117.0, 116.8, 21.1; MS ( $m/z$ ) 262 (M<sup>+</sup>).

**3d:** <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  7.91-7.85 (m, 1H, Ar-H), 7.79-7.72 (m, 2H, Ar-H), 7.65-7.55 (m, 2H, Ar-H), 7.51-7.38 (m, 2H, Ar-H), 7.24-7.14 (m, 2H, Ar-H), 2.36 (s, 3H, CH<sub>3</sub>); MS ( $m/z$ ) 304 (M<sup>+</sup>).

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1. A CONVENIENT PREPARATION OF STERICALLY CROWDED 1,9-DISUBSTITUTED DIBENZOTHIOPHENES AND 3,3'-DISUBSTITUTED DIARYL SULFIDES.  
Naomichi Furukawa, Takeshi Kimura, Yoji Horie, and Satoshi Ogawa, *Heterocycles*, **32**, 675 (1991).
2. GENERATION OF NEW DITHIA DICATIONS FROM STERICALLY CONGESTED 1,9-DITHIODIBENZOTHIOPHENES AND THEIR MONOOXIDES IN CONCENTRATED SULFURIC ACID.  
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3. STRUCTURES OF STERICALLY ENCUMBERED 1,9-BIS(ARYLTIO)DIBENZOTHIOPHENES AND DETECTION OF THEIR DITHIA DICATIONS IN CONCENTRATED SULFURIC ACID BY  $^1\text{H}$ -NMR.  
Takeshi Kimura, Yoji Horie, Satoshi Ogawa, Hisashi Fujihara, Fujiko Iwasaki, and Naomichi Furukawa, *Heterocycles*, in press.
4. FIRST PREPARATION OF A NEW STABLE DIBENZO[*bc,fg*][1,4]DITHIO-PENTALENE AND DETERMINATION OF THE STRUCTURE BY X-RAY ANALYSIS.  
Takeshi Kimura, Yasuhiro Ishikawa, Satoshi Ogawa, Takehiko Nishio, Ikuo Iida, and Naomichi Furukawa, Submitted.
5. PHOTOCHEMICAL NEW SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF TRIPHENYLENO[4,5-*bcd*]THIOPHENE DERIVATIVES AND TRIPHENYLENO-[4,5-*bcd*]SELENOPHENE.  
Takeshi Kimura, Yasuhiro Ishikawa, Satoshi Ogawa, and Naomichi Furukawa, Submitted.
6. PREPARATION OF STERICALLY CONGESTED 1,9-DISUBSTITUTED DIBENZO-SELENOPHENES BY LIGAND COUPLING REACTIONS AND FORMATION OF NEW DITHIA AND DISELENA DICATIONS ON CHEMICAL AND ELECTROCHEMICAL OXIDATIONS.  
Naomichi Furukawa, Yasuhiro Ishikawa, Takeshi Kimura, and Satoshi Ogawa, Submitted.
7. PREPARATION AND OXIDATION REACTION OF STERICALLY CONGESTED 1,9-DISUBSTITUTED DIBENZOTHIOPHENES AND SELENOPHENES: GENERATION OF NEW DITHIA AND DISELENA DICATIONS IN CONCENTRATED SULFURIC ACID.  
Submitted.

Others

8. SYNTHESIS AND REACTIONS OF NEW CYCLICPOLYSULFIDES. 6,10-DISUBSTITUTED[1,2,3]TRITHIOLO[5,4-*h*]BENZOPENTATHIEPINS.  
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