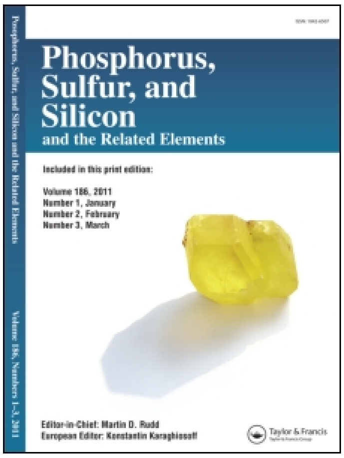

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Formation of Unusual Valent Organic Sulfur and Selenium Compounds via Transannular Interaction

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FORMATION OF UNUSUAL VALENT ORGANIC SULFUR AND SELENIUM COMPOUNDS VIA TRANSANNULAR INTERACTION

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Abstract 1,5-Dithia- and diselenacyclooctane [1,5-DTCO and 1,5-DSeCO] were prepared and converted to the dication salts using $NOPF_6$ or conc. H_2SO_4. The structures of the salts were determined by the x-ray crystallographic analysis revealing that σ-bond is formed between the two sulfur or selenium atoms. Several other sterically congested dications derived from dibenzothiocin, 1,9-disubstituted dibenzothiophenes and the corresponding selenium compounds were synthesized and their structures were estimated on the basis of their ^1H-, ^{13}C- and ^{77}Se nmr spectroscopy. The dications of trissulfide, 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]-dithiocin and the selenium analog were generated. Inspection of their nmr spectra revealed that the central sulfur or selenium atom in these salts should have a hypervalent bonding structure, 10-S-4(C_2S_2), or 10-Se-4(C_2Se_2) which was further confirmed by the ^{77}Se-nmr coupling constants.

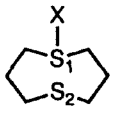
INTRODUCTION

Transannular interaction is a generally observable phenomenon in organic molecules or reactions[1]. When the two heteroatoms are arranged appropriately in space, an attractive force works between the two atoms and creates a new bonding which is identified by various spectroscopic methods. The transannular interaction tends to be observed in the medium sized cyclic compounds more than seven membered ring systems bearing two heteroatoms such as nitrogen and sulfur.

As a typical example, the two sulfur atoms in 1,5-dithiacyclooctane[1,5-DTCO] (**1**) and the related cyclic compounds approach close together due to the characteristic conformational property observed in 8-membered cyclic compound and hence should have an attractive force even in the neutral state. Moreover, when the compound (**1**) is converted to the partially mono charged species such as monosulfoxide (**2**)2), monosulfilimine (**3**)3) and monosulfonium salt (**4**)4), a stronger attractive interaction exerts between the two sulfur atoms since the x-ray crystallographic analysis reveals that the distances between the two sulfur atoms in the molecules are shorter than that of the starting compound (**1**) being whithin the Van der Waals S-S contact (3.75 Å) as shown in Table 1.

Table 1 1,5-DTCO derivatives

Compounds	X	S-S (Å)	<XSS (°)	Ref.
1	lone pair	3.58	-	
2	O	3.14	175.4	2)
3	NTs	3.14	177.8	3)
4	CH_2COCH_3	3.12	178.9	4)



1-4

Interestingly, for example, the x-ray analysis of sulfilimine (**3**) demonstrates that the angle of N-S_1-S_2 is nearly 180°. This indicates clearly that the central sulfur atom (S_1) in **3** should have a quasi sulfurane structure bearing nitrogen and sulfur atoms as the two axial ligands and two carbon atoms and a lone electron pair as the remaining three equatorial ligands.

This result predicts that how one can design and provide various hypervalent molecules of heteroatoms by using transannular interaction.

Furthermore, one electron oxidation of compound **1** using one electron oxidant such as $NOBF_4$5), under anodic oxidation6) and pulse radiolysis7) has been reported to afford 1,5-dithiacyclooctane cation radical [1,5-DTCO$^{\underset{\cdot}{+}}$] (**5**) which is further oxidized to the corresponding dication [1,5-DTCO]$^{+2}$ (**6**). Similarly, the compounds bearing two sulfenyl sulfur atoms separated by more than three methylene linkages undergo one or two electron oxidation to afford the corresponding cation radicals or dications either from acyclic or cyclic compounds8). We have also interested in studying the transannular interaction in organic sulfur and selenium compounds and found that the dication (**6**) and that of other cyclic and acyclic compounds are generated by treating the sulfoxide (**2**) or sulfilimine (**3**) with conc. sulfuric acid9). The detection of dication (**6**) formation in conc. sulfuric acid was carried out by using ^{1}H- and ^{13}C-NMR spectroscopy. A typical spectrum of monooxide (**2**) in conc. D_2SO_4 is shown in Fig. 1.

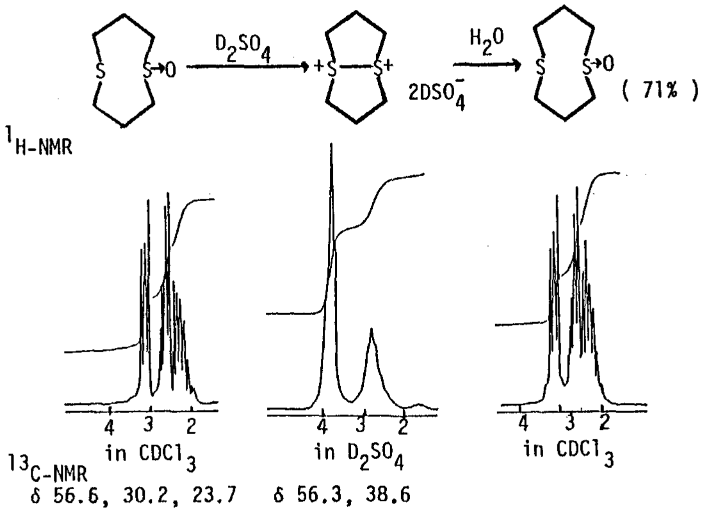


Fig. 1 ^{1}H-NMR of 1,5-DTCO in conc. D_2SO_4

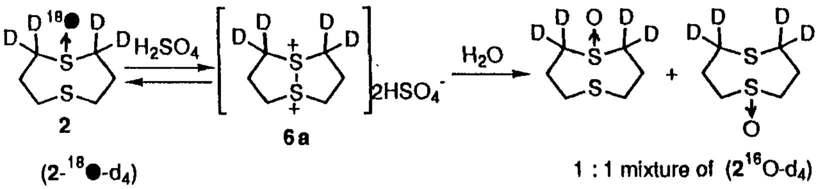
According to the ideas to design the dithiadication salts via transannular interaction, we prepared several cyclic sulfur and selenium compounds bearing more than two sulfur (and selenium) atoms besides **1** and treated them in conc. H_2SO_4 or with one electron oxidizing agents. This paper represents our recent results on the preparation and detection of dications of sulfur and selenium compounds and also the preparation of new hypervalent molecules of sulfur and selenium atoms.

Here, we wish to describe the formation of the following three dication species.

1. First isolation and structural determination of 1,5-DTCO dication salt and its selenium analog [1,5-DSeCO] by x-ray crystallographic analysis.
2. Formation of dications of sterically congested compounds such as dibenzothiocins and 1,9-disubstituted dibenzothiophenes.
3. New hypervalent compounds of dibenzodiciocin and -selenocin derivatives i.e., [1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin and -selenocin] via transannular interaction on oxidation.

1. a: Formation of 1,5-DTCO Dication Salt (**6**)

Formation of the dication of 1,5-DTCO(**6**) has been reported by Musker, Asmus, and Alder[5)-7)]. The structure of the salt (**6**) was assigned on the basis of UV, ^{13}C-nmr and elemental analysis. Alternatively we found that the sulfoxide (**2**) is readily converted to the dication of **1** on dissolution in conc. sulfuric acid. The formation of **6** was confirmed directly by observing the ^{1}H- and ^{13}C-nmr chemical shifts of **1** in D_2SO_4. The D_2SO_4 solution of **1** gave the starting sulfoxide (**2**) after treatment with water. The formation of dithiadication (**6**) was further confirmed by the following D- and ^{18}O-tracer experiments using D- and ^{18}O-labeled compound[10].



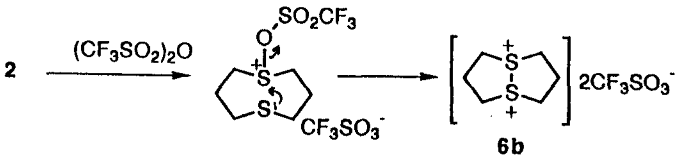
Scheme 1

After quenching the H_2SO_4 solution of 2,2,8,8-tetradeuterated-1,5-DTCO(**2**-d_4) with H_2O, a mixture of both 2,2,8,8 and 4,4,6,6 tetradeuterated-1,5-DTCO was obtained in a 1:1 ratio. The reaction is illustrated in Scheme 1.

b: Crystal Structures of Disulfide and Diselenide Dication Salts of 1,5-DTCO and 1,5-DSeCO.

We found that the reaction of sulfoxide **2** with triflic anhydride, $(CF_3SO_2)_2O$[≡Tf_2O] gives a remarkably stable disulfide dication salt 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethane-sulfonate) (**6b**)[9].

This reaction proceeds via the initial formation of the trifluoromethanesulfonyloxysulfonium cation which is converted to the disulfide dication (**6b**) by the intramolecular nucleophilic displacement of ttrifluoromethanesulfonate ion ($CF_3SO_3^-$) by the second sulfur atom as shown in Scheme 2.



Scheme 2

The crystal structure of **6b** was determined by x-ray crystallographic analysis. According to the x-ray analysis, there are two independent dication, **A** and **B**, in the crystals, each of which has an exact two fold axis coincide with the crystal symmetry. The crystal structure of dication **A** of **6b** is shown in Fig. 2.

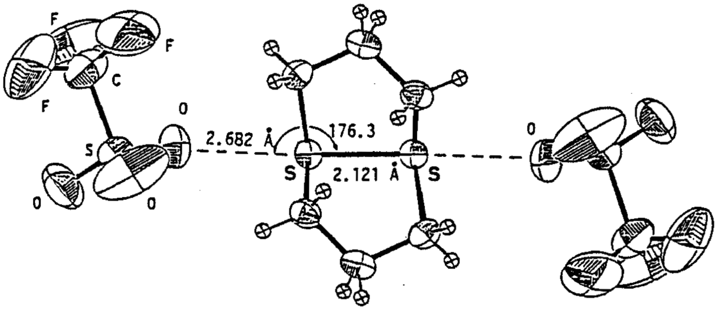
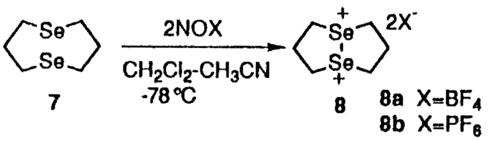


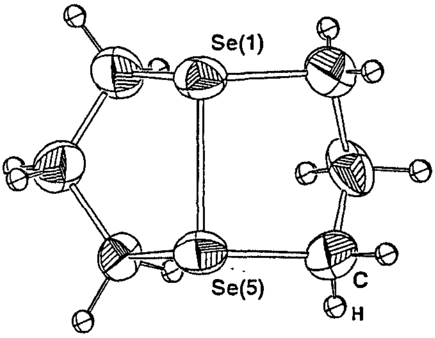
Fig.2 ORTEP of $[1,5\text{-DTCO}]^{2+}\cdot 2BF_4^-$

The S(1)-S(2) length is 2.121 Å, which is only slightly longer than the normal S-S single bond (2.08 Å) in 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 very strong interaction can be observed between the S^+ of the dication, and the oxygen atoms of the triflate counter anion. The distance of $S^+\cdots O$ is 2.682 Å, which is markedly shorter than the Van der Waals contact of 3.35 Å. The angle of $S\text{-}S\cdots O$ is 176.3°. Nearly collinear interaction of $O\cdots S\text{-}S\cdots O$ is formed with central two fold symmetry. This strong interaction between the cation and the anion also contributes to the stabilization of the crystals. The optimized transannular S-S distance is 3.307 Å for 1,5-DTCO (**1**) and 2.140 Å for $1,5\text{-DTCO}^{2+}$ by ab initio MO calculation based on the STO-3G basis set12). Similarly 1,5-diselenacyclooctane[1,5-DSeCO](7) was prepared and its oxidation with two equiv. $NOPF_6$ or $NOBF_4$ afforded the corresponding 1,5-diselenadication salt (**8**)[13] as shown in Scheme 3.



Scheme 3

The ^{77}Se-nmr of **7** in CH_3CN appears at δ 141.3ppm (s), while that of **8a** shifts to enormous downfield at δ 806.5 (s) indicating the formation of dicationic species (standard: $Me_2Se{=}O$). Furthermore, the x-ray crystallographic analysis of **8a** reveals that the Se^+-Se^+ distance is 2.38 Å which is nearly identical to the normal Se-Se single bond[14]. The distance between the fluorine atom of BF_4^- and the Se^+ atom is 2.68-3.25 Å which is also within Van der Waals contact of Se···F (3.37 Å). The ORTEP drawing of **8a** is shown in Fig. 3.

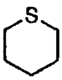
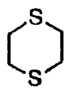
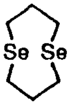


Se-Se: 2.38 Å

Fig. 3 ORTEP of $[1,5\text{-DSeCO}]^{2+}\cdot 2BF_4^-$

Interestingly, in the case of selenium compounds, 1,4-diselenacyclohexane dication (**9**) was isolated as a first crystalline compound of six membered dication which has the ^{77}Se-nmr chemical shift at δ 1202 ppm as a singlet. Besides the short distance between the S-S or Se-Se in these 1,5-dithia and 1,5-diselenacyclooctane, the other characteristic physical property for these compounds is that they have extremely lower oxidation potentials than the standard monothia (or selena) compound. The oxidation potentials of several thia[15] and selena[16] derivatives were measured by cyclic voltammetry and the representative Ep values are shown in Table 2.

Table 2. Oxidation potentials (Ep) of dithia (and selena) ethers

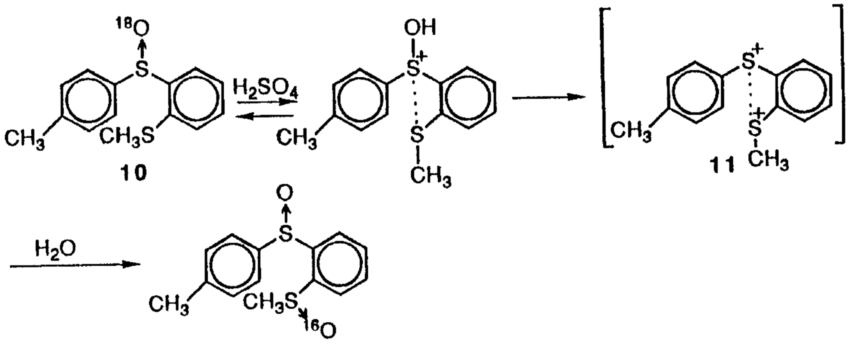
compound						$(n\text{-Hex})_2Se$
Ep (V)	1.32	1.25	1.14	0.343	0.25	0.95

(Ag/Ag^+ CH_3CN)

Thus the low oxidation potential should be one of the essential factors for transannular interaction.

2. Dithiadication Salts of Dibenzothiocin and other Sterically Congested Systems.

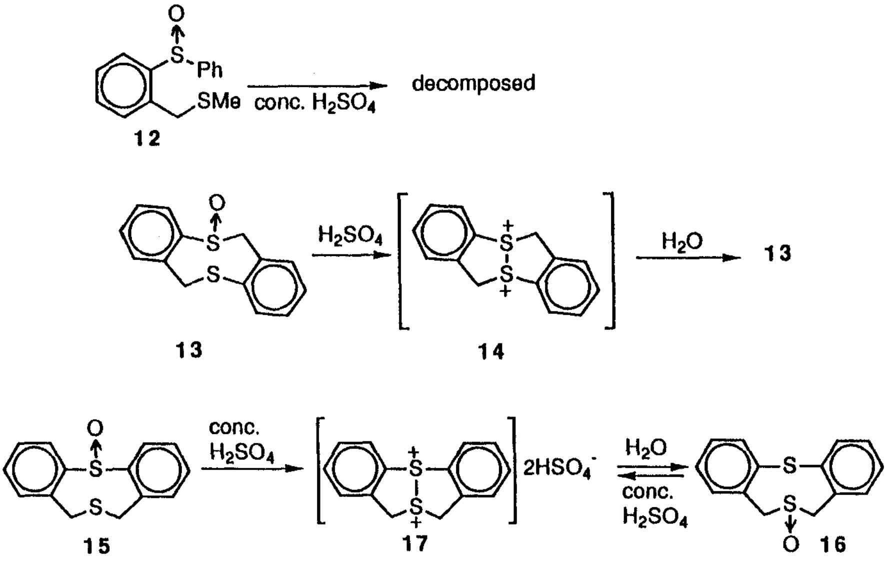
Earlier, intramolecular formation of dithiadications has been postulated by Shine[17)] and Oae[18)] in the reactions of thianthrene monooxide and o-methylphenyl p-tolyl sulfoxide (**10**) in conc. H_2SO_4. In the compound (**10**), kinetic study and stereochemistry for oxygen migration and racemization reactions revealed the presence of dithiadication (**11**) as an intermediate though it was not detected. (Scheme 4)



Scheme 4

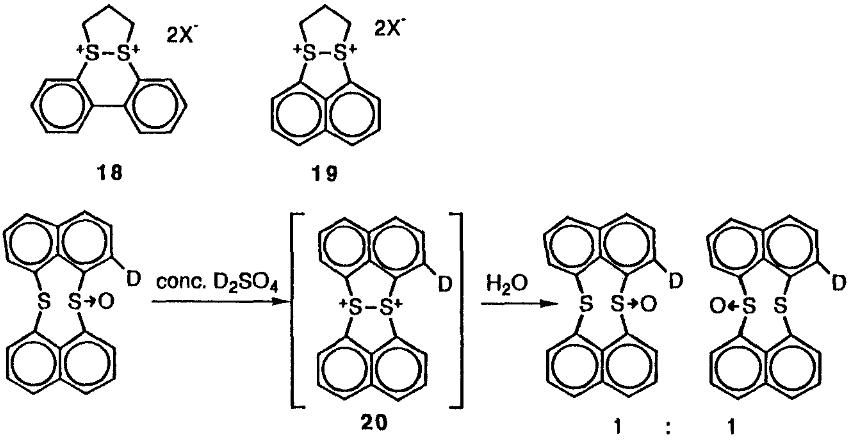
We have intended to detect or to isolate other dithia- and diselenadications of aromatic systems since they should be easily prepared and handled. Therefore, we synthesized the following sterically congested dithiaethers bearing phenyl or naphthyl groups. i. e., dibenzothiocins (**13**) (**15**) (**16**), 1,8-dithiasubstituted naphthalenes (**19**) (**20**) 1,9-dithiasubstituted dibenzothiophenes (**21**). Generation of dications from these compounds was performed using either one of the following procedures ; (i) the sulfides were treated with 2 equiv. of one electron oxidant such as $NOPF_6$. (ii) the sulfides were initially converted to the sulfoxides and then were treated in conc. H_2SO_4. Although the sulfoxide (**12**) was decomposed soon in conc. H_2SO_4, other cyclic sulfoxides (**13**) and (**15**) were stable in conc. H_2SO_4 and the generation of dithiadications (**14**) and (**17**) was confirmed by the observation of the ^1H- and ^{13}C-nmr spectroscopy.

On dissolution of sulfoxides (**15**) and (**16**) in conc. D_2SO_4, typical ^1H- and ^{13}C-nmr spectroscopic behaviors were observed demonstrating that the dithiadications (**14**) and (**17**) are actually generated. After quenching the conc. H_2SO_4 solution of **14** and **17** with H_2O, sulfoxides (**13**) and (**16**) were obtained as sole products and in case of **17** none of **15** was detected at all (Scheme 5)19).



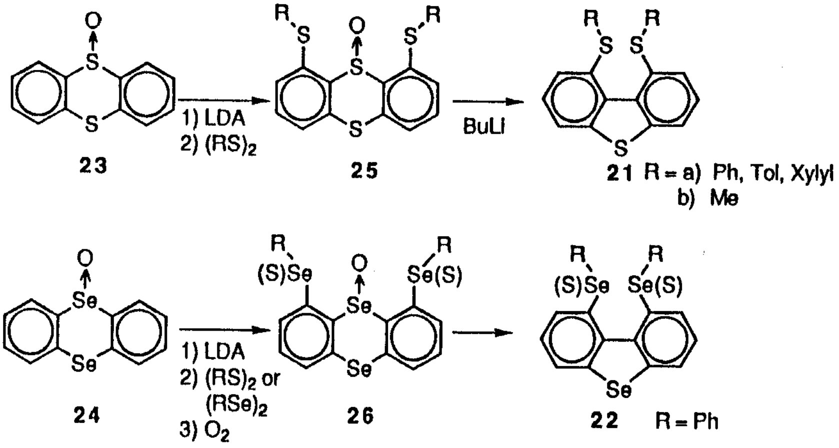
Scheme 5

Besides these dibenzothiocins, o,o'-dithiasubstituted biphenyl20), 1,8-dithiasubstituted naphthalene21) also afforded the corresponding dithiadications (**18**)-(**20**) via transannular interaction on oxidation of the sulfides or on treatment of the sulfoxides with conc. H_2SO_4.(Scheme 6)



Scheme 6

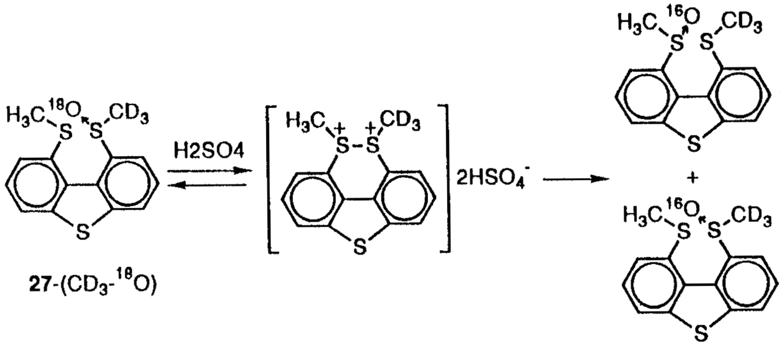
These dithiadications have been isolated and the spectroscopic data have been accumulated. In these dithia derivatives, the sulfur atoms are fixed close together within Van der Waals contact of S-S. As an extension of these studies, we synthesized more sterically congested bissulfides (or bisselenides), 1,9-dithia (or diselena) substituted dibenzothiophenes (**21**) and (**22**) starting from thianthrene monooxide (**23**) (or selenanthrene monooxide (**24**)). The compounds (**23**) and (**24**) which were obtained by oxidation of thianthrene or selenanthrene with mcpba (m-chloroperbenzoic acid) were treated with two eq. of LDA (lithium diisopropyl amide) and then with disulfides (or diselenides) to give the corresponding 4,6-bisdithiasubstituted thianthrenes (**25**) (or selenanthrene (**26**)). Then **25** was treated with BuLi to give 1,9-disubstituted **21** (or **22**) in moderate yields via ring contraction reactions as shown in Scheme 7[22].



Scheme 7

The x-ray crystallographic analyses of **21a** (R=Ph) and its monooxide (**22a**) revealed that the S-S distances in **21a** and **22a** are 3.012, 3.016 Å respectively. These values are shortest ever known as a Van der Waals S-S contact[22]. Furthermore, the two benzene rings in the fused thiophenes are distorted and the dihedral angles composed of the two outer sulfur and carbon atoms in the rings are 20.9°. These short S-S distances and large distorsion of the two phenyl groups suggest that the transannular interaction in **21a** and **22a** should take place readily to make a σ-bond on oxidation. The ^{1}H- and ^{13}C-nmr spectra of the monooxide of **21b** (R=Me) (**27**) were measured in conc. D_2SO_4. In the ^{1}H-nmr, the two methyl peaks for the sulfoxide (**27**) observed at δ 2.79, 2.33 ppm in $CDCl_3$ coalesced to δ

3.04 ppm as a singlet in conc. D_2SO_4. On dissolution in D_2SO_4 the sulfide (**21b**) also appears an identical ^{1}H-nmr spectrum with that of the monooxide (**27**). These results indicate that the dithiadication is actually generated from **27** and **21b** in D_2SO_4. Furthermore, the sulfoxide (**27**) labeled with ^{18}O and deuterium was used in the reaction and the mechanism involving the initial formation of the dication was confirmed[23]. Similarly, treatment of the sulfide (**21a**) with conc. H_2SO_4 also gave the dication salt as a colorless solid which was actually isolated as a crystalline compound. The reactions are illustrated in Scheme 8.



Scheme 8

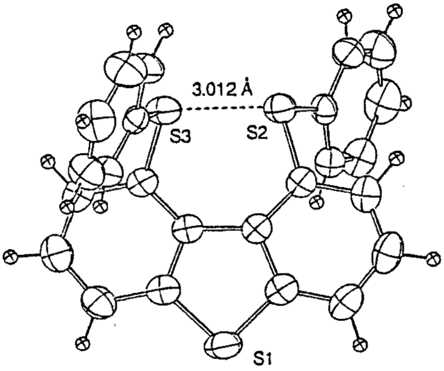
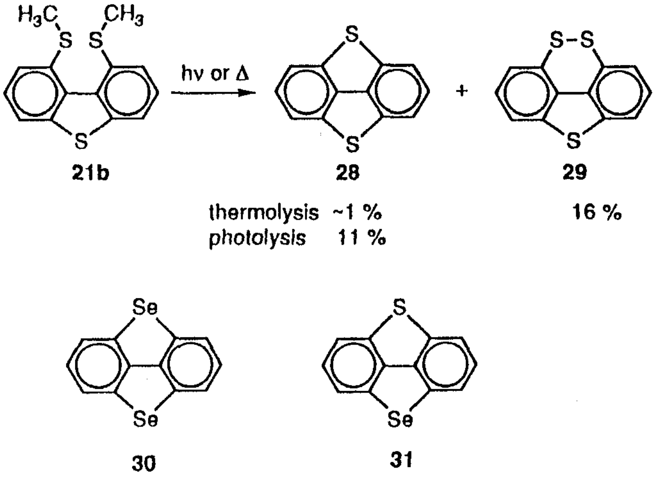


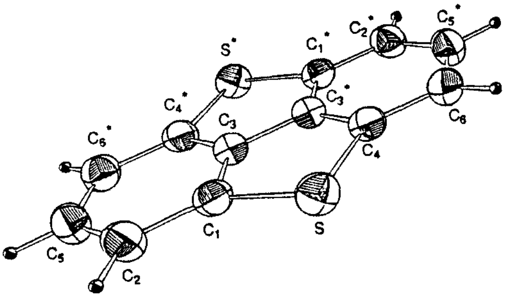
Fig. 4

During these studies, we found that the pyrolysis of **21b** gave unexpectedly 1,5-dithiapentalene; dibenzo[bc, fg][1,4]dithiapentalene (**28**) in a trace amount, while the yield of **28** increased to 11 % together with the disulfide (**29**) in 16 % yield on photolysis. Although the mechanism for formation of **28** by thermolysis or photolysis is ambiguous at this moment, the facile conversion of **21b** into **28** has been estimated involving the transannular S-S interaction to give the dication species from which the demethylation or dethiomethylation takes place. The results are shown in Scheme 9. This is the first example for peparation of phenyl substituted dithiapentalene[24]. Similarly, 1,5-diselenapentalene (**30**) and 1,5-selenathiapentalene (**31**) were prepared by thermolysis and photolysis of the corresponding 1,9-dithia and diselenasubstituted dibenzoselenophenes[25].



Scheme 9

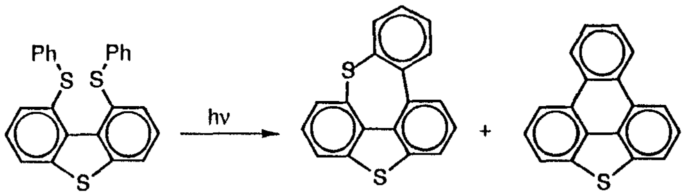
The x-ray crystallographic analysis of pentalenes, **28**, **30** and **31** has been conducted and the typical ORTEP drawing of **28** is shown in Fig. 5.



Bond Length (Å)	
S-C_1	1.791(2)
C_3-C_3*	1.386(3)
Bond Angle (deg.)	
C_1-S-C_4	92.3(1)
C_2-C_1-C_3	116.1(2)
C_1-C_2-C_5	116.8(2)
C_2-C_5-C_6*	125.7(2)
C_1-C_3-C_4*	128.5(2)

Fig. 5 ORTEP of **28**

Inspection of the x-ray analysis reveals that the structure of **28** is a completly planar molecule involving the two phenyl rings and the two sulfur atoms. The C-S bond length (1.791 Å) is rather longer as compared to those of other known pentalenes or benzothiophenes and the central C-C bond is shorter (1.386 Å) and hence should have a double bonded character[26]. The molecules in the crystals stack vertically with a 4.000 Å intermolecular S-S distance. Similarly **30** and **31** were found to be planar molecules as well as **28**. On the other hand, although pyrolysis of **21a** at 450 °C recovered the starting material, photolysis of **21a** afforded not the pentalene (**28**) at all but the dibenzothiepin (**32**) and triphenylenothiophene (**33**) in 12 and 44 % yields respectively as shown in Scheme 10[27].



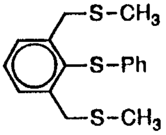
21a **32** 12 % **33** 44 %

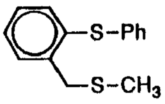
Scheme 10

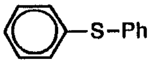
Thus, photolysis and thermolysis of these sterically congested 1,9-disubstituted dibenzothiophenes and selenophenes provide various structurally attractive aromatic compounds which have never been synthesized and these compounds promise to be worthy compounds for synthesis of new functional materials, such as an electroconductive material.

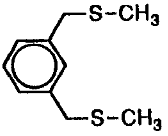
3. Dications of Cyclic Trissulfide and Trisselenide. : New Hypervalent Molecules

2,6-Bismethylthiomethylphenyl phenyl sulfide (**34**) and related sulfides (**35**)-(**37**) were prepared and their oxidation potentials (Ep vs. SCE) were measured by cyclic voltammetry[28]. The Ep values of these compounds are 34, 1.15 V; 35 , 1.34 V; 36, 1.55 V; 37, 1.82 V respectively[28]. The lowest Ep value of **35** suggests that the transannular interaction between the three sulfur atoms may take place for the formation of a new type of $>S^+-\overset{|}{\underset{|}{S}}-S^+<$ bonding. The x-ray crystallographic analysis of monooxide (**39**) indicates that the two sulfur atoms S_1 and S_2 in a crystal are arranged closely within the Van der Waals contact of S-S 3.47Å while the third sulfur atom is far from the central sulfur atom as shown in Fig. 6[29]. The sulfoxide (**39**) or (**40**) was dissolved into conc. D_2SO_4, and the ^1H-nmr spectrum measured in D_2SO_4 indicates the formation of dication (**41**) via transannular interaction between the three sulfur atoms. On treatment of the D_2SO_4 solution of **41** with H_2O, the three products were obtained in 6:1:1 ratio[28] as shown in Scheme 11 .

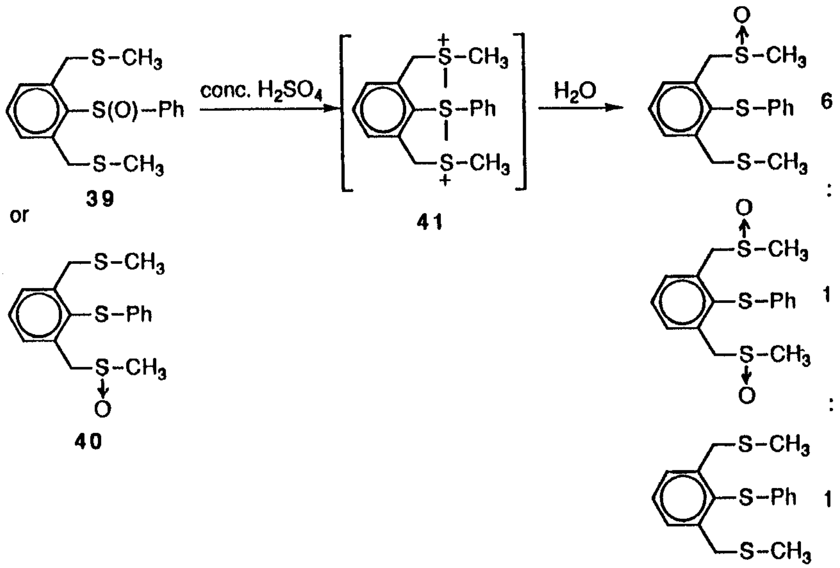








	34	**35**	**36**	**37**
E_p	1.15 V	1.34 V	1.55 V	1.82 V



Scheme 11

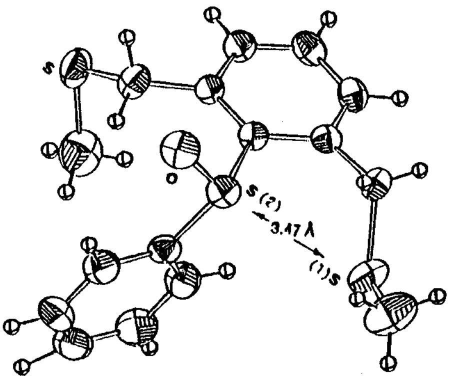


Fig.6 ORTEP of **39**

This result demonstrates that the dication (**41**) is a plaussible intermediate in which the central sulfur atom is a sulfurane structure [10-S-4(C_2S_2)]. In order to obtain further clear evidence for formation of this new type of sulfurane having two apical sulfur ligands, more rigid 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin (**42**) was synthesized$^{30)}$. The x-ray crystallographic analysis of **42** shows that the 8-membered ring is a chair-chair conformation and the distances between the three sulfur atoms are separated beyond the Van der Waals contact of S-S$^{29)}$. This conformation of **42** in solution is rigid and it does not change at the temperature range between 150 °C and -60 °C since the ^{1}H-nmr of the -CH_2- of **42** in $CDCl_3$ appeared at δ 3.89, 4.94 (J = 14 Hz) as AB quartets does not change at all in that temperature range. The ORTEP drawing of **42** is shown in Fig. 7.

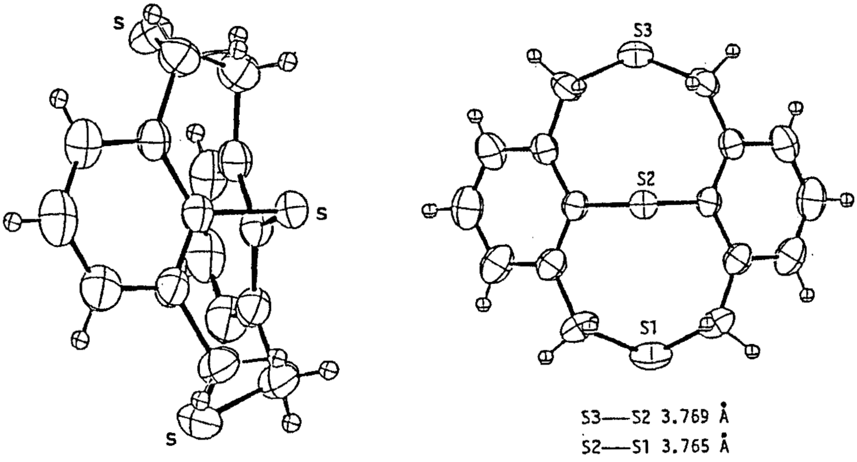
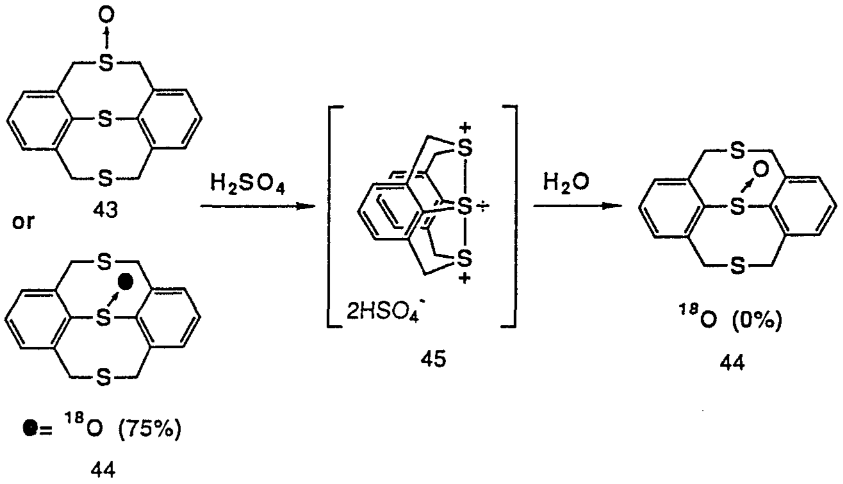


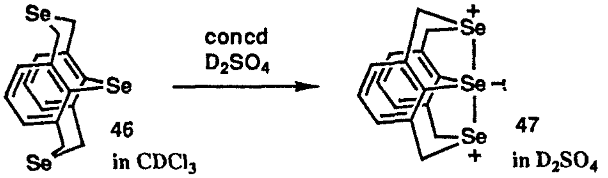
Fig. 7 ORTEP of **42**

The sulfoxides **43** and **44** were prepared and dissolved into conc. D_2SO_4 for ^{1}H- and ^{13}C-nmr measurement$^{30)}$. The two methylene quartets of **43** appeared at δ 3.87, 4.93 (J=14 Hz) and 4.29, 5.54 (J=12 Hz) in $CDCl_3$ change dramatically to the one set of AB quartet at δ 4.11, 4.63 (J= 17 Hz) in conc. D_2SO_4 indicating that the conformational change of the chair-chair to the boat-boat form should take place at once to give a dication species (**45**) by the transannular bond formation with the three sulfur atoms. The ^{13}C-nmr spectrum also supports the formation of **44** since the ^{13}C-nmr spectrum appeared at δ 40.1, 64.9 in $CDCl_3$ changes to at δ 43.6 in D_2SO_4 as a single peak.



Scheme 12

This ^{1}H- and ^{13}C-nmr spectral results reveal the formation of the dication **45** in which the central sulfur atom is a sulfurane structure having the two apical sulfur ligands [10-S-4(C_2S_2)]. Surprisingly, when the conc. H_2SO_4 solution of **45** was dissolved into H_2O and separation of the products, only the sulfoxide **44** was obtained and not the sulfoxide **43**. This result is markedly contrasted to the similar reaction of benzothiocin in conc. H_2SO_4 in where H_2O attacks only at the benzylic sulfur atom to give the corresponding sulfoxide as shown in Scheme 5. The formation of **44** was confirmed by comparing the spectrum with that of the authentically prepared sulfoxide (**44**). As one of the plausible explanation for the change of the attacking site from the alkyl to the aryl sulfur atom by water in the hypervalent bond of **45**, the central sulfur atom in the sulfurane (**45**) is orthogonal to the π bonds of the two phenyl ligands and hence the cationic charge at the central sulfur atom can not be delocalized into the phenyl ring to accumulate at the aryl sulfur atom which is attacked more preferentially by H_2O than the alkyl sulfur atoms. The isolation of the dication (**45**) was performed by treating the sulfoxide (**44**) with $(CF_3SO_2)_2O$ as a crystalline salt which afforded the starting sulfoxide (**44**) with H_2O. Similarly, the trissulfide (**42**) was converted to the dication (**45**) by using two equiv. of $NOPF_6$ as a crystalline compound. Similar transannular interaction of the selenium compound was observed using trisselenium derivative (**46**)$^{31)}$. When **46** was dissolved into conc. H_2SO_4 or on treatment with two equiv. $NOPF_6$, the corresponding diselenadication (**47**) in which the central selenium is a selenurane structure bearing two selenium atoms as apical ligands. The formation of hypervalent $>Se^{+}\text{-}\overset{|}{\underset{|}{Se}}\text{-}Se^{+}<$ bond was confirmed by ^1H-, ^{13}C- and ^{77}Se-nmr. Interestingly, in the ^{77}Se-nmr of **47**, clear satelite peaks were observed indicating the formation of Se-Se bonding of the two main peaks of the ^{77}Se-nmr at δ 830 (-SeAr) and 535 ($-SeCH_2Ph$) ppm with $J_{Se\text{-}Se} = 200$ Hz.



46 in $CDCl_3$

^{77}Se δ 209 (-SeAr),
366 ($-SeCH_2Ar$)

^1H δ 3.88, 5.33
(ABq, J=13Hz:CH_2)
^{13}C δ 32.9 (CH_2)

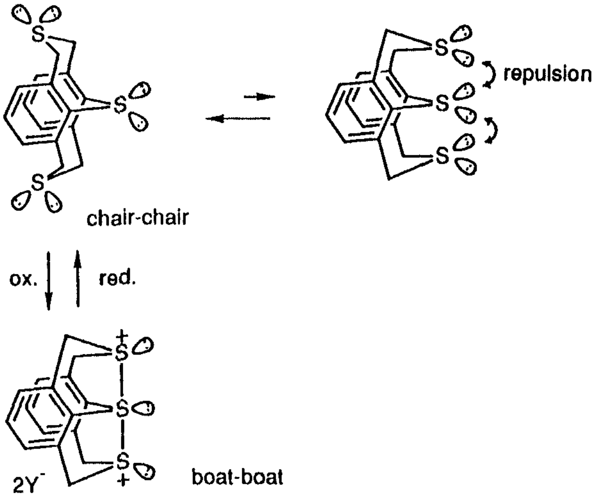
47 in D_2SO_4

^{77}Se δ 817 (-SeAr),
544 ($-SeCH_2Ar$)
$^1J_{Se\text{-}Se} = 210$ Hz

^1H δ 4.07, 4.59
(ABq, J=16Hz:CH_2)
^{13}C δ 41.3 (CH_2)

Scheme 13

A similar Se-Se coupling was also observed when the ^{77}Se-nmr of the selenide (**46**) was measured in D_2SO_4. The selenurane (**47**) can be reduced quantitatively to the corresponding selenide (**46**) using nucleophilic reagents or reducing agents such as PhSH and Sm_2I_2. The sulfide (**42**) and the selenide (**46**) take the most stable chair-chair conformation which does not change conformationally to the boat-chair or the boat-boat form probably because of the large repulsive force works between the lone pair electrons in the three sulfur or selenium atoms. On the other hand, on oxidation of **42** or **46**, the electron-electron repulsive force is diminished to become the boat-boat form which is a more prefered conformation for making hypervalent bonding as shown in Scheme 14.



Scheme 14

CONCLUSION

1,5-Dithia- and diselenacyclooctane were converted to the dithia or diselenadication salts of which structures were determined by x-ray crystallography as first dithia and diselenadications. Several other dithia- and diselenadications were also prepared. Furthermore, trissulfide and trisselenide were pepared and on oxidation of these compounds new type of hyprvalent sulfurane and selenurane were prepared.

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