Bull. Chem. Soc. Jpn., **70**, *2571—2591 (1997)*

Accounts

Studies on Dichalcogena Dications of 2-Center-2-electron and 3-Center-4-electron Bonds: Isolation and Intermediary Formation

Naomichi Furukawa

Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received April 25, 1997)

1,5-(Dithia and diselena)cyclooctanes gave the dithia and diselena dications. Their structures were determined by X-ray crystallographic analyses. Similarly, dithia and diselena dications were produced on oxidation with 2 equiv of $NOBF_4$ or $NOPF_6$ or on treatment of the corresponding monooxides with Tf_2O or concd H_2SO_4 from the sterically congested bis-sulfides or bis-selenides, such as 1,9-bis(thio- or seleno-substituted)dibenzochalcogenophene, 1,8-bis(thio- or seleno-substituted)naphthalenes and 2,2′-(thio- or seleno-substituted) 1,1′-biphenyls. These dications, however, were found to be unstable and to release the substituents attached at the chalcogen atoms. These either generated reactive species, i.e., quinodimethane and alkyl cations or demonstrated new reactions such as thio-Claisen rearrangement or photochemical conversion of naphtho[1,8-*de*]-1,3-dithiin derivatives.

Diphenyl chalcogenides bearing 2,6-bis(methylthiomethyl), 2,6-bis(methylselenomethyl) and 2,6-bis[(dimethylamino)methyl] substituents produced the hypervalent chalcogenuranes(λ^4). Their structures were determined by X-ray crystallographic analyses and their charge distributions were estimated by the ab initio MO-calculation and ^{77}Se- or ^{125}Te-NMR spectroscopy. Methyl 2,6-bis[(dimethylamino)methyl]phenyl selenide and telluride gave stable monoselenenium and monotellurenium cations on oxidative demethylation by the reaction with *t*-BuOCl. These are the first monovalent selenenium and tellurenium cation species.

Transannular interaction is a well-known phenomenon in organic compounds.[1)] Particularly, when more than two chalcogen atoms in a molecule are arranged appropriately in space, a repulsive force between the atoms dominates initially. However, on removal of one or two electrons from the chalcogen atom, an attractive force operates between the two chalcogen atoms to create a new chemical bond, called a "dication":[2)] 2-center-2-electron [2c–2e] bond (**I**), or a "cation radical":[3)] 2-center-3-electron [2c–3e] bond. Furthermore, when a lone pair of electrons attached to a third chalcogen atom transannularly participate in the formation of dichalcogena dications, new dication species in which the central atom is a hypervalent tetracoordinated atom bearing two chalcogen atoms as the apical ligands are formed:[4)] 3-center-4-electron [3c–4e] bond (**II**). These molecular models are schematically illustrated in Fig. 1.

These dichalcogena dications, **I** and **II**, have not been studied extensively and hence are of considerable interest for investigation. The producibility and stability of **I** and **II** remarkably depend on the structures of the substrates: namely, size of the rings, conformations, substituents attached at the chalcogen atoms, and the nature of the chalcogen atoms.

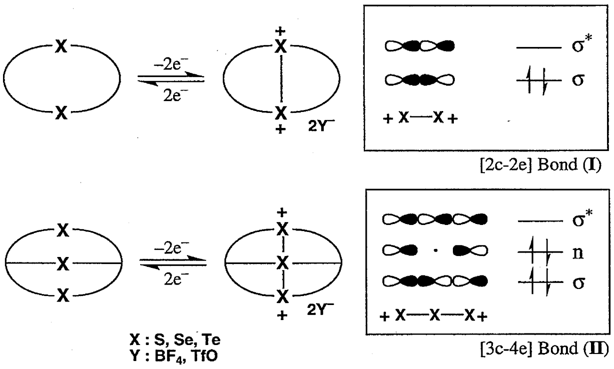


Fig. 1. Schematic illustration of two types of bonds of dication species.

This account presents our recent investigations on the dichalcogena dications bearing the [2c–2e] and the [3c–4e] bonding systems. The following topics are discussed.

I) Dications of [2c–2e] (**I**) bond

I-1) 1,5-Dithiacyclooctane (1,5-DTCO) and 1,5-diselenacyclooctane (1,5-DSeCO) dications

I-1-1) Preparation and detection of 1,5-DTCO and 1,5-

DSeCO and Te analog and their dications
I-1-2) Crystal structures of 1,5-DTCO and 1,5-DSeCO dications
I-1-3) Reactivity of 1,5-DTCO and 1,5-DSeCO dications
I-2) Preparation of aromatic ring-fused dichalcogena dications and their reactions
I-2-1) 1,9-Bis(thio- or seleno-substituted) dibenzothiophene dications
I-2-2) First preparation of 4,8-dithiacyclopenta[*def*] fluorene
I-3) Preparation and reactions of 1,8-bis(thio- or seleno-substituted) naphthalenes and related dications
I-3-1) Thio-Claisen rearrangement
I-4) Facile dealkylation and formation of cyclic thiosulfonium salts via S···S through-space interaction
I-5) Molecular activation and generation of active species via dithia or diselena dications
I-5-1) Quinodimethane formation
I-5-2) Photochemical reactions of 2-substituted and 2,2-disubstituted naphtho[1,8,*de*]-1,3-dithiin derivatives
I-5-2-1) Photolysis of monooxides of naphtho[1,8-*de*]-1,3-dithiins
I-5-2-2) Photolysis of *N*-tosylsulfilimines derived from naphtho[1,8-*de*]-1,3-dithiins
I-5-2-3) Photolysis of monoylides of naphtho[1,8-*de*]-1,3-dithiins
II) Dications of hypervalent species of [3c–4e] bond
II-1) Preparation of hyperdications
II-2) First RSe^+ and RTe^+ salt; 2,6-bis(dimethylaminomethyl)phenyl selenenium and tellurenium compounds

Numbering Note. Since we describe many compounds and active species in this account, we employed a systematic numbering method to explain the compounds. Throughout this account, we used the following numberings: dications are always described as suffix ($\mathbf{X^{2+}}$); oxides, sulfilimines and ylides are shown as **X–O**, **X–NTs**, $\mathbf{X{-}C^{-}R_2}$; substituents attached at S or Se atoms are shown as **a** = Ph, **b** = Me, **c** = Et, **d** = $-(CH_2)_3-$, **e** = $-CH_2-CH{=}CH_2$ as **Xa**, **Xa–NTs** etc., where **X** always means the skeletal structure.

I. Dications of [2c–2e] (I) Bond

I-1) 1,5-Dithiacyclooctane (1,5-DTCO) and 1,5-Diselenacyclooctane (1,5-DSeCO) Dications. As a typical example for the transannular interaction between chalcogen atoms, the two sulfur atoms in 1,5-dithiacyclooctane [1,5-DTCO] (**1**) and the related cyclic compounds approach close together and hence should experience an attractive force between the two sulfur atoms.[2,3,5] Moreover, when the compound (**1**) is converted to the mono-sulfoxide (**1a**),[6] -sulfilimine (**1b**)[7] and -sulfonium salt (**1c**),[8] the stronger attractive force between the two sulfur atoms dominates, since the X-ray crystallographic analyses of **1a**—**1c** reveal that the distances between the two sulfur atoms in the molecules are shorter than in compound (**1**) and shorter than within the van der Waals S–S distance(3.70 Å). The X-ray crystallographic analyses also reveal that the angles of $X{-}S_1{-}S_2$ of **1a**—**1c** are nearly 180°. These results clearly indicate that the central sulfur atoms of **1a**—**1c** exist as a quasi-sulfurane, which is converted readily to the corresponding dication species (Table 1).

1,5-Dithiacyclooctane (**1**) and its selenium (**2**) and tellurium (**3**) analogs are the best candidates to prepare the dichalcogena dications. One most reliable diagnosis for generation of dications having a [2c–2e] (**I**) bond, is to examine the oxidation potentials and wave patterns including reversibilities of the substrates by cyclic voltammetry.[5] Representative oxidation potentials (E_p) are shown in Table 2. These results show that the lower the oxidation potentials, the more stable the detectable dications.[9—11]

I-1-1) Preparation and Detection of 1,5-DTCO and 1,5-DSeCO and Te Analog and Their Dications. Several procedures are known to generate the dications with a [2c–2e] (**I**) bond. Anodic oxidation[12] and pulse radiolysis[13] of **1** have been reported as physical methods. In the latter procedure, 1,5-DTCO cation radical [$1,5\text{-DTCO}^{+\bullet}$] ($\mathbf{1}^{+\bullet}$) is formed and further oxidation to the corresponding dication ($\mathbf{1}^{2+}$) occurs. As chemical methods, one-electron oxidants such as Ti(III)–H_2O_2,[14] $NOBF_4$ or $NOPF_6$ are useful to generate $\mathbf{1}^{+\bullet}$ and then $\mathbf{1}^{2+}$.[15] These procedures can be applied to produce other cyclic and acyclic dichalcogena dications. We found that the dications ($\mathbf{1}^{2+}$), ($\mathbf{2}^{2+}$), and ($\mathbf{3}^{2+}$) are produced by treating the corresponding monooxide (**1a**) or monoimine (**1b**) with concd H_2SO_4 or by an acid anhydride such as $(CF_3SO_2)_2O[Tf_2O]$.[16] The preparation of $\mathbf{1}^{2+}$ is illustrated

Table 1. Structural Data from X-Ray Crystallographic Analyses

Compounds	X	$S_1 \cdots S_2$ (Å)	$\angle X{-}S_1{-}S_2$ (°)
1	Lone pair	3.58	—
1a[6]	O	3.14	175.4
1b[7]	NTs	3.14	177.8
1c[8]	$^{-}CH_2COOCH_3$	3.12	178.9

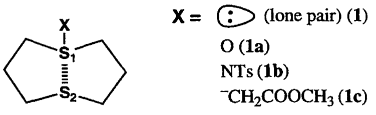
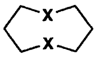
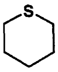
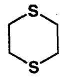
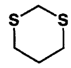
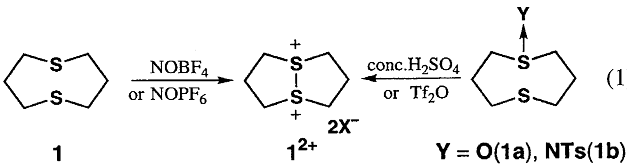


Table 2. Oxidation Potentials of Several Sulfur-Containing Compounds[5]

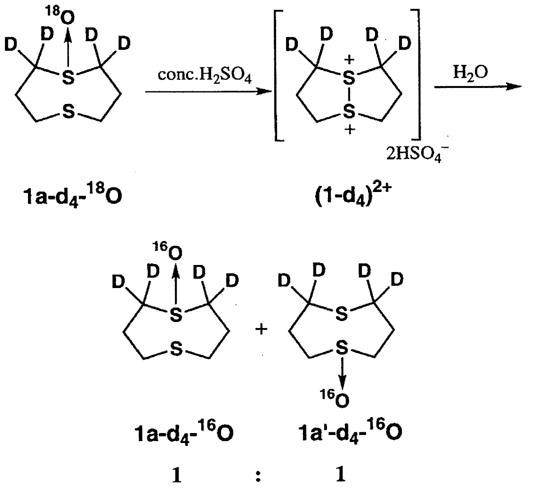
Compounds					
E_p (V) (Ag/AgClO$_4$)	X=S (1)	0.34 (reversible)			
	=Se (2)	0.25 (reversible)	1.32	1.25	1.14
	=Te (3)	−0.02 (reversible)			

in Eq. 1.



(1)

The detection of 1^{2+} in concd H_2SO_4 was carried out by ^1H- and ^{13}C NMR. The formation of 1^{2+} was further confirmed by following D(^{2}H)- and ^{18}O-tracer experiments using D- and ^{18}O-labeled 2,2,8,8-tetradeuterated 1,5-DTCO monooxide (**1a-d_4-^{18}O**). After quenching the H_2SO_4 solution of **1a-d_4-^{18}O** with H_2O, a mixture of 2,2,8,8- and 4,4,6,6-tetradeuterated 1,5-DTCO monooxides (**1a-d_4-^{16}O** and **1a′-d_4-^{16}O**) was obtained in a 1 : 1 ratio as shown in Eq. 2.

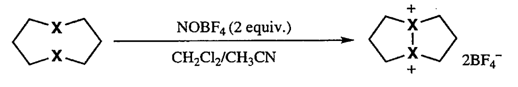


(2)

^{77}Se and ^{125}Te NMR spectroscopies are also efficient techniques for the detection of the dications of Se (2^{2+})[17] and Te (3^{2+}).[10] Several examples of ^{77}Se and ^{125}Te NMR data of 2^{2+} and 3^{2+} are shown in Fig. 2.

I-1-2) Crystal Structures of 1,5-DTCO and 1,5-DSeCO Dications. Recently, we have succeeded in the preparation of two kinds of dication salts (1^{2+})[18,19] and (2^{2+})[20] as crystalline compounds. Their structures were determined by X-ray crystallographic analyses, as shown in Fig. 3.

According to the X-ray results[19] of 1^{2+}, the S(1)–S(2) length is 2.12 Å, which is only slightly longer than the normal S–S single bond (2.08 Å) of disulfides. The bond angle of ∠C–S–C is 104.1° and that of ∠S–S–C is 92.7°. It is interesting to note that a very strong interaction is observed between the sulfur atom (S^+) of the dication and the oxygen atom of the triflate counter anion. The S–O (TfO) distance is 2.682 Å, which is markedly shorter than the sum of van der Waals radii of sulfur and oxygen atoms (3.35 Å). The angles of $\angle S^+–S^+\cdots O$ is 176.3°. A nearly collinear interaction of $O\cdots S^+–S^+\cdots O$ is observed with a central twofold symmetry. The optimized transannular S–S distance is 3.307 Å for 1,5-DTCO (**1**) and 2.140 Å for 1^{2+}, as postulated by an ab initio RHF MO calculation based on the STO-3-21G$^{(*)}$ basis set.[21]



2 (X = Se): ^{77}Se δ 141 ppm
3 (X = Te): ^{125}Te δ 163 ppm
2^{2+} (X = Se): ^{77}Se δ 806 ppm
3^{2+} (X = Te): ^{125}Te δ 1303 ppm

Fig. 2. Values of chemical shift in ^{77}Se and ^{125}Te NMR spectroscopic measurements of dications 2^{2+} and 3^{2+}.

Similarly, the 1,5-diselenacyclooctane dication (2^{2+}) was prepared from the bis-selenide (**2**) with two equivalents of $NOBF_4$ or $NOPF_6$. The X-ray crystallographic analysis of BF_4^- salts of 2^{2+} revealed that the $Se^+–Se^+$ distance is 2.38 Å, which is roughly identical to the normal Se–Se single bond.[20] The distances between the fluorine atoms of BF_4^- and the Se^+ atom are in the range 2.68—3.25 Å, which is also within the van der Waals contact of $Se\cdots F$ (3.37 Å).

I-1-3) Reactivity of 1,5-DTCO and 1,5-DSeCO Dications. Although dithia and diselena dications (1^{2+} and 2^{2+}) are stable enough to be isolated, they are expected to be highly reactive species since the two positive charges are localized at the two adjacent chalcogen atoms and repulsive forces operate between them. In fact, dications 1^{2+} and 2^{2+} behave as an electron acceptor. They react with several nucleophilic reagents to give either respectively substituted or oxidized products. The reactions of (1^{2+})[22] and (2^{2+})[23] are shown in Scheme 1. The reactivity of tellurium analog (3^{2+}) has been examined to some extent.[10,24]

I-2) Preparation of Aromatic Ring-Fused Dichalcogena Dications and Their Reactions. As a further extension of the dication chemistry, we tried to prepare dichalcogena di-

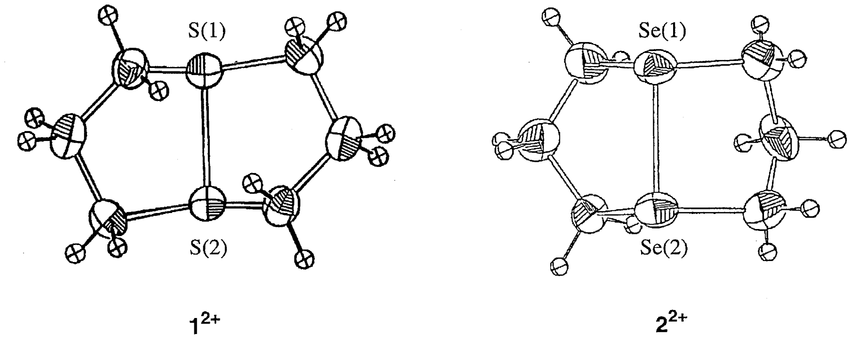
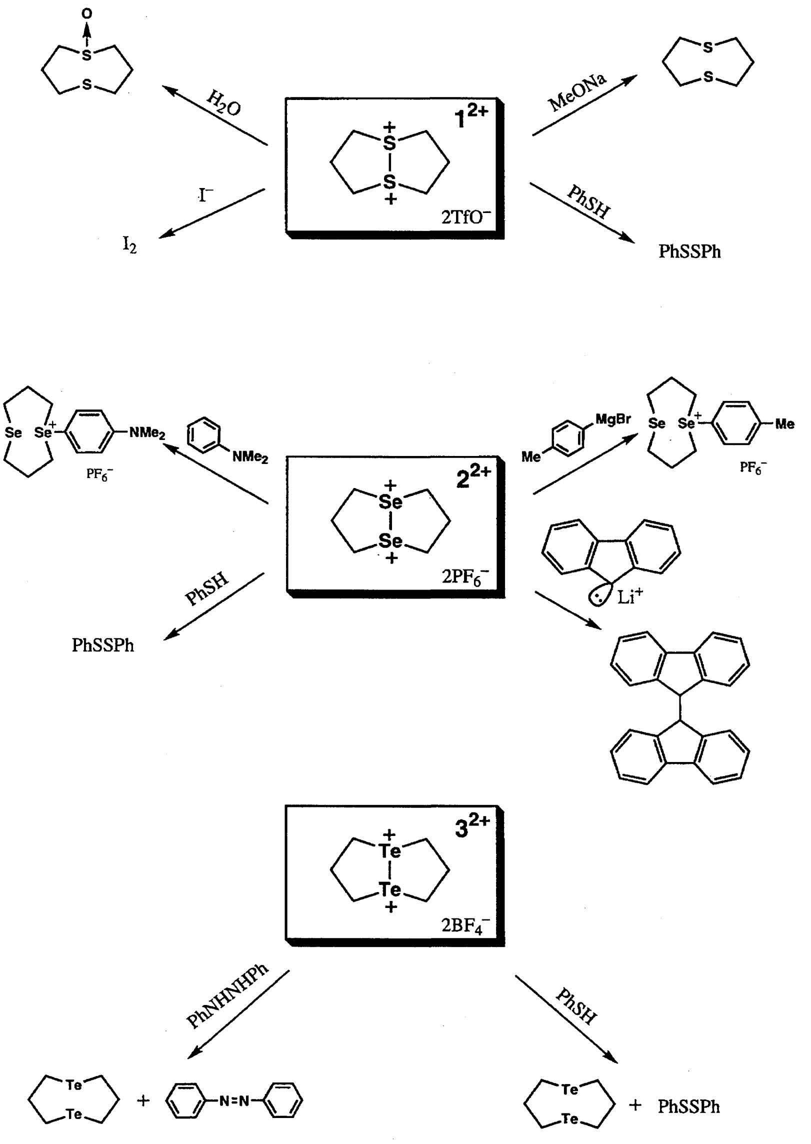


Fig. 3. ORTEP drawings of 1,5-DTCO dication (1^{2+}) and 1,5-DSeCO dication (2^{2+}).



Scheme 1.

cations bearing aromatic rings. Such dications will be obtained from the following sterically congested bis-chalcogenides bonded to phenyl or naphthyl groups, i.e., 1,8-bis(thio-substituted) naphthalenes (A), 1,9-bis(thio-substituted) dibenzothiophenes (B), 2,2′-bis(thio-substituted) 1,1′-biphenyls (C) (Chart 1). Dithia dications from these compounds are obtained using one of the following two common procedures: (i) the sulfides are treated with 2 equivalents of $NOBF_4$ or $NOPF_6$; (ii) the sulfides are initially oxidized to the monosulfoxides, which are treated with concd H_2SO_4 or Tf_2O to give the respective dithia dications. Similarly, the selenium and tellurium analogs can be converted to the diselena and ditellura dications.

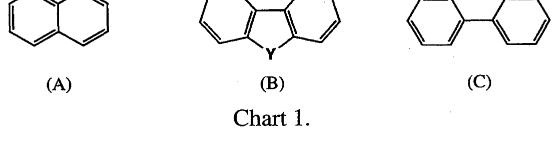
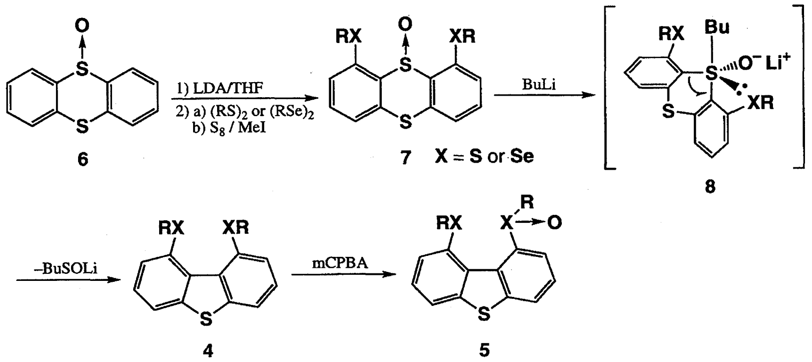


Chart 1.

I-2-1) 1,9-Bis(thio- or seleno-substituted) Dibenzothiophene Dications.[11] We found a convenient procedure for preparation of 1,9-bis(thio-substituted) dibenzothiophenes (**4**) starting from thianthrene monooxide (**6**).[25] The monooxide (**6**) was treated with two equivalents of LDA (lithium diisopropylamide) and then with disulfides to give the corresponding 1,9-bis(thio-substituted) thianthrene 10-oxides (**7**). These were then treated with BuLi to give **4** in moderate yields, probably proceeding through an intramolecular ligand-coupling reaction via the sulfurane intermediate (**8**) which is formed initially by the attack of BuLi on the sulfinyl sulfur atom. All reactions for preparing **4** are shown in Scheme 2. The dibenzoselenophene analogs (**9**) were prepared in a similar way.[26]

Dibenzothiophene (**4a**) and its monooxide (**5a**) were obtained as crystalline materials. The X-ray crystallographic analyses of **4a** and **5a** revealed that the S···S distances are 3.012 and 3.016 Å, respectively.[27] These values are shorter than the sum of the van der Waals radii of sulfur atoms (3.70 Å). Furthermore, the two benzene rings in the fused

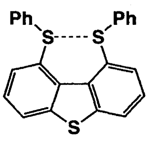


RX	Yield(%)
PhS	65[a)]
p-TolS	46[a)]
p-ClPhS	59[a)]
MeS	22[b)]

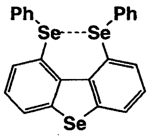
Scheme 2.

Table 3. Interatom Distances, Torsional Angles and Oxidation Potentials (E_p)

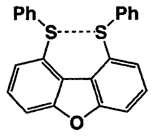
Compounds	S(Se)···S(Se) (Å)	Torsional angles (°)	E_p (V)
4a	3.012	20.7	0.86
9b	3.072	19.5	0.54
11	3.190	5.3	1.02



4a



9a



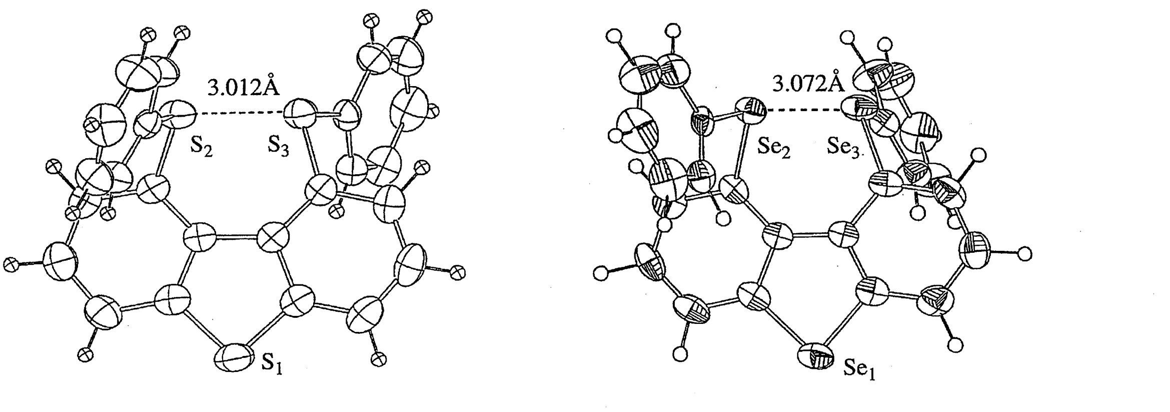
11

thiophene are considerably distorted and the dihedral angles consisting of the two outer sulfur and ring carbon atoms are ca. 20°. These short S–S distances and large distortion of the two benzene rings suggest that the through-space interaction between the two sulfur atoms in **4a** and **5a** should take place readily to form a dicationic S···S σ-bond on oxidation.

The Se–Se distance and torsional angle of dibenzoselenophene analog (**9a**) indicate similar trends with those of **4a**.[28)] These dibenzothiophene (**4a**) and dibenzoselenophene (**9a**) have unusually low oxidation potentials as compared with those of dibenzofuran derivative (**11**) which is nearly a planar molecule and hence has no torsional strain unlike **4a** and **9a**. The oxidation potentials and S···S and Se···Se distances are summarized in Table 3 and Fig. 4.

On dissolution of **4a** and **9a** in concd D_2SO_4, the formation of the corresponding dications (**4a**$^{2+}$) and (**9a**$^{2+}$) was observed.[25a,26)] The ^{1}H- and ^{13}C NMR spectra of the corresponding sulfoxide (**5a**) and selenoxide (**10a**) in concd D_2SO_4 also were identical with those of **4a** and **9a**, while **11** was found to decompose in D_2SO_4. Hydrolysis of **4a**$^{2+}$ and **9a**$^{2+}$ in concd D_2SO_4 solutions afforded the corresponding monooxides (**5a**) and (**10a**) in high yields.

The formation of the dication between the two selenium atoms could be detected by ^{77}Se NMR spectroscopy. In the ^{77}Se NMR spectrum of **9a**, two signals were observed at $\delta = 427.0$ and 468.7 in 2 : 1 intensity ratio in $CDCl_3$. On dissolution **9a** into concd D_2SO_4, those two signals greatly shifted to downfield to give two signals at $\delta = 534.8$ and 699.1 in 1 : 2 intensity ratio. The mono-selenoxide (**10a**) in concd D_2SO_4 exhibits a similar ^{77}Se NMR behavior. In the ^{77}Se NMR spectrum of **10a**, three signals are observed: at $\delta = 896.4$ (SeO), 423.3 (Se), and 484.0 (selenophene), and the satellite peaks having a coupling constant ($J_{\text{Se–Se}} =$



4a **9a**

Fig. 4. ORTEP drawings of compounds **4a** and **9a**.

372 Hz) corresponding to the two Se atoms of SeO and Se are also seen. This clearly indicates that the through-space interaction takes place between the two selenium atoms in **10a**. These results reveal that even the divalent S or Se species are converted to the dications in concd H_2SO_4.[26]

The clear-cut evidence for the formation of the dication ($\mathbf{4b}^{2+}$) using a methyl derivative (**4b**) was observed. A typical example is shown in the following Scheme 3.[29]

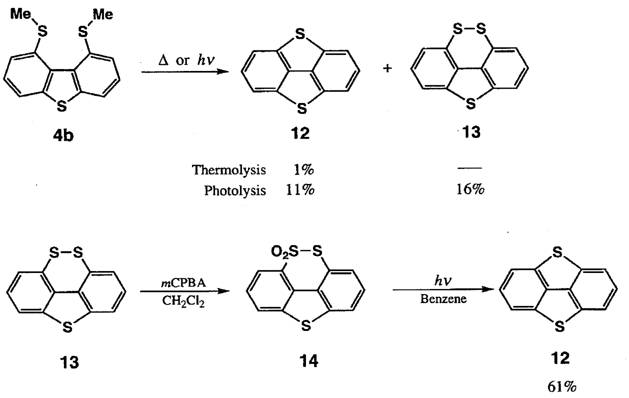
In the ^{1}H NMR spectrum, the two methyl signals for the sulfoxide (**5b**) are observed at $\delta=2.79$ and 2.33 in $CDCl_3$. These coalesced to $\delta=3.04$ as a singlet peak in concd D_2SO_4. In concd D_2SO_4, the ^{1}H NMR spectrum of **4b** is identical to that of **5b**. Furthermore, hydrolysis by adding H_2O to the concd D_2SO_4 solution of **5b** labeled with ^{18}O and deuterium gave a mixture of sulfoxides (**5b-d_3-^{16}O**) and (**5b′-d_3-^{16}O**) in 1 : 1 ratio and the ^{18}O in **5b-d_3-^{18}O** was completely exchanged with ^{16}O. This result also demonstrates the formation of dication (**4b^{2+}-d_3**). In contrast to the methyl derivative, the dications of ethyl or higher alkyl homologs were found to be unstable in concd H_2SO_4.[30]

I-2-2) First Preparation of 4,8-Dithiacyclopenta[*def*]-fluorene.

In the course of the studies on the dibenzothiophene dications, it was found that the thermolysis of **4b** at 500 °C serendipitiously gave 4,8-dithiacyclopenta[*def*]fluorene (**12**) in a trace amount, while on photolysis with a high pressure mercury lamp, the yield of **12** increased to 11% together with 4,8,9-trithiacyclopenta[*def*]phenanthrene (**13**) in 16% yield.[31] Although the mechanism for the formation of **12** has not been understood, the transformation of **13** to **12** via thiosulfonate (**14**) was successfully carried out in a 61% yield, as shown in Scheme 4, according to Meinwald's photodesulfurization procedure of thiosulfonate.[32] Few analogous compounds of **12** have been reported,[33] but the above is a first example for the preparation of a 3,7-dichalcogenabicyclo[3,3,0]octane including a biphenyl ring. Similarly, 4,8-diselenacyclopenta[*def*]fluorene (**15**) and 4-thia-8-selenacyclopenta[*def*]fluorene (**16**) were prepared by thermolysis or photolysis of the dibenzoselenophene derivatives, using the same procedure as in the case of the dibenzothiophene.[34)]

The X-ray crystallographic analyses of **12**, **15**, and **16** were successfully performed. Their ORTEP drawings are shown in Fig. 5.[34b)]

The structural results of **12** revealed that it is a completely planar molecule. The C–S bond length (1.791 Å) is rather long compared with the lengths of the known derivatives of

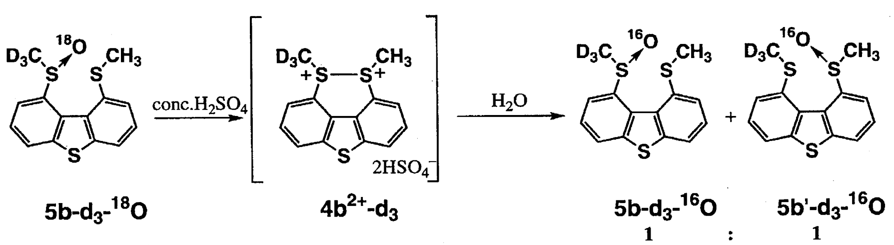


Scheme 4.

3,7-dichalcogenabicyclo[3,3,0]octane or dibenzothiophenes. The central C–C bond length is relatively short (1.386 Å) and should be comparable to a double bond. In the crystal structure, 4,8-dithiacyclopenta[*def*]fluorene molecules stack vertically with a 4.00 Å intramolecular S···S distance. Similarly, **15** and **16** also have planar structures, as demonstrated by the X-ray crystallographic analysis. These dichalcogena derivatives of fluorenes, **12** and **15**, behave as electron-donor molecules and can be converted to the corresponding CT complexes upon treatment with a suitable acceptor molecule such as TCNQ (tetracyanoquinodimethane). The CT complex of **12** and TCNQ each forms violet crystals, in which **12** and TCNQ stack with each other forming a column. This CT complex has, however, only a semiconducting-character.[35] The oxidation potentials for **12** and **15** are the same or slightly lower than that of dibenzothiophene (**4**) or dibenzoselenophene (**9**), respectively.[34b)] Therefore, if one uses these dichalcogena derivatives of fluorenes as electro-conducting materials, further modification is awaited.

Cyclic voltammetry of **12** shows an irreversible redox system in the voltammogram ($E_p=1.16$ V, $Ag/AgNO_3/CH_3CN$). On repeated scanning as shown in Fig. 6,[31] the intensities of oxidation and reduction potentials increase, it suggests that ring opening and polymerization of the thiophene ring may give a electro-conducting polymer whose structure and molecular weight have not been determined as yet.

In contrast to the 1,9-bis(methylthio)dibenzothiophene, arylthio derivatives of **4** are thermally stable, whereas, i.e., photolysis of the bis(phenylthio) derivative (**4a**) did not afford the expected fluorene derivative at all, but produced the dibenzothiepin (**17**) and triphenylenothiophene (**18**) in 26 and 72% yields, respectively as shown in Eq. 3.[28,36,37]



Scheme 3.

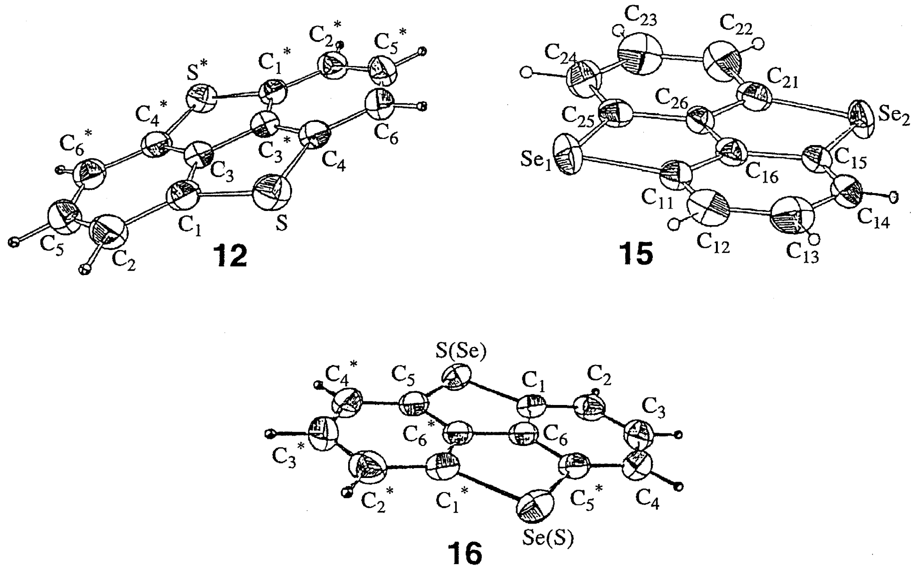


Fig. 5. ORTEP drawings of 4,8-dichalcogenacyclopenta[*def*]fluorenes **12**, **15**, and **16**.

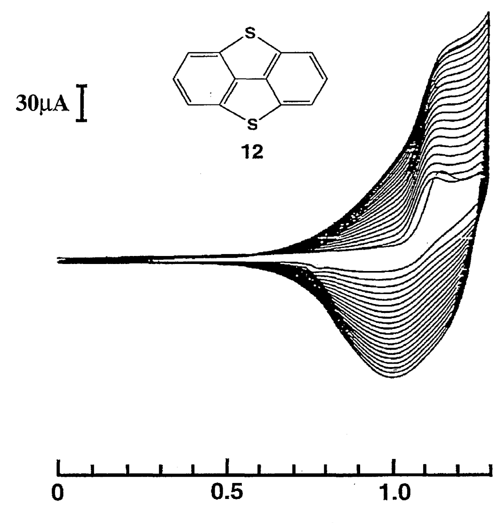
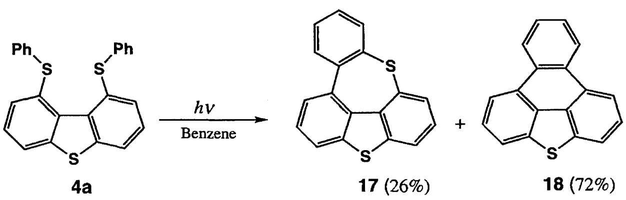


Fig. 6. Cyclic Voltammogram (CV) of **12** (0.82 mM) after 20 times scannings in CH_3CN at 20 °C (Pt electrode, Ag/0.01 M $AgNO_3$ as reference electrode, 0.1 M $NaClO_4$ as electrolyte, scan rate: 200 mV s^{-1}).

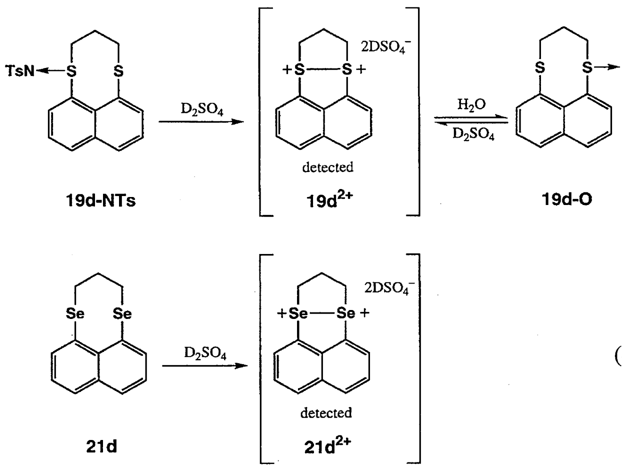


(3)

Photolysis and themolysis of these sterically congested 1,9-bis(thio or seleno-substituted) dibenzothiophenes (**4**) and (**9**) provide various structurally attractive aromatic compounds which have rarely been prepared by ordinary procedures. Such dibenzothiophene and dibenzoselenophene derivatives are promising for the synthesis of new functional materials such as opto- or electro-conducting materials.

I-3) Preparation and Reactions of 1,8-Bis(thio- or seleno-substituted) Naphthalenes and Related Dications.[38,39)] 1,8-Bis(thio-substituted) naphthalene derivatives (**19**) are readily prepared from naphtho[1,8-*cd*]-1,2-dithiole (**20**). These naphthalene derivatives possess a sterically rigid system suitable for examining whether the substituents at the 1- and 8-positions of the naphthalene interact with each other via a through-space interaction and hence provide new stable dications. Naphtho[1,8-*bc*]-1,5-dithiocin (**19d**) and its monooxide (**19d-O**) and monosulfilimine (**19d-NTs**) were prepared in order to generate the dication (**19d**$^{2+}$).[40)]

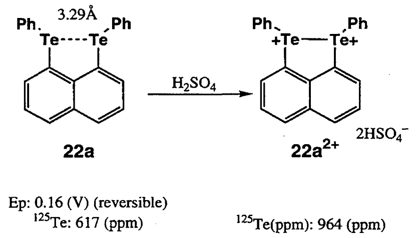
Glass and his co-workers reported the preparation of dithiocin (**19d**) and its monooxide (**19d-O**).[41)] They found that the S···S distances in **19d** and **19d-O** are 3.23 and 3.00 Å, respectively, which are within the van der Waals S–S contact of 3.70 Å. Hence they show the existence of through-space interaction between the two sulfur atoms. The angle of $\angle S_1–S_2–O$ in **19d-O** is 174.2° indicating that the S_2 atom has approximately a sulfurane structure, like that of 1,5-DTCO monooxide. However, on the basis of an MO calculation using the Hartree–Fock method with STO-3G basis set, it was proposed that there is no bond formation, even incipiently, between the two sulfur atoms in **19d-O**.[38c)] On dissolution in concd H_2SO_4, **19d-O** is converted to the dithia dication (**19d**$^{2+}$), which after hydrolysis with H_2O, **19d-O** was recovered with retention of the configuration at the sulfinyl sulfur atom. We have also examined the oxygen-exchange reaction of **19-O** in concd H_2SO_4 and obtained results identical with those by Glass et al. Furthermore, *N*-tosylsulfilimine (**19d-NTs**) also produces **19d**$^{2+}$ in concd D_2SO_4 as seen by following the change in the ^{1}H NMR spectra (Eq. 4).[40)] The ^{1}H NMR spectra indicate that the conformation of **19d**$^{2+}$ is a boat form with respect to the thiocin moiety, since the signal corresponding to the central methylene protons in the trimethylene bridge separates into two signals, centered at $\delta = 1.8$ and 3.6, as two broad doublets. The experiment using a D-labeled compound also indicates the formation of dication. In the case of the selenium derivative, even the bisselenide (**21d**) gives the diselena dication (**21d**$^{2+}$) directly in concd D_2SO_4 as shown in Eq. 4.[42]



(4)

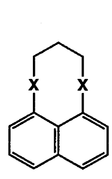
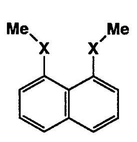
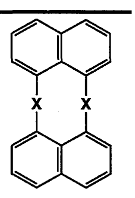
Electrochemical oxidation of these sulfur and selenium derivatives by cyclic voltammetry shows extremely low oxidation potentials (E_p), which imply that these dications are stable[39] enough to be detected. The oxidation potentials (E_p) of naphthalene derivatives are shown in Table 4.

The tellurium analog, 1,8-bis(phenyltelluro) naphthalene (**22a**), was synthesized and was dissolved in concd H_2SO_4 to give the dication (**22a**$^{2+}$), which was identified by ^1H-, ^{13}C- and ^{125}Te NMR spectroscopy[43] (Eq. 5).



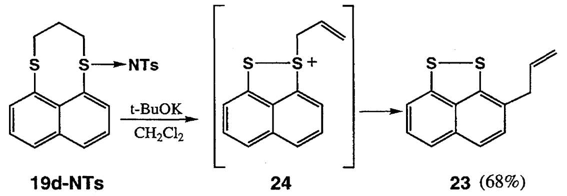
(5)

Table 4. Oxidation Potentials (E_p) of Naphthalene Derivatives

				
E_p (V)[a]	X=S	0.47[b] irreversible	0.70[b] irreversible	0.70 reversible
	X=Se	0.18 reversible	0.48 reversible	0.33[c] reversible

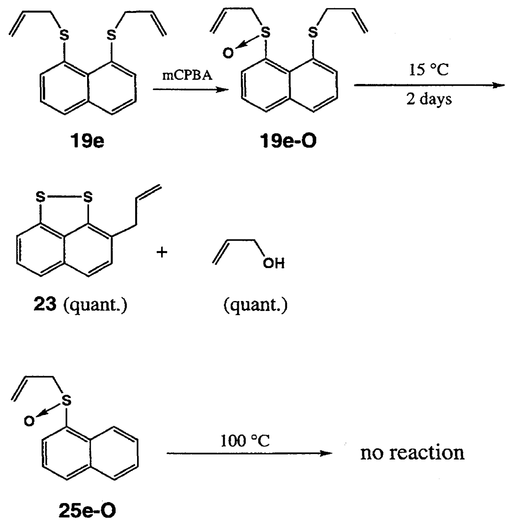
a) Cyclic voltammetry was carried out at a glassy carbon electrode, 300 mV s^{-1} scan rate, and measured in acetonitrile, 0.1 M in sodium perchlorate, versus Ag/0.01 M $AgNO_3$ in acetonitrile reference electrode. b) Determined at a Pt electrode, 100 mV s^{-1} scan rate, and measured in acetonitrile, 0.1 M in lithium perchlorate, versus Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. c) Measured in acetonitrile–dichloromethane (= 4 : 1), 0.08 M in sodium perchlorate.

I-3-1) Thio-Claisen Rearrangement. In the reaction of sulfilimine (**19d-NTs**) with *t*-BuOK in CH_2Cl_2, 3-allylnaphtho[1,8-*cd*]-1,2-dithiole (**23**) was obtained as the major product probably via [3,3] sigmatropic allylic shift from the sulfonium salt (**24**) as shown in Eq. 6.



(6)

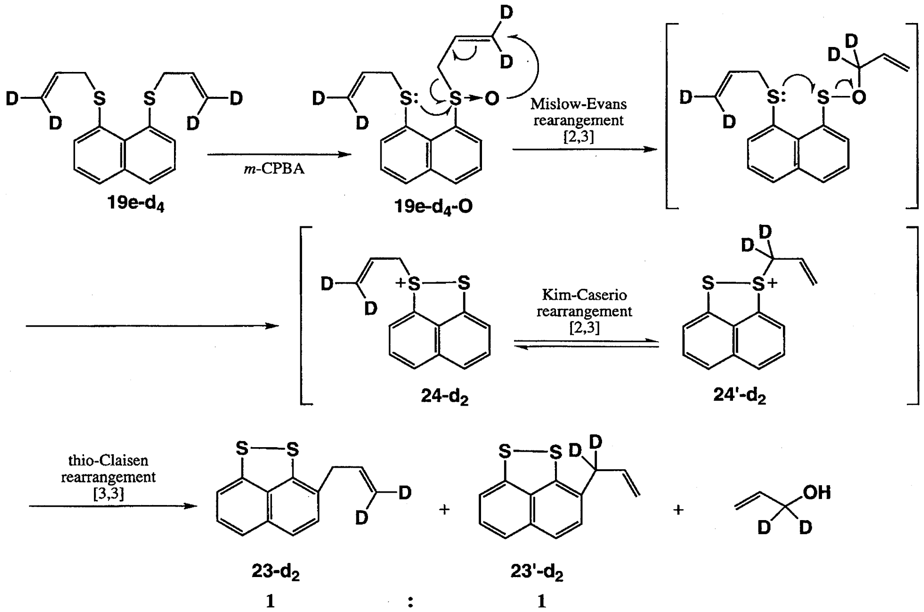
In order to ascertain the mechanism for this new reaction, 1,8-bis(allylthio)naphthalene (**19e**) and its monooxide (**19e-O**) were prepared. Although **19e** does not undergo the thio-Claisen rearrangement, **19e-O** undergoes the thio-Claisen rearrangement at room temperature to afford both **23** and allyl alcohol in quantitative yields. This rearrangement was not observed in the reactions of 1-(allylsulfinyl)naphthalene (**25e-O**), even at 100 °C (Eq. 7).[44]



(7)

As to the mechanism for this rearrangement, the following two [2,3] and one [3,3] sigmatropic rearrangements take place consecutively: Namely, the initial Mislow–Evans rearrangement[45] should be the rate-determining step which must be triggered by the through-space interaction between the sulfenyl and the sulfinyl sulfur atoms enhancing the reactivity of the sulfinyl oxygen atom for migration.

These conceivable mechanisms were confirmed by using D-labeled compounds (**19e-*d*$_4$-O**). After the reaction, **19e-*d*$_4$-O** 3-allylnaphtho[1,8-*cd*]-1,2-dithiole (**23e-*d*$_2$**) and D-labeled allyl alcohol were obtained and then were purified and the D-labeled positions and D-contents of them were determined by ^1H NMR spectroscopy (Scheme 5). As a result, deuterium atoms in the allyl alcohol were found at the 1-position exclusively, while deuterium atoms of the allylic group in **23e** were distributed at the 1- and 3-positions in roughly 1 : 1 ratio. These results demonstrate clearly that the initial Mislow–Evans rearrangement proceeds to give the sulfe-

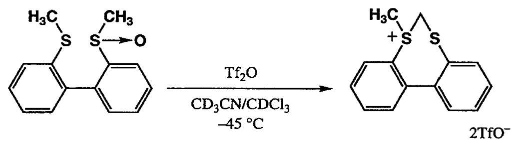


Scheme 5.

nate, which undergoes intramolecular S_N2-type reaction[46] to afford an equilibrium mixture of sulfonium salts (**24-d_2**) and (**24′-d_2**). Finally, the sulfonium salts undergo the thio-Claisen rearrangement to result in the formation of **23-d_2** (and **23′-d_2**).

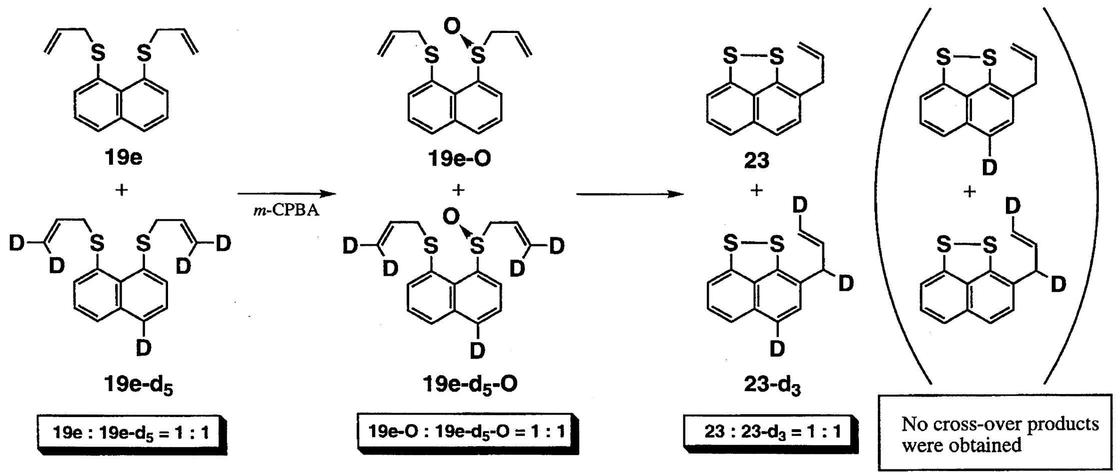
This new thio-Claisen rearrangement[47] was found to proceed via an intramolecular manner exemplified by the crossover experiment shown in Scheme 6.

I-4) Facile Dealkylation and Formation of Cyclic Sulfonium Salts via S···S Through-Space Interaction. As a further extension of the dichalcogena dication chemistry, we tried to synthesize alkyl substituted dications, which would subsequently produce the reactive species. As appropriate candidates for the preparation of reactive dications, 2,2′-bis(alkylthio- or alkylseleno-substituted) 1,1′-biphenyls (**26**) and (**27**) were utilized as the desired precursors. 2,2′-Bis(methylthio) 1,1′-biphenyl monosulfoxide (**26b-O**) was prepared and treated with Tf_2O at −45 °C in $CD_3CN/CDCl_3$.[48] Surprisingly, the formation of dication (**26b**$^{2+}$) was not observed by ^{1}H NMR spectroscopy at −45 °C, but **26b-O** was converted to the cyclic sulfonium salt (**28b**) in high yield as shown in Eq. 8.



26b-O **28b** (quant.) (8)

Normally, one would think that in this reaction the Pummerer-type reaction[49] should take place by an initial *O*-sulfonylation, followed by deprotonation from the methyl group and finally an intramolecular attack by the other sulfur atom to give the cyclization product (**28b**).[50] However, when

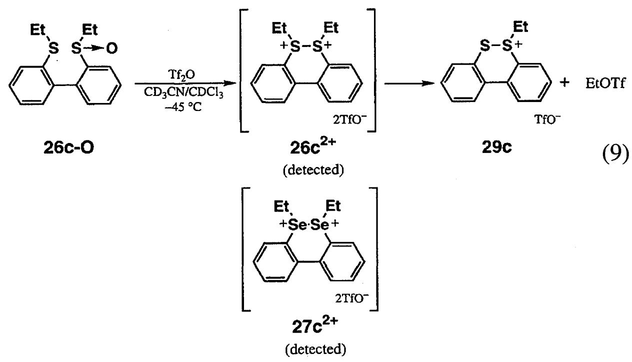


Scheme 6.

the trideuterated sulfoxide (**26b-d_3-O**) was treated with Tf_2O at −45 °C, the deuterium atoms in the sulfonium salt (**28b-d_2**) and (**28b-d_3**) were observed at the methylene groups of **28b-d_2** and the methyl groups of **28b-d_3** in 0.17 : 0.83 ratio. If the reaction proceeded via only the Pummerer-type process b) in Scheme 7, then the deuterium atoms should be observed only at the methylene position and not at the methyl group as found in **28b-d_2**. Thus the present result strongly rules out the simple Pummerer reaction, instead it supports the formation of the dication (**26b^{2+}-d_3**) prior to proton abstraction. The isotope ratio reflects on the isotope effect due to the proton abstraction from **26b^{2+}-d_3**. This is illustrated in Scheme 7.

Furthermore, interestingly, when the mono-sulfoxide of diethyl derivative (**26c-O**) was similarly treated with Tf_2O in an NMR tube at −45 °C, two signals corresponding to the two types of the ethyl groups in **26c-O** coalesced to give a symmetrically coupled signal in ^{1}H NMR spectroscopy. This ethyl signal is attributed to the formation of the bis-(sulfonium) dication (**26c^{2+}**) which on elevating the temperature to −20 °C, was split into two symmetric signals; then new ethyl signals were observed.[51] In a large scale preparation, a crystalline compound was isolated and its ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies indicate the formation of the monosulfonium salt (**29c**).[46,52] Ethyl triflate was observed as a counter-part by measuring the ^{1}H NMR described above as new methylene and methyl signals, which agree with that of ethyl triflate authentically prepared. The formation of **26c^{2+}** shows that **26c-O** is highly activated after the conversion to the dication (**26c^{2+}**), from which the removal of one ethyl group takes place quite rapidly. Similarly, isopropyl, *t*-butyl- and benzyl-substituted biphenyl derivatives of **26** afford the corresponding monosulfonium salts (**29**) (Eq. 9).

A selenium analog of dication (**27c^{2+}**) was also detected by ^{1}H NMR spectroscopy under the same conditions.[51]

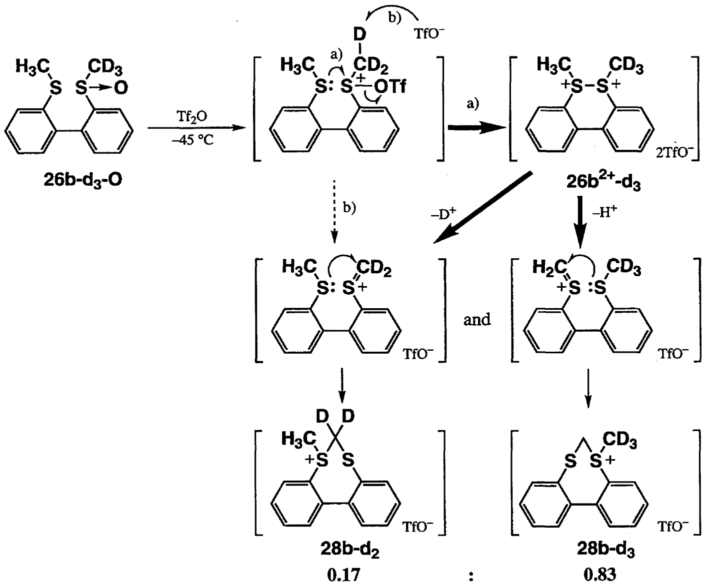


(9)

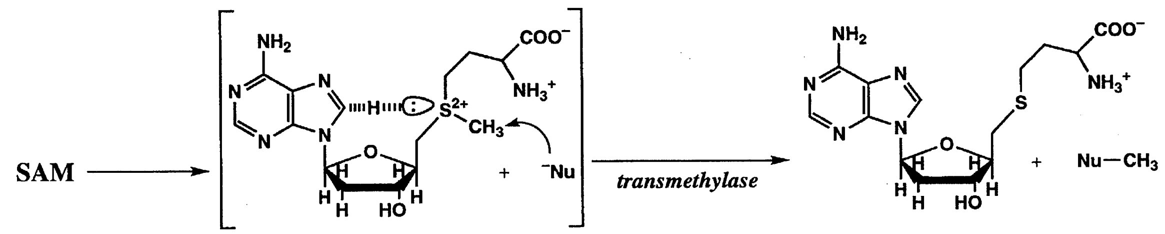
In general, dealkylation of sulfonium salts requires high temperature, while **26c^{2+}** has an usually high reactivity which is enough to allow the transethylation even at −40 °C.[53] *S*-Adenosylmethionine (SAM) is know to serve as a transmethylating reagent in vivo at room temperature in the presence of an enzyme.[54] Our present experiment suggests that SAM should be highly activated by the through-space interaction between the sulfur atom and other heteroatoms in the molecule to form a highly reactive monosulfonium salt prior to the transmethylation process. Recently, an interesting concept for the activation of SAM has been presented by Brajeswar et al.[55] They have proposed that the central sulfur atom in the sulfonium moiety of SAM is converted to a sulfurane-like dication intermediate, from which the methyl group is transferred readily to the nucleophiles, as shown in Scheme 8.

An unsymmetrical sulfonium dication was also generated by a similar treatment of 2-methylthio-2′-ethylsulfinyl 1,1′-biphenyl (vise versa) (**30** or **30′**), with Tf_2O affording an unstable dithia dication (**31**) which decomposes to give the corresponding mono-sulfonium salts (**29b**) and (**29c**) in a ratio of 1 : 6, as shown in Scheme 9.[51]

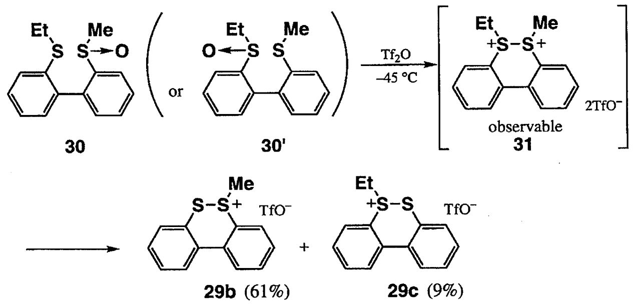
In the case of the benzyl methyl derivatives, **32** and **32′**, on treatment with Tf_2O in CD_3CN or $CDCl_3$, both sulfox-



Scheme 7.

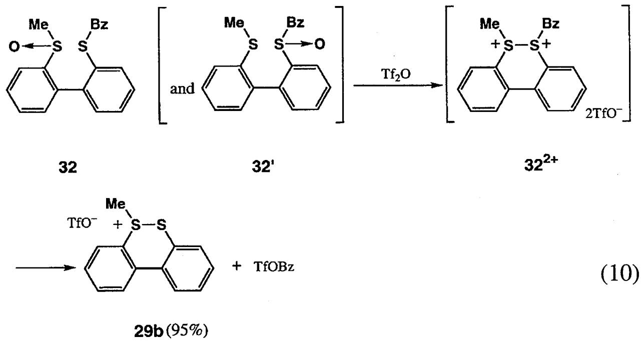


Scheme 8.



Scheme 9.

ides give the *S*-methylsulfonium salt (**29b**) as a sole product, suggesting that the dication ($\mathbf{32}^{2+}$) should be formed initially. Then the removal of the benzyl group takes place exclusively from this dication (Eq. 10).[51]



(10)

The kinetic study of the thermal decomposition of dithia dication ($\mathbf{26c}^{2+}$) gave good first-order rate constants k (s^{-1}) of 1.11×10^{-3} (−30 °C), 3.56×10^{-4} (−35 °C), 1.56×10^{-4} (−40 °C), 5.64×10^{-5} (−45 °C) and the activation parameters $\Delta H^{\ddagger}=21.0\pm1.1$ (kcal mol^{-1}), $\Delta S^{\ddagger}=14.8\pm4.5$ (eu). The large positive entropy value and the removability among the alkyl moieties (Bz>Et>Me) substituted at the sulfur atoms suggest that the dealkylation may proceed either via an S_N1 process or a ligand-coupling reaction and that an S_N2 pathway can be excluded.[51]

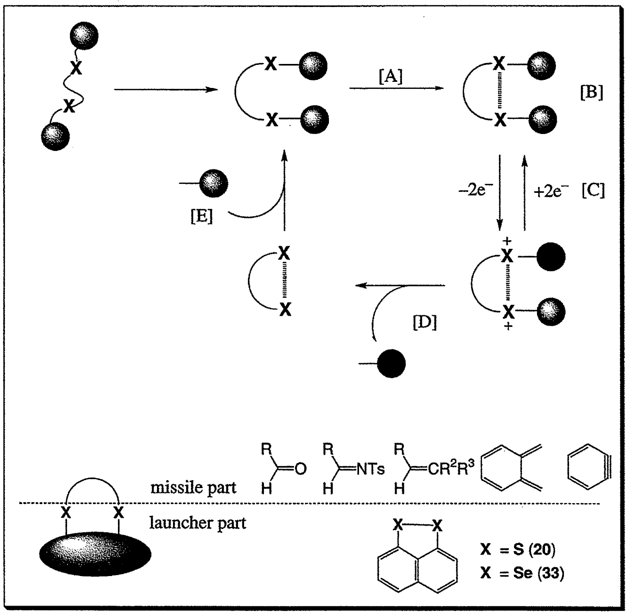
This facile deethylation of $\mathbf{26c}^{2+}$ by the extremely low nucleophilic anion, i.e. TfO$^-$, demonstrates that the formation of the dithia dication converts the *S*-alkyl groups to the highly reactive alkylating agents.[56] Similarly, naphthalene derivatives (**19**) also afford the corresponding dithia dications ($\mathbf{19}^{2+}$) which finally give the *S*-monosulfonium salts.[57]

I-5) Molecular Activation and Generation of Active Species via Dithia or Diselena Dications. The formation of dithia (or diselena) dications via the through-space interaction between chalcogen atoms as mentioned above activates the molecules producing the highly labile moieties. Another possible procedure to activate the molecules is the photolysis of the compounds which may excite one electron on the chalcogen atom to the residual naphthalene ring by n–π* excitation. This photo-excitation produces an electron-deficient radical-cation-like state at the one chalcogen group, from which the S–S or Se–Se bond formation takes place transannularly to convert the molecules into highly activated states.[58] From this activated state, the substituents attached at the chalcogen atoms are released to liberate the active species together with thermodynamically stable disulfides or diselenides. This concept may create a new methodology for generating new reactive species. We call this a missile system which is composed of a potential missile part and a launcher part.

There are many conceivable functional groups which can be extruded readily from the system as a missile, whereas the molecule as a launcher part should possess a thermally and photochemically stable skeleton. Examples include aromatic or heterocyclic compounds which are readily recovered and recycled after the reactions. There are several ignition systems, such as photolysis, which trigger the reactions for generating active species. This concept is not only useful for creating a new methodology but also provides an environmentally benign process for synthetic organic chemistry. The model is illustrated in Scheme 10.

I-5-1) Quinodimethane Formation. 8,13-Dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin (**35**) was prepared[59] and was exposed to sunlight in the presence of air. The decomposition of **35** took place gradually to give a *o*-quinodimethane dimer (**38**) and naphtho[1,8-*cd*]-1,2-diselenole (**33**) quantitatively.[60] This reaction may involve quinodimethane (**36**) as a transient intermediate after the formation of the photoexcited diselena dication ($\mathbf{35}^{2+}$) by photoinduced activation. The formation of **36** was identified by the trapping experiment in the presence of olefins under UV irradiation. This reaction gives tetrahydronaphthalene derivatives (**37**) in high yields, together with 100% recovery of **33**. The reaction is shown in Scheme 11 and the trapping experimental results are summarized in Table 5.

The photolysis of 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]dithionin (**34**) gave almost the same results as the selenium derivatives.[61] The results are summarized in Table 5. There are several procedures reported for the generation of quinodimethane.[62,63] However, our present method gives the olefin adducts and the starting disulfide or diselenide in high yields. Therefore, our method has an advantage for the generation of *o*-quinodimethane under photolysis conditions.



[A] : *hv*, Δ
[B] : Transannular interaction
[C] : Activation
[D] : Generation of active apecies
[E] : Recycle

Scheme 10.

Table 5. Trapping Experiment of *o*-Quinodimethane (**36**)

Substrates	Olefins R	Olefins R′		Yield (%) **37**
34	H	CO_2Me		62
	CO_2Me	CO_2Me	(*cis*)	54
	CO_2Me	CO_2Me	(*trans*)	79
35	H	CO_2Me		97
	CO_2Me	CO_2Me	(*cis*)	94
	CN	CN	(*trans*)	99

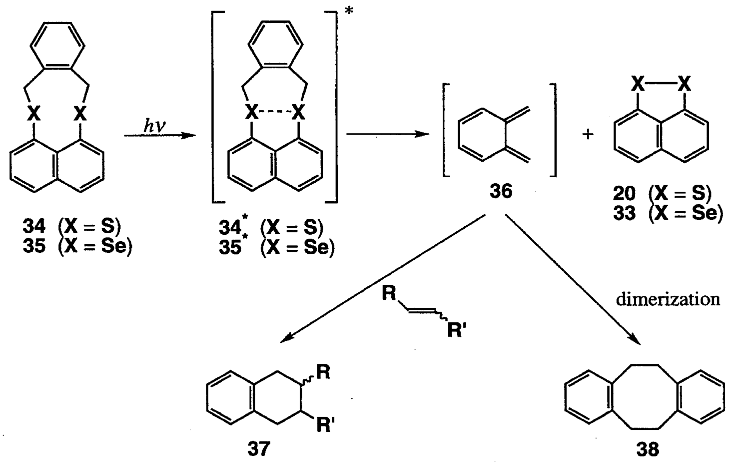
I-5-2) Photochemical Reactions of 2-Substituted and 2,2-Disubstituted Naphtho[1,8-*de*]-1,3-dithiin Derivatives.

In the modern organic syntheses, organic sulfur compounds play quite important roles.[64,65] As one such brilliant success, the concept of "Umpolung" has been introduced by Corey and Seebach, using typically 1,3-dithianes.[66] There are many procedures to remove 1,3-propanedithiol for deprotection,[67] which may involve the transannular interaction between the sulfur atoms, after converting divalent sulfur to the trivalent state.[68] Among these deprotection of aldehydes and ketones photochemical conversion is of considerable interest.[58] If one used naphthalene-1,8-dithiol (**39**) instead of 1,3-propanedithiol, the photolytic deprotection of the dithiol should occur quite readily to recover the ketones or the aldehydes and naphtho[1,8-*cd*]-1,2-dithiole (**20**) which can be recycled for the preparation of starting materials.

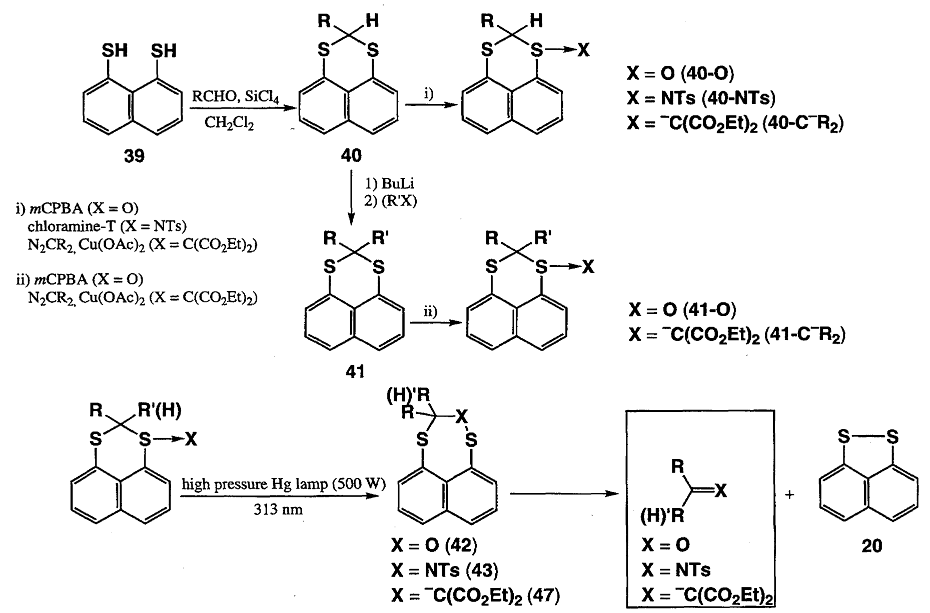
We prepared various derivatives of 2- and 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiin (**40**) and converted them to the corresponding monooxides (**40-O**), monosulfilimines (**40-NTs**) and mono-*S*-ylides (**40-C⁻R₂**), respectively. In fact, these three dithiin derivatives undergo photolysis to give aldehydes, ketones, imine derivatives and olefins in almost quantitative yields with the recovery of **20** as shown in Scheme 12.[69]

I-5-2-1) Photolysis of Monooxides of Naphtho[1,8-*de*]-1,3-dithiins. Although dithiins (**40**) and (**41**) are thermally and photochemically stable molecules, monooxides (**40-O**) and (**41-O**) are decomposed to the corresponding aldehydes and ketones quantitatively with complete recovery of **20** on exposure to high-pressure Hg lamp in benzene for 20 h.[75] The photolysis procedure is independent of the nature of the solvents. The results obtained are summarized in Table 6.

When the ^{1}H NMR signals of **40a-O** were followed, new peaks corresponding to those of the rearranged intermediate product (sulfenate) (**42a**) appeared but disappeared again completely. The formation of **42a** was identified as the cyclic sulfenate by examining the ^{1}H-, ^{13}C NMR and mass-spectra after the isolation of the crude compound. Finally the spectra were converted to that of a 1 : 1 mixture of **20** and benzaldehyde. *Cis–trans*-isomerization of the substrate (**40a-O**) was also observed. The time course of the photolysis is illustrated in Fig. 7.



Scheme 11.



Scheme 12.

Table 6. Photolysis of Dithioacetal Monooixde and Dithioketal Monooxide in Benzene a)

Substrates (**40-O** or **41-O**)		Yield (%) b)	
R	R′	Aldehyde or ketone	**20**
Ph	H	>99	>99
$CH_3(CH_2)_5$	H	>99	>99
PhCH=CH	H	>99	>99
Ph	CH_3	>99	>99
Ph	Py	>99	>99
Ph	PhCH(OH)–	>99	>99

a) 400 W high pressure Hg lamp, $\lambda > 300$ nm, Substrates (0.1 mmol), Benzene (5 ml). b) Yields were determined by gas chromatography and ^{1}H NMR spectroscopy.

The effect of light intensity on the photolysis of **40a-O** and the quantum yield measurements demonstrate that photoreaction of **40a-O** proceeds via the mechanism shown in Scheme 13. An excited singlet state (n–π^*) initiates the cleavage of the C–S bond in (**40a-O**)* giving the diradical (**40a-O**)$^{*\bullet}$ to form the sulfenate (**42a**) as an intermediate via the S–S through-space interaction. Finally, the sulfenate (**42a**) should be converted to benzaldehyde and **20** via also through-space interaction.

The photolysis of sulfoxides reported before gives the corresponding sulfenate ester as an intermediate. The mechanism has been exemplified by the quantum yield analysis and the stereochemistry of the sulfoxides employed.71)

I-5-2-2) Photolysis of *N*-Tosylsulfilimines Derived from Naphtho[1,8-*de*]-1,3-dithiins. The sulfilimines (**40-NTs**)72) also undergo intramolecular photo-imino rearrangement giv-

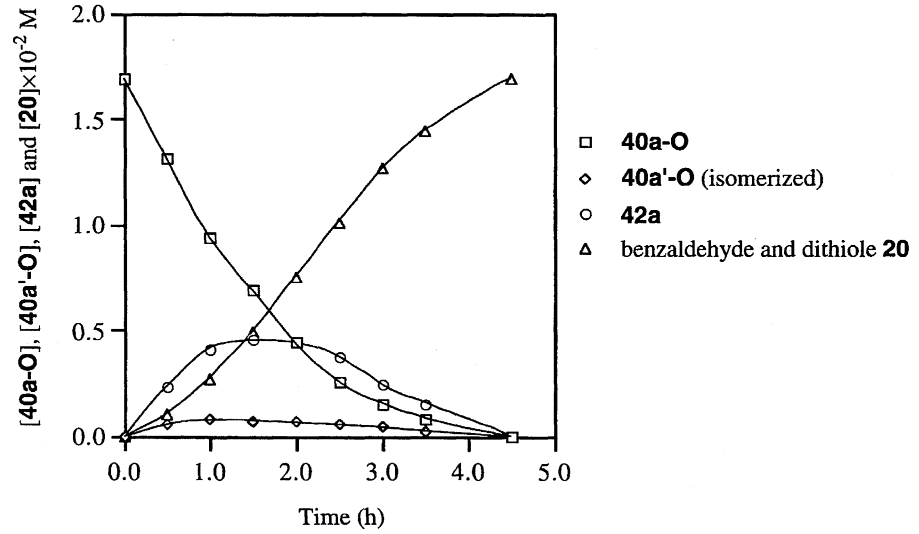
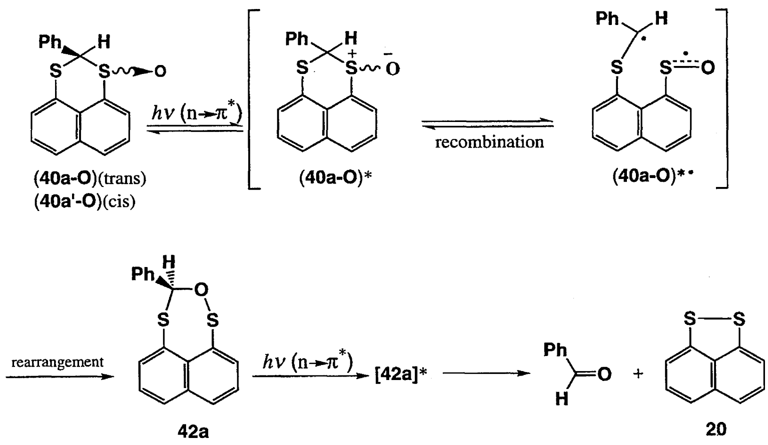


Fig. 7. Time course of photolysis of 1-phenyl-naphtho[1,8-*de*] 1,3-dithiane-1-oxide (**40a-O**) ([**40a**−O]$_0$=1.69×10^{-2} M in $CDCl_3$).



Scheme 13.

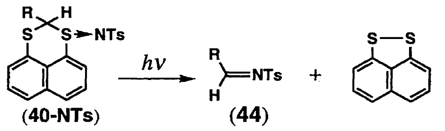
ing *N*-tosyl aldimines (**44**) quantitatively together with **20**.[73] Typical examples are shown in Table 7. The photolysis of **40-NTs** gives not only aromatic aldimines[74] but also aliphatic aldimines quantitatively, regardless of the solvents employed.

The photo-decomposition mode of the sulfilimine (**40a-NTs**) was similar to that of the sulfoxide (**40a-O**).

The monitoring results of the photolysis of **40a-NTs** by the ^{1}H NMR as shown in Fig. 8 clearly indicate the formation of an intermediate (**43a**) : 2,3-Dihydro-3-phenyl-2-tosylnaphtho[1,8-*ef*]-1,4,2-dithiazepine which was successfully separated and its structure was determined by X-ray crystallographic analysis. This dithiazepine (**43a**) decomposes to the final product, again via the S–S through-space interaction.

Interestingly, besides the photolysis, the 1-*N*-tosylsulfilimines (**40-NTs**) on treatment with BF_3–Et_2O undergo the imino-group migration to give aldimine–BF_3 complexes (**45**)

Table 7. Photolysis of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines in Benzene[a)]



R	Yield of aldimine (**44**) %[b)]
Ph	>99
Et	>99
$CH_3(CH_2)_5$	>99
PhCH=CH	>99
2-Furyl	>99

a) 400 W high pressure Hg lamp, λ > 300 nm, Substrates (0.1 mmol), Benzene (5 ml). b) Yields were determined by gas chromatography and ^{1}H NMR spectroscopy.

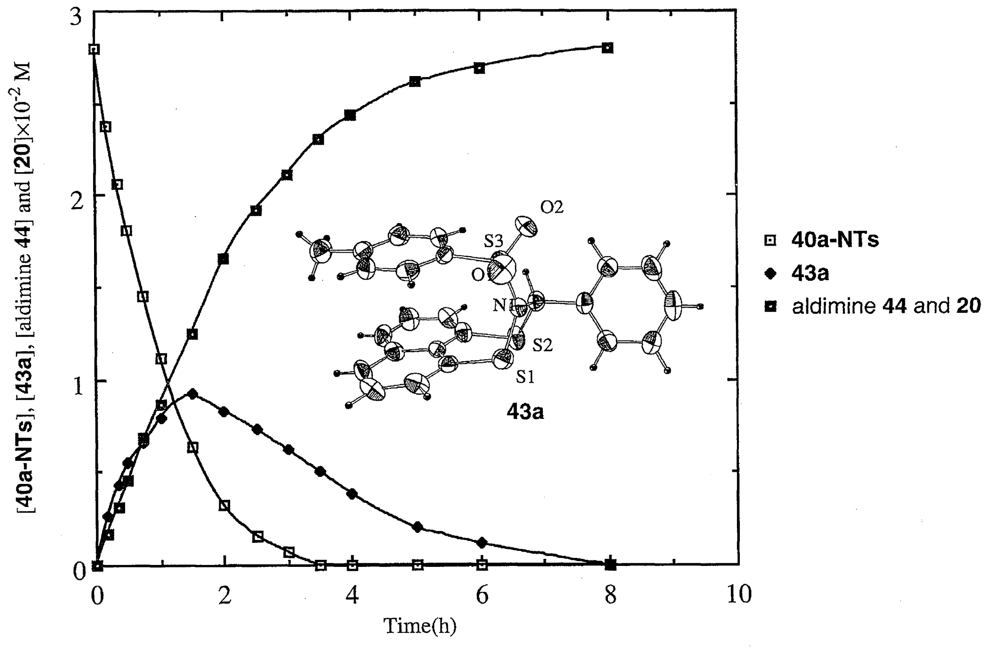


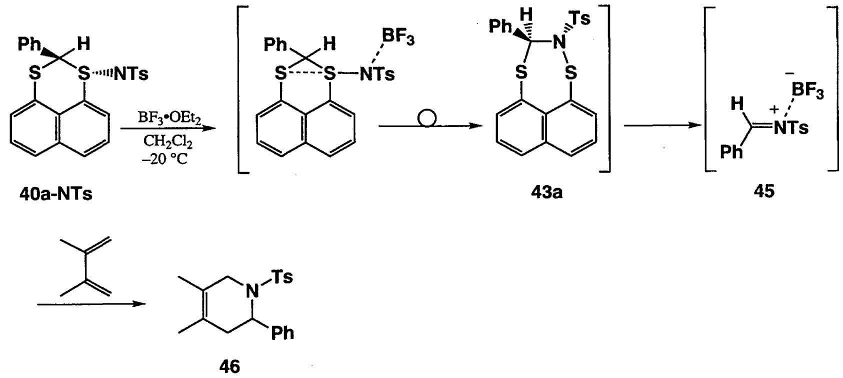
Fig. 8. Time course of photolysis of 1-phenyl-naphtho[1,8-*de*] 1,3-dithiane-1-*N*-tosylsulfilimine (**40a-NTs**) ([**40a**−**NTs**]$_0$=2.8×10^{-2} M in $CDCl_3$) and ORTEP drawing of intermediate **43a**.

as reactive intermediates which are trapped by dienes via imino [4+2] cycloaddition to give *N*-tosyltetrahydropyridine derivatives (**46**) in high yields.[75] The reactions are illustrated in Scheme 14 and the results are summarized in Table 8.

I-5-2-3) Photolysis of Monoylides of Naphtho[1,8-*de*]-1,3-dithiins. Naphtho[1,8-*de*]-1,3-dithiin-1-onium bis(ethoxycarbonyl)methylides (**40-C$^-$R$_2$**) were photolyzed under conditions similar to those used in the reactions of the sulfoxides (**40-O**) and the sulfilimines (**40-NTs**) as described before.

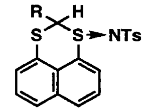
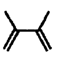
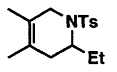
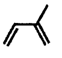
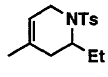
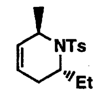
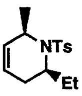
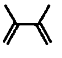
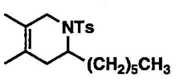
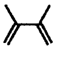
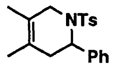
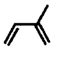
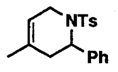
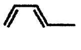
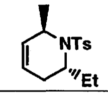
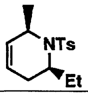
The modes of the photolysis of the ylides (**40-C$^-$R$_2$**) are similar to those of the sulfoxides and the sulfilimines. Namely, the photolyses of **40-C$^-$R$_2$** are clean and give the olefins and **20** quantitatively. The intramolecular migrational mode, light intensity dependence, and intermediary formation of the ring-expanded intermediate (**47**: R=Ph, R′=COOEt) are consistent with the features of the photolysis of **40-O** and **40-NTs**.[76] Tetrasubstituted ethylenes can be obtained quantitatively, demonstrating that the photolysis of **40-C$^-$R$_2$** is a synthetically important procedure.

In order to understand the mechanism of the photolysis, an ab initio calculation was carried out by using, 2,3-dihydronaphtho[1,8-*ef*]-1,4-dithiepin (**48**) as a model compound in the S$_1$ (singlet state) as well as S$_0$ (ground state) (Fig. 9). The RHF method was applied to the S$_0$, and the CIS method to the S$_1$ using STO-3G* basis set. The optimized S···S distances in S$_0$ and S$_1$ are 3.06 (3.13 Å) and 2.516 Å respectively. This bond shortening of ca. 0.5 Å at the S$_1$ promotes the reactivity of **48** by the through interaction between two sulfur atoms, and is related to the clean photo decomposition of the dithiepins (**47**).

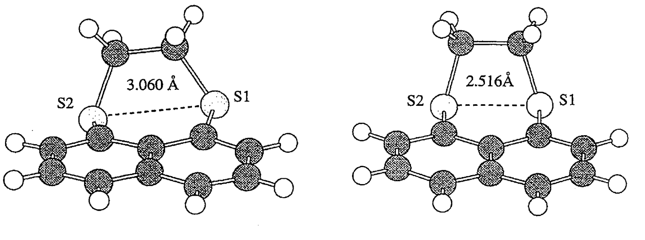


Scheme 14.

Table 8. Diels–Alder Cycloaddition of *N*-Tosylaldimines Generated in situ[a)]

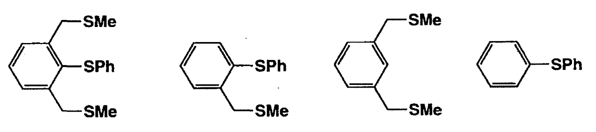
Substrate	R	Diene	Products		Yield (%)[b)]
	Et				81
	Et				88
	Et		 (2:1)[c)]		88
	CH$_3$(CH$_2$)$_5$				83
	Ph				56
	Ph				48
	Ph		 (3:1)[c)]		52

a) Substrates (0.22 mmol), Diene (0.22 mmol), BF$_3$(OEt$_2$) (0.22 mmol), CH$_2$Cl$_2$ (10 cm^{-3}). b) Isolated yields. c) Stereochemistry was established by ^{1}H NMR NOE.



48 (S_0) **48** (S_1)

Fig. 9. Three-dimensional view for RHF/STO-3G$^{(*)}$ optimized S_0 structure (left) and CIS/STO-3G$^{(*)}$ optimized S_1 structure (right) of **48**.



49

1150 mV$^{a)}$ 1340 mV$^{a)}$ 1400 mV$^{a)}$ 1550 mV$^{a)}$

Fig. 10. Oxidation potentials of 2,6-bis(methylthiomethyl)-phenyl phenyl sulfide (**49**) and related sulfides. a) Conditions: Pt electrode vs. saturated calomel electrode, 0.1 M n-Bu_4NClO_4 (electrolyte), CH_3CN (solvent), 200 mV s^{-1} (scan rate).

II) Dications of Hypervalent Species of [3c–4e] Bond

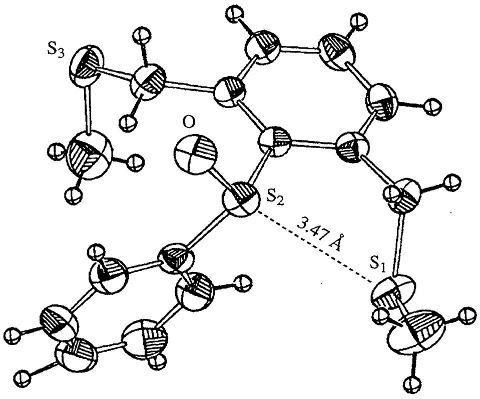
II-1) Preparation of Hyperdications. Accumulation of transannular or through-space interaction among more than three chalcogen atoms creates a new dication species as shown in Fig. 1. In this model, the chalcogen dications derived from the tris-sulfides or their monooxides are connected by a central hypervalent atom[77] and the atoms of the cationic center serve as electropositive ligands.

The preparation of these new hypervalent bonded compounds is carried out by one of two methods. The first is the oxidation process using one electron oxidants such as $NOBF_4$, whereas the second method is the treatment of monooxide with concd H_2SO_4 or acid anhydrides.[2a—2c] 2,6-Bis(methylthiomethyl)phenyl phenyl sulfide (**49**) and related sulfides were prepared. Their oxidation potentials (E_p vs. SCE) were measured by cyclic voltammetry. The E_p values of these compounds are shown in Fig. 10.

The lowest E_p values of the tris-sulfide (**49**) suggests that this may give a desired dication species (**49**$^{2+}$) after removing electrons from one sulfur atom. As shown in Fig. 10, the E_p values decrease every 200 mV by adding one *ortho*-methylthiomethyl group to diphenyl sulfide, while *m*-bis(methylthiomethyl)benzene has a higher oxidation potential than **49**.[78]

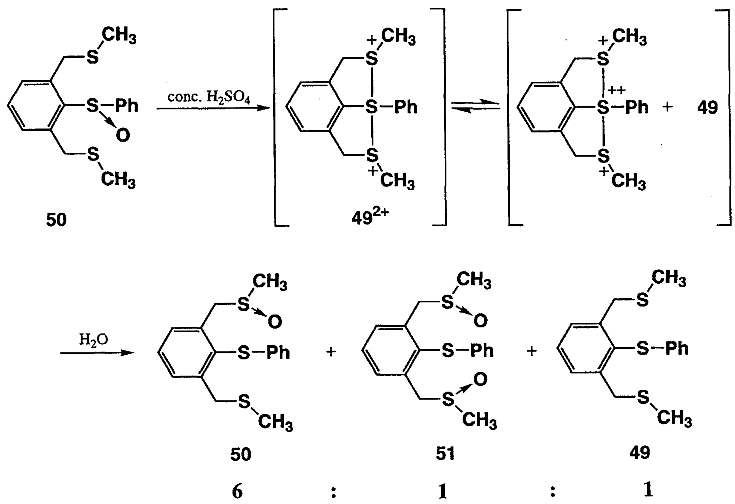
The X-ray crystallographic analysis of the monooxide (**50**) indicates that the two sulfur atoms S_1 and S_2 in the solid state are arranged within the van der Waals contact of S–S (3.70 Å), while the third sulfur atom (S_3) is far from the central sulfur atom, as shown in Fig. 11.[78] The sulfoxides (**50**) and (**50′**) were dissolved in concd D_2SO_4. Their measured ^{1}H NMR spectra indicate the formation of dication (**49**$^{2+}$) via through-space interactions between the three sulfur atoms. On treatment of a D_2SO_4 solution of **49**$^{2+}$ with H_2O, the three products (**49**), (**50′**), and (**51**) were obtained in 1 : 6 : 1 ratio as shown in Scheme 15. Selenides behave similarly to the sulfides.[80]

The formation of **49** and **51** suggests the disproportionation



50

Fig. 11. ORTEP drawing of monooxide **50**.



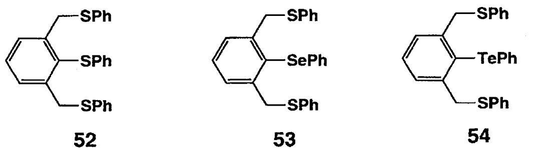
Scheme 15.

of **49^{2+}**, as shown in Scheme 15.

As an interesting extension of this reaction, diphenyl chalcogenides bearing 2,6-bis(phenylthiomethyl) groups (**52**—**54**) were prepared and their E_p values vs. Ag/AgCl in 3 M KCl/CH_3CN were measured (1 M = 1 mol dm^{-3}) (Fig. 12). Subsequently, these compounds were converted to the dications.[81)]

The three compounds (**52**), (**53**), and (**54**) have one cathodic and anodic peaks between −1500 mV to +1500 mV in the CV measurement, suggesting that oxidation potentials between the cation radicals and dications are too narrow to be distinguished by the present method. However, the oxidizing ability order of the three chalcogenides is Te > Se > S, which is the same as the trend observed for the oxidation potentials of the chalcogen atoms.[86)]

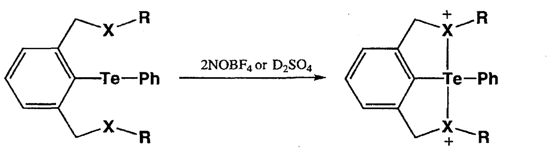
The tellurides (**54**), (**55**), and (**56**) and their monooxides were prepared and treated with either concd D_2SO_4 or $NOBF_4$ as an oxidant in an NMR-tube (Eq. 11). The ^1H NMR spectra of these compounds show the formation of the dication species (**57**), (**58**), and (**59**). The structures of these chalcogen dications were determined by X-ray crystallographic analysis after isolation. The ORTEP drawings of telluranes (**57**), (**58**), and (**59**) are show in Fig. 13.



52 **53** **54**

1103 mV[b)] 926 mV[a)] 666 mV[a)]

Fig. 12. Oxidation potentials of 2,6-bis(phenylthiomethyl)-phenyl phenyl sulfide (**52**), selenide (**53**), and telluride (**54**).

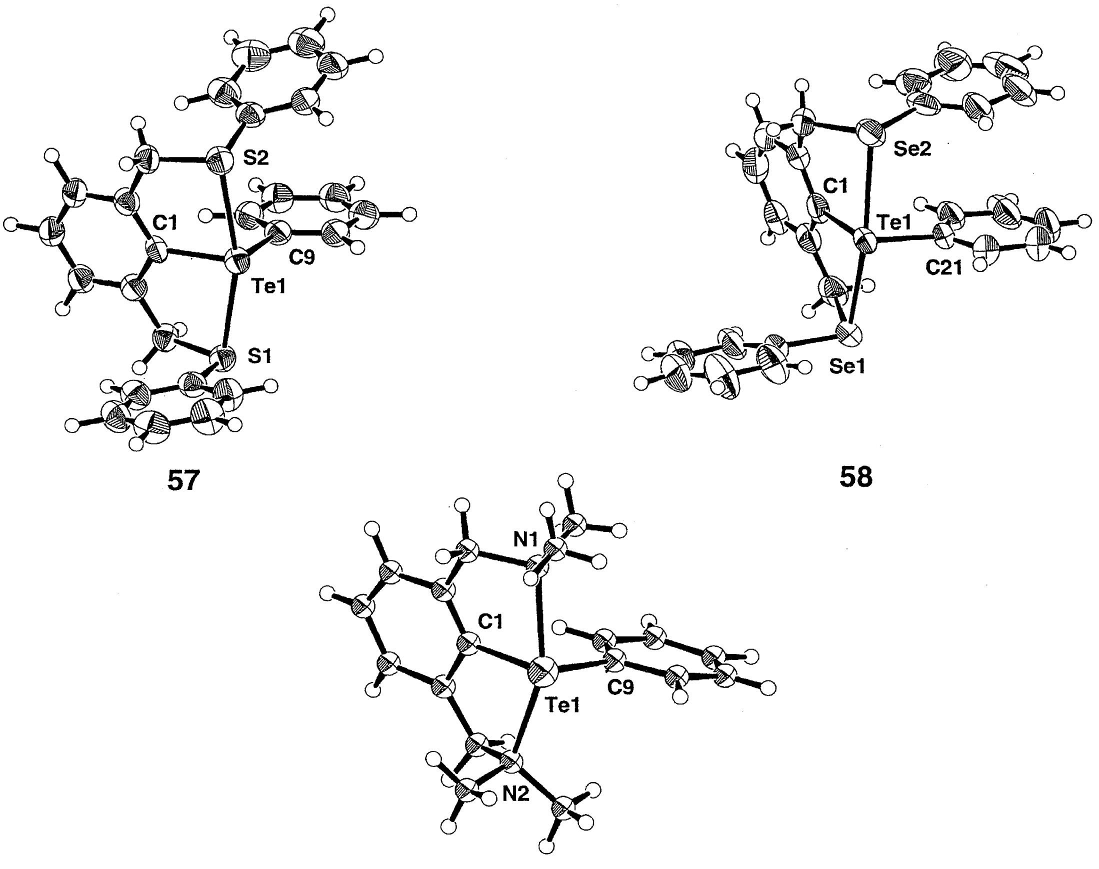


(11)

RX = SPh (**54**)
RX = SePh (**55**)
RX = N(CH₃)₂ (**56**)

RX = SPh (**57**)
RX = SePh (**58**)
RX = N(CH₃)₂ (**59**)

The dication (**57**) has a trigonal bipyramidal structure at the central Te atom, in which the two sulfonio groups occupy the axial positions, while the two phenyl rings and the lone electron-pair compose the equatorial ligands, with significantly longer Te–S bond distances: 2.652 and 2.654 Å, compared with the normal Te–S σ-bond length of 2.36 Å. From the view of **57** down the Te(1)–C(1) axis, it is seen that the phenyl rings are almost perpendicular to the S(1)–Te(1)–S(2) bond. Furthermore, surprisingly, the arrangement of the three phenyl groups are of a *cis–trans*-conformation,



57 **58** **59**

Fig. 13. ORTEP drawings of 2,6-bis[(phenylsulfonio)methyl]phenyl phenyl telluane (**57**), 2,6-bis[(phenylselenonio)methyl]phenyl phenyl tellurane (**58**), and 2,6-bis[(dimethylammonio)methyl]phenyl phenyl telluane (**59**).

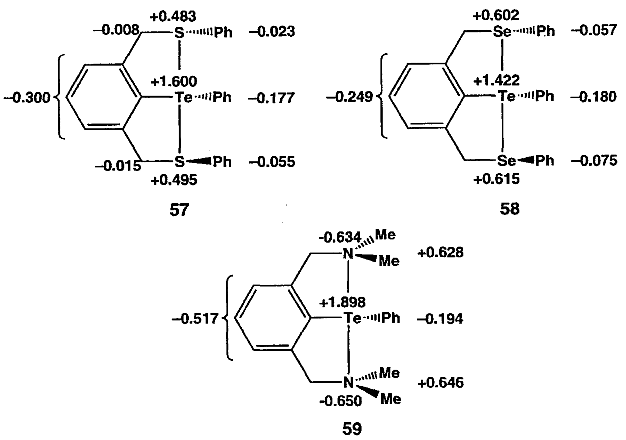
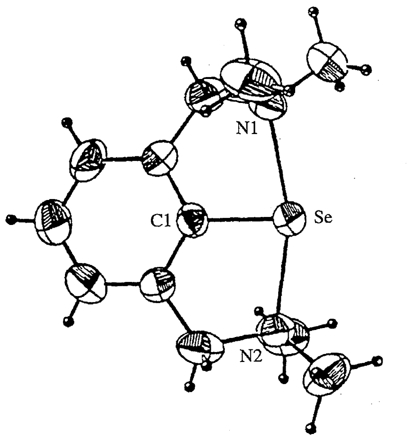


Fig. 15. Charge distribution of the tellurane dications (**57**), (**58**), (**59**) by single-point ab initio RHF/3-21G$^{(*)}$ calculation using the X-ray structures. The charges were calculated by the Natural Population Analysis (NPA) method.



62

Fig. 16. ORTEP drawings of selenenium salt (**62**).

which is marked contrast to the expected *trans–trans* conformation, as shown in Fig. 14. The distance between *cis* oriented phenyl rings is in the range 3.258—4.280 Å, indicating that π–π stacking may play an important role of this conformer of **57** in the solid state.

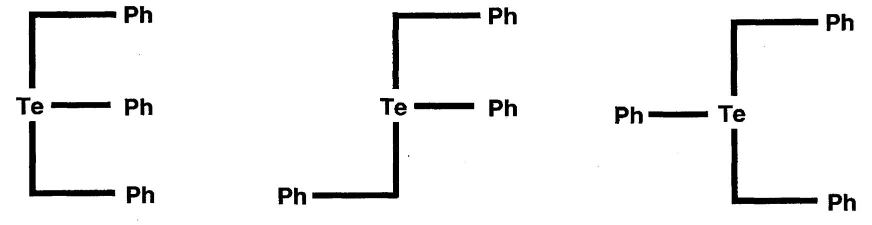
The charge densities and bond orders of the hypervalent bond of these telluranes (**57**), (**58**), and (**59**) were calculated by the ab initio RHF-method on the basis of 3-21G$^{(*)}$.[82] The results are shown in Fig. 15.

Interestingly, these ab initio calculations reveal that the positive charges at the hyperavalent bond of **57** and **58** are distributed among the S–Te and Se–Te bonds and positive charges are delocalized into neither the phenyl rings nor the methylene groups. But in the tellurane (**59**), the positive charges of the hypervalent bond are found at the central Te atom and the two nitrogen ligands are negatively charged; moreover, in these cases the population of 5d orbital is around 3%, indicating that the d-orbital participation is negligible.

Accordingly, these telluranes (**57**), (**58**), and (**59**) should have doubly positively charged structures at the Te atom rather than the hypervalent bonds.

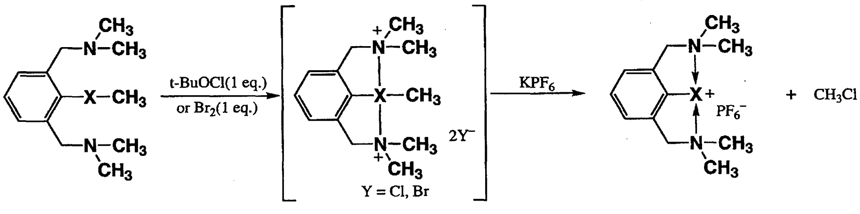
II-2) First RSe$^+$ and RTe$^+$ Salts; 2,6-Bis(dimethylaminomethyl)phenyl Selenenium and Tellurenium Cationic Compounds. The preparation of an monovalent sulfur cation (RS$^+$) species has been long awaited. Although many attempts have been conducted and the formation of it has been reported,[83] its existence still gives rise to controversial problems. Analogous selenenium and tellurenium cations (RSe$^+$, RTe$^+$) are also standing in line for investigation.[84]

As described in the previous sections, selenides and tellurides with two 2,6-dimethylaminomethyl groups on the 2,6-position of the phenyl ring, which are called a Koten's arm (ligand),[85] can stabilize the cations generated at the central Se and Te atoms by the through-space interaction enormously. Furthermore, the formation of dications highly activates the molecules to release the alkyl substituents attached at the



cis-cis conformation *cis-trans* conformation *trans-trans* conformation

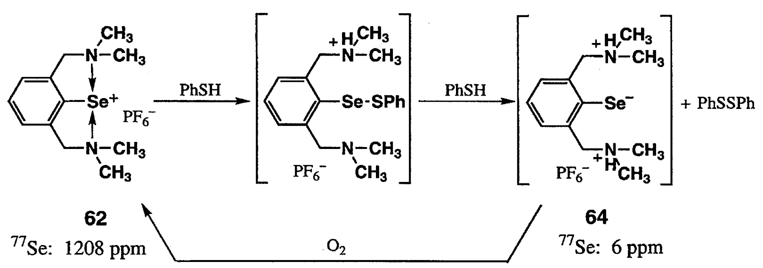
Fig. 14. Three types of conformers of 2,6-bis[(phenylsulfonio)methyl]phenyl phenyl telluane (**57**).



X = Se (60) ^{77}Se: 90.0 ppm
X = Te (61) ^{125}Te: 287.2 ppm

X = Se (62) ^{77}Se: 1208.3 ppm
X = Te (63) ^{125}Te: 1949.4 ppm

Scheme 16.



Scheme 17.

central chalcogen atom as electrophiles.

A combination of these procedures may produce the desired selenenium and tellurenium compounds (RSe^+, RTe^+). We prepared the following selenide (**60**) and telluride (**61**) and treated them with *t*-BuOCl and then KPF_6 for the anion exchange. As we expected, the selenenium salt (**62**) and tellurenium analog (**63**) were isolated, as shown in Scheme 16.[86)]

The selenenium salt (**62**) was isolated and the structure was determined by X-ray crystallographic analysis. The ORTEP drawing is shown in Fig. 16.

The PF_6^- anion is separated from the cationic center and makes no contact within the van der Waals contact. The bond lengths between the Se and two nitrogen atoms are 2.154(7) and 2.180(7) Å, which are much shorter than the sum of the van der Waals Se–N contact of 3.45 Å, although the distance is slightly longer than the sum of a covalent radii of Se–N bond. The positively charged character of the Se atom is also estimated by ^{77}Se NMR spectroscopy. The enormous down-field shift of the cationic species (**62**) as compared with the starting material (**60**) demonstrates the formation of a positive charge at the Se atom. The tellurenium species (**63**) was also confirmed by ^{125}Te NMR spectroscopy. Ab initio RHF calculations with STO-3-21G$^{(*)}$ as a basis set of these two new chalcogen species also confirm their existence.[87)]

Monovalent chalcogen species such as RSe^+ should react with olefins, but the present selenenium and tellurenium cations do not react with olefins at all due to the sterically bulky ligands which may prevent the approach of the Se^+ center to the olefinic carbon.

On the other hand, the selenenium cation (**62**) reacts with 2 equiv PhSH to give diphenyl disulfide and selenolate anion (**64**) which is converted back to the starting selenenium cation (**62**) on exposure to the selenolate in air, as shown in Scheme 17.

This is the first example of the isolation of selenenium and tellurenium cation species.

Conclusion

This account summarized the recent advancement in the chemistry of dichalcogena dications having 2-center-2-electron and 3-center-4-electron bonds. We have developed the chemistry of dichalcogena dications obtained from sterically congested bis- and tris-dichalcogenides. These dication species may not only provide us with new concepts in the chemical bondings of heteroatom compounds but also may produce new chemical reactions and functionally important materials such as molecular hysteresis in future.

Finally, the author wishes to thank to many co-workers, particularly Professor H. Fujihara, Dr. K. Kimura, Dr. T. Fujii, Dr. R. Akaishi, Dr. O. Takahashi, Dr. H. Mima, Dr. H. Shima, and many graduate students.

Finally, the author wishes to express gratitude for the financial support by the Ministry of Education, Science, Sports and Culture, [Grant Nos. 05236205, 07216211, and 08740484] and the Fund of Tsukuba Advanced Research Alliance (TARA) project [University of Tsukuba].

References

1) a) N. J. Leonard, *Acc. Chem. Res.*, **12**, 423 (1979); b) R. W. Alder, *Acc. Chem. Res.*, **16**, 321 (1983); c) K.-y. Akiba, K. Takee, K. Ohkata, and F. Iwasaki, *J. Am. Chem. Soc.*, **105**, 6965 (1983); d) K.-y. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, *J. Am. Chem. Soc.*, **108**, 6320 (1986); e) K.-y. Akiba, *Nippon Kagaku Kaishi*, **1987**, 1130; f) S. N. Tandura, M. G. Voronkov, and N. V. Alekseev, *Top. Curr. Chem.*, **131**, 99 (1986); g) J. G. Verkade, *Acc. Chem. Res.*, **26**, 483 (1993).

2) a) N. Furukawa, *Nippon Kagaku Kaishi*, (*J. Chem. Soc. Jpn.*), **1987**, 1118; b) H. Fujihara and N. Furukawa, *J. Synth. Org. Chem.* (*Jpn.*), **49**, 636 (1991); c) H. Fujihara and N. Furukawa, *J. Mol. Struct.* (*Theochem.*), **186**, 261 (1989); d) H. Fujihara and N. Furukawa, *Rev. Heteroatom Chem.*, [Myu, Tokyo], **6**, 263 (1992).

3) a) K.-D. Asmus, *Acc. Chem. Res.*, **12**, 436 (1979); b) W. K. Musker, *Acc. Chem. Res.*, **13**, 200 (1980); c) J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, **103**, 1159 (1981); d) K. Ohkata, K. Okada, and K.-y. Akiba, *Tetrahedron Lett.*, **26**, 4491 (1985).

4) H. Fujihara and N. Furukawa, "Sulfur-Centered Reactive Intermediate in Chemistry and Biology," NATO-ASI Series, Life Sciences, ed by C. Chatagilialoglu and K.-D. Asmus, Plenum Press, London and New York (1990), p. 193.

5) a) M. D. Ryan, D. D. Swanson, R. S. Glass, and G. S. Wilson, *J. Phys. Chem.*, **85**, 1069 (1981); b) G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *J. Am. Chem. Soc.*, **101**, 1040 (1979); c) W. N. Setzen and R. S. Glass, "Conformational Analysis of Medium-Sized Heterocycles," ed by R. S. Glass, VCH, New York (1988), Chap. 4, p. 151.

6) J. T. Doi, R. M. Kessler, D. L. de Leeuw, M. M. Olmstead, and W. K. Musker, *J. Org. Chem.*, **48**, 3707 (1983).

7) F. Iwasaki and N. Furukawa, *Acta Crystallogr., Sect. C*, **C43**, 80 (1987).

8) S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc. B*, **1970**, 1603.

9) H. Fujihara, R. Akaishi, and N. Furukawa, *Chem. Lett.*, **1990**, 549.

10) H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, and N. Furukawa,

Tetrahedron Lett., **32**, 4537 (1991).

11) N. Furukawa, *Phosphorous Sulfur Silicon*, **74**, 261 (1993).

12) J.-G. Gourcy, G. Jeminet, and J. Simonet, *J. Chem. Soc., Chem. Commun.*, **1974**, 634.

13) a) D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, **1975**, 238; b) M. Bonifâcič, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 675.

14) B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1748.

15) a) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976); b) R. S. Glass, M. Hojjatie, A. Petsom, and G. S. Wilson, *Phosphorus Sulfur*, **23**, 143 (1985).

16) a) N. Furukawa, A. Kawada, and T. Kawai, *J. Chem. Soc., Chem. Commun.*, **1984**, 1151; b) H. Fujihara, A. Kawada, and N. Furukawa, *Heterocycles*, **24**, 17 (1986); c) H. Fujihara, A. Kawada, and N. Furukawa, *J. Org. Chem.*, **52**, 4254 (1987).

17) H. Fujihara, R. Akaishi, T. Erata, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1989**, 1789.

18) H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1987**, 930.

19) F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **61**, 2563 (1988).

20) F. Iwasaki, M. Morimoto, M. Yasui, R. Akaishi, H. Fujihara, and N. Furukawa, *Acta Crystallogr., Sect. C*, **C47**, 1463 (1991).

21) N. Nakayama, O. Takahashi, O. Kikuchi, and N. Furukawa, Abstract II of "72th Japan Chemical Society Meeting," Tokyo, 1997, Abstr., p. 1153.

22) a) H. Fujihara, R. Akaishi, and N. Furukawa, *Chem. Lett.*, **1988**, 709; b) H. Fujihara, R. Akaishi, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **62**, 616 (1989); c) H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1989**, 147.

23) a) H. Fujihara, A. Nakamura, R. Akaishi, and N. Furukawa, *Chem. Lett.*, **1990**, 393; b) H. Fujihara, R. Akaishi, A. Nakamura, and N. Furukawa, *Tetrahedron Lett.*, **31**, 6375 (1990); c) H. Fujihara, R. Akaishi, and N. Furukawa, *Tetrahedron*, **49**, 1605 (1993).

24) a) H. Fujihara, Y. Takaguchi, T. Ninoi, T. Erata, and N. Furukawa, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 2583; b) H. Fujihara and N. Furukawa, *Phosphorus Sulfur Silicon*, **67**, 131 (1992).

25) a) T. Kimura, Y. Horie, S. Ogawa, F. Iwasaki, N. Furukawa, and H. Fujihara, *Heterocycles*, **33**, 101 (1992); b) N. Furukawa, T. Kimura, Y. Horie, and S. Ogawa, *Heterocycles*, **32**, 675 (1991); c) N. Furukawa, S. Ogawa, K. Matsumura, T. Shibutani, and H. Fujihara, *Chem. Lett.*, **1990**, 979; d) T. Kimura, Y. Horie, F. Iwasaki, S. Ogawa, N. Furukawa, and F. Iwasaki, *Heteroatom Chem.*, **4**, 243 (1993).

26) N. Furukawa, Y. Ishikawa, T. Kimura, and S. Ogawa, *Chem. Lett.*, **1992**, 675.

27) M. Yasui, S. Murata, F. Iwasaki, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **68**, 744 (1995).

28) T. Kimura, Y. Ishikawa, K. Ueki, Y. Horie, and N. Furukawa, *J. Org. Chem.*, **59**, 7117 (1994).

29) N. Furukawa, T. Kimura, Y. Horie, S. Ogawa, and H. Fujihara, *Tetrahedron Lett.*, **33**, 1489 (1992).

30) a) Y. Izumi, The Dissertation of the Masters Degree, University of Tsukuba, 1995; b) T. Kimura, Y. Izumi, E. Horn, and N. Furukawa, *Heteroatom Chem.*, **7**, 313 (1996).

31) T. Kimura, Y. Ishikawa, S. Ogawa, T. Nishio, I. Iida, and N. Furukawa, *Tetrahedron Lett.*, **33**, 6355 (1992).

32) J. Meinwald, S. Knapp, K. Obendorf, and R. E. Hughes, *J. Am. Chem. Soc.*, **98**, 6643 (1976).

33) a) M. P. Cava and M. V. Lakshmikantham, *Acc. Chem. Res.*, **8**, 139 (1975); b) J. Nakayama, A. Ishii, Y. Kobayashi, and M. Hoshino, *J. Chem. Soc., Chem. Commun.*, **1988**, 959; c) M. P. Cava and G. E. M. Husbands, *J. Am. Chem. Soc.*, **91**, 3952 (1969); d) K. J. Miller, K. F. Moschner, and K. T. Potts, *J. Am. Chem. Soc.*, **105**, 1705 (1983); e) B. M. Gimarc, *J. Am. Chem. Soc.*, **105**, 1979 (1983); f) S. Yoneda, K. Ozaki, T. Inoue, A. Sugimoto, K. Yanagi, and M. Minobe, *J. Am. Chem. Soc.*, **107**, 5801 (1985); g) A. Tsubouchi, N. Matsumura, H. Inoue, and K. Yanagi, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 909; h) A. Ishii, J. Nakayama, J. Kazami, Y. Ida, T. Nakamura, and M. Hoshino, *J. Org. Chem.*, **56**, 78 (1991).

34) a) T. Kimura, Y. Ishikawa, and N. Furukawa, *Chem. Lett.*, **1993**, 635; b) T. Kimura, Y. Ishikawa, Y. Minoshima, and N. Furukawa, *Heterocycles*, **37**, 541 (1994).

35) T. Kimura, The Dissertation of the Doctors Degree, University of Tsukuba, 1992.

36) T. Kimura, Y. Ishikawa, and N. Furukawa, *Heterocycles*, **35**, 53 (1993).

37) T. Kimura and N. Furukawa, *Tetrahedron Lett.*, **36**, 1079 (1995).

38) a) H. Fujihara, J.-J. Chiu, and N. Furukawa, *Chem. Lett.*, **1990**, 2217; b) R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, and G. S. Wilson, *J. Am. Chem. Soc.*, **111**, 4036 (1989); c) R. S. Glass, *Main Group Chem. News*, **2**, 4 (1994).

39) a) H. Fujihara, M. Yabe, J.-J. Chiu, and N. Furukawa, *Tetrahedron Lett.*, **32**, 4345 (1991); b) M. Yabe, The Dissertation of The Masters Degree, University of Tsukuba, 1992.

40) N. Furukawa, H. Shima, and S. Ogawa, *Heteroatom Chem.*, **6**, 559 (1995).

41) a) R. S. Glass, J. L. Broeker, and H. Firouzabadi, *J. Org. Chem.*, **55**, 5739 (1990); b) R. S. Glass, L. Adamowicz, and J. L. Broeker, *J. Am. Chem. Soc.*, **113**, 1065 (1991).

42) H. Fujihara, M. Yabe, and N. Furukawa, *J. Chem. Soc., Perkin Trans 1*, **1996**, 1783.

43) H. Fujihara, H. Ishitani, Y. Takaguchi, and N. Furukawa, *Chem. Lett.*, **1995**, 571.

44) a) N. Furukawa, H. Shima, and T. Kimura, *J. Chem. Soc., Chem. Commun.*, **1993**, 1762; b) H. Shima and N. Furukawa, *Tetrahedron.*, **51**, 12239 (1995).

45) a) R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970); b) D. A. Evans, C. L. Sims, and G. C. Andrews, *J. Am. Chem. Soc.*, **99**, 5453 (1977); c) S. Braverman, "The Chemistry of Sulphones and Sulphoxides," ed by S. Patai, Z. Rappoport, and C. J. M. Stirling, John Wiley & Sons, New York (1988), Chap. 14, p. 717; d) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).

46) a) J. K. Kim and M. C. Caserio, *J. Org. Chem.*, **44**, 1897 (1979); b) M. Klin, N. Beutous, J. K. Kim, and M. C. Caserio, *J. Org. Chem.*, **44**, 1904 (1979).

47) R. P. Lutz, *Chem. Rev.*, **84**, 205 (1984).

48) H. Shima, R. Kobayashi, T. Nabeshima, and N. Furukawa, *Tetrahedron Lett.*, **37**, 667 (1996).

49) On the Pummerer Reaction, see: S. Oae, "Yuki Iou Kagaku," Kagaku-Dojin, Kyoto (1982), Vol. 1, Chap. 7, p. 413.

50) Y. Kita, *J. Synth. Org. Chem. Jpn.*, **52**, 746 (1994).

51) H. Shima, M. Goto, and N. Furukawa, unpublished results.

52) a) H. Minato, T. Miura, and M. Kobayashi, *Chem. Lett.*, **1975**, 1055; b) G. Capozzi, O. Delucchi, V. Lucchini, and G. Modena, *Synthesis*, **1976**, 677.

53) a) D. N. Kevill and S. W. Anderson, *J. Am. Chem. Soc.*, **108**, 1579 (1986); b) D. N. Kevill and S. W. Anderson, *J. Org. Chem.*,

51, 5029 (1986).

54) G. A. Maw, "The Chemistry of the Sulfonium Group," ed by C. J. M. Stirling and S. Patai, John Wiley & Sons, New York (1981), Chap. 17.

55) P. Brajeswar, "211th ACS National Meeting," New Orleans, LA, 1996, Abstr., No. 211 and 214.

56) Similar trends are observed in idonanes, see: a) T. Okuyama, T. Takino, T. Sueda, and M. Ochiai, *J. Am. Chem. Soc.*, **117**, 3360 (1995); b) N. Hartz, G. Rasul, and G. A. Olah, *J. Am. Chem. Soc.*, **115**, 1277 (1993); c) T. Kitamura, *J. Synth. Org. Chem. Jpn.*, **53**, 893 (1995).

57) On the detailed chemistry of this area, H. Shima, R. Kobayashi, M. Goto, and N. Furukawa, papers are in preparation.

58) I. W. J. Still, "The Chemistry of Sulphones and Sulphoxides," ed by S. Patai, Z. Rappoport, and C. J. M. Stirling, John Wiley & Sons, New York (1988), Chap. 18, p. 873.

59) H. Fujihara, R. Saito, M. Yabe, and N. Furukawa, *Chem. Lett.*, **1992**, 1437.

60) H. Fujihara, M. Yabe, and N. Furukawa, *J. Org. Chem.*, **58**, 5291 (1993).

61) Y. Higuchi and N. Furukawa, unpublished results.

62) a) W. Oppolzer, *Synthesis*, **1978**, 793; b) J. J. McCullough, *Acc. Chem. Res.*, **13**, 270 (1980).

63) Y. Ito, M. Nakatsuka, and T. Saegusa, *J. Am. Chem. Soc.*, **102**, 863 (1980).

64) D. N. Jones, "Comprehensive Organic Chemistry," Pergamon Press, New York (1979), Vol. 3.

65) E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York (1978).

66) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975).

67) P. C. B. Page, M. B. Van Niel, and J. C. Prodger, *Tetrahedron*, **45**, 7643 (1989).

68) K. Ogura, M. Yamashita, M. Suzuki, S. Furukawa, and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **57**, 1637 (1984).

69) T. Fujii, The Dissertation of The Doctor's Degree, University of Tsukuba, 1996.

70) N. Furukawa, T. Fujii, T. Kimura, and H. Fujihara, *Chem. Lett.*, **1994**, 1007.

71) a) Y. Guo and W. S. Jenks, *J. Org. Chem.*, **60**, 5480 (1995); b) C. Sheu, C. S. Foote, and C.-L. Gu, *J. Am. Chem. Soc.*, **114**, 3015 (1992); c) E. L. Clennan, D.-X. Wang, K. Yang, D. J. Hodgson, and A. R. Oki, *J. Am. Chem. Soc.*, **114**, 3021 (1992).

72) Sulfilimines: S. Oae and N. Furukawa, "Sulfilimines and Related. Derivatives, ACS Monograph," ACS, Washington D. C. (1983).

73) T. Fujii, T. Kimura, and N. Furukawa, *Tetrahedron Lett.*, **36**, 1075 (1995).

74) a) J. Sisko and S. M. Weinreb, *J. Org. Chem.*, **55**, 393 (1990); b) W. B. Jenningo and C. J. Lovely, *Tetrahedron*, **47**, 5561 (1991); c) B. E. Love, P. S. Raje, and T. C. Williams, *Synlett*, **1994**, 493; d) B. M. Trost and C. Marrs, *J. Org. Chem.*, **56**, 6468 (1991).

75) T. Fujii, T. Kimura, and N. Furukawa, *Tetrahedron*, **36**, 4813 (1995).

76) a) T. Fujii, H. Sakuragi, and N. Furukawa, *Tetrahedron Lett.*, **36**, 8039 (1995); b) T. Fujii, O. Takahashi, and N. Furukawa, *J. Org. Chem.*, **61**, 6233 (1996).

77) R. A. Hayes and J. C. Martin, "Organic Sulfur Chemistry. Theoretical and Experimental Advances," in "Sulfurane Chemistry," ed by F. Bernardi, I. G. Csizmadia, and A. Mangini, Elsevier, Amsterdam (1985), Chap. 8, p. 408.

78) H. Fujihara, J.-J. Chiu, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1986**, 1359.

79) F. Iwasaki, N. Toyoda, N. Yamazaki, H. Fujihara, and N. Furukawa, *Acta Crystallogr., Sect. C*, **C46**, 2154 (1990).

80) H. Fujihara, Y. Higuchi, H. Mima, and N. Furukawa, *Chem. Lett.*, **1994**, 619.

81) A. R. Berghold, E. Horn, O. Takahashi, S. Sato, K. Kobayashi, and N. Furukawa, submitted to *J. Am. Chem. Soc.*

82) N. Furukawa, K. Kobayashi, E. Horn, S. Sato, and O. Takahashi, unpublished results

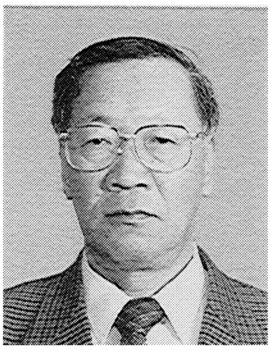
83) a) H. Kwart and K. G. King, "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur," Springer, New York (1977).

84) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, John Wiley and Sons, New York (1986), Vol. 1, (1987), Vol. 2.

85) a) G. van Koten, *Pure Appl. Chem.*, **61**, 1681 (1989); b) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek, and J. C. Shoone, *J. Organomet. Chem.*, **148**, 233 (1978); c) G. van Koten, J. Terheijden, J. A. M. van Beek, I. C. M. Wehman-Ooyevaar, F. Muller, and C. H. Stan, *Organometallics*, **9**, 903 (1990); d) C. J. Carmalt and A. H. Cowley, *Main Group Chem. News*, **4**, 4 (1996).

86) H. Fujihara, H. Mima, and N. Furukawa, *J. Am. Chem. Soc.*, **117**, 10153 (1995).

87) O. Takahashi, H. Ono, O. Kikuchi, and N. Furukawa, "the 74th. Japan Chemical Society Meeting," Tokyo, 1997, Abstr., Vol. II, p. 1153.



Naomichi Furukawa is professor of organic chemistry at Tsukuba University. He obtained his B. S. from Kyoto University in 1960 and then joined the Chemistry Department of the Radiation Center of Osaka Prefecture. In 1964, he moved to Osaka City University as a research associate where he obtained his PhD, in 1968. He then came to Tsukuba University as an associate professor in 1974 and was promoted to a professor in 1984. He has been a professor of newly founded Tsukuba Advanced Alliance Center at Tsukuba University since 1995. His research interest is organic heteroatom chemistry, particularly on chalcogen atoms and heterocyclic chemistry containing sulfur atom. He is the author of about 300 scientific that deal mostly with organic chalcogen chemistry. He spent one and half year at Brookhaven National Laboratories from 1968 to 1970.