

超原子価をもつヘテロ原子化合物の設計と合成
- イオウ、セレン、テルルを含む環状化合物の現在と未来 -

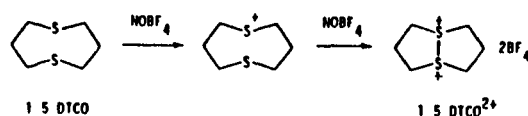
筑波大学化学系

古川尚道

ジチアヂカチオンの分子構造とその化学の展望

INTRODUCTION

The role of dithia dications ($\text{>S}^+-\text{S}^+\text{<}$) as either a reaction intermediate or a new organosulfur species is currently becoming more important in the reactions of mesocyclic or acyclic dithioethers under oxidative conditions, and is described in Musker's recent review [1]. The photoelectron spectra of cyclic dithioethers, such as 1,5 dithiacyclooctane (1,5 DTCO) suggest that the lone electron pairs on the two thioether groups in one molecule interact intramolecularly even in the ground state, namely via a through space transannular interaction. Conformational analysis of 1,5 DTCO indicates that the electron transfer is favored by interaction destabilization due to the lone pair-lone pair interaction in 1,5 DTCO as well as the stabilization in the oxidation products by the bond forming participation between the two thioether groups. Evidence for neighboring group participation on sequential one electron oxidation in 1,5 DTCO has been observed. As an example, Musker and co workers have reported that oxidation of 1,5 DTCO with one equivalent of nitrosonium tetrakisfluoroborate (NO^+BF_4^-) produces a corresponding stable cation radical [2]. Further oxidation of the cation radical gives a dication (Scheme 1).



Scheme 1

Furthermore, electrochemical studies of 1,5 DTCO also support these observations. The peak potential (E_p , vs $\text{Ag}/0.1 \text{ M Ag}^+$) for oxidation of 1,5 DTCO is 0.34 V and the oxidation is reversible [3,4]. This oxidation potential

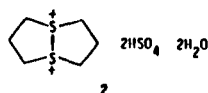
is 0.8 V lower than that for the corresponding monothioether analogue, i.e., heptamethylene sulfide. This large difference of the oxidation potential between the two compounds demonstrates the contribution of the transannular interaction between the two sulfur atoms in 1,5-DTCO. The detailed analysis of the current-voltage curves of 1,5-DTCO reveals the two closely spaced, one-electron transfer steps in which the second electron transfer is about 20 mV easier than the first [4]. This somewhat electronically surprising behavior of 1,5-DTCO can be explained by considering the electronic structure of the cation radical. Asmus and co-workers have suggested that the odd electron should be placed in an antibonding S-S orbital (σ^*) [5]. Removal of this electron for formation of the dication creates an energetically more favorable situation than the cation radical in spite of the increase in bonding between the two sulfur atoms. Although Musker et al., Asmus et al. and others have reported on the structure of dithia dications based on spectroscopic evidences, they have neither described the X-ray crystal structural analysis nor the reactivities on the dithia dications.

This review presents our recent exploration of the almost unknown territory on the detailed structure and the reactions of dithia dication salts.

PREPARATION OF DITHIA DICATION

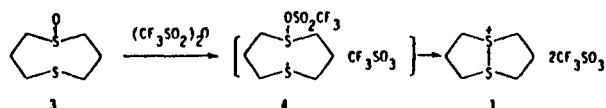
Musker and co-workers [2] reported that the oxidation of 1,5-DTCO with 2 equivalents of NOBF_4 gave the dithia dication salt which is assigned its structure by ^{13}C NMR and elemental analyses (Scheme 1).

We found that the bis(hydrogen sulfate) salt **2** of the dication of 1,5-DTCO was isolated by pouring the H_2SO_4 solution of 1,5-DTCO 1-oxide (**3**) (vide infra) into ice-cooled anhydrous diethyl ether, whereupon colorless crystals of **2** precipitated [6]. Although the crystalline salt **2** is very hygroscopic, becoming liquid on exposure to air, it was identified as the structure **2** by examining the elemental analysis (Scheme 2).



Scheme 2

However, the reaction of sulfoxide **3** with trifluoromethanesulfonic anhydride $(\text{CF}_3\text{SO}_2)_2\text{O}$ gave a remarkably stable dithia dication salt, 1,5-dithionabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**1**) [7] (Scheme 3).



Scheme 3

This reaction proceeds via the initial formation of the trifluoromethanesulfonyloxy sulfonium salt (4) which is subsequently converted into the disulfide dication 1 by an intramolecular nucleophilic displacement of the trifluoromethanesulfonate ion (CF_3SO_3^-) by the second sulfur atom as shown in Scheme 3. Then, the crystal structural analysis of 1 can be performed by X-ray crystallography (vide infra).

STRUCTURE OF DITHIA DICATION

The crystal structure of 1,5-dithionibicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (1) has been determined by the X-ray method, thus elucidating an actual structure of the dithia dication [8]. According to the X-ray analysis, there are two independent dications A and B, in the crystals, each of which has an exact two fold axis coincident with the crystal symmetry. The crystal structures of the dication 1 are shown in Figs. 1 and 2.

The S(1)-S(2) lengths are 2.126 Å for A and 2.122 Å for B, which are only slightly longer than the normal S-S single bond (2.08 Å) in disulfides. Some sulfur-bonded 1-thionia-5-thiacyclooctane salts and 1,5-DTCO derivatives have been found to have relatively short transannular S...S contact in the range of 3.121-3.271 Å [9-12] which is apparently within the van der Waals' contact (Table 1). The S-C lengths are 1.842 and 1.828 Å for A and 1.829 and 1.830 Å for B. These values are also slightly longer than the normal S-C single bond length, while the C-C lengths (1.509 Å for A and 1.516 and 1.527 Å for B) are slightly shorter than the normal $\text{Csp}^3\text{-Csp}^3$ bond. The bond angles of C-S-C are 104.1° and 104.6° for A and B, respectively and those of S-S-C are 92.7-95.9°. The conformation of the eight-membered ring is a distorted chair-chair form. It is interesting to note that very strong interactions were observed between the S^+ of the dication and the oxygen atoms of the counteranions tri-

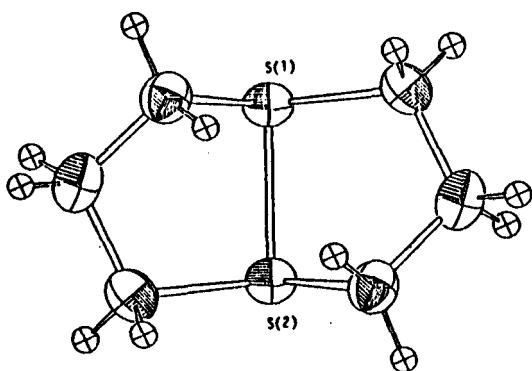


Fig. 1. The crystal structure of dication A.

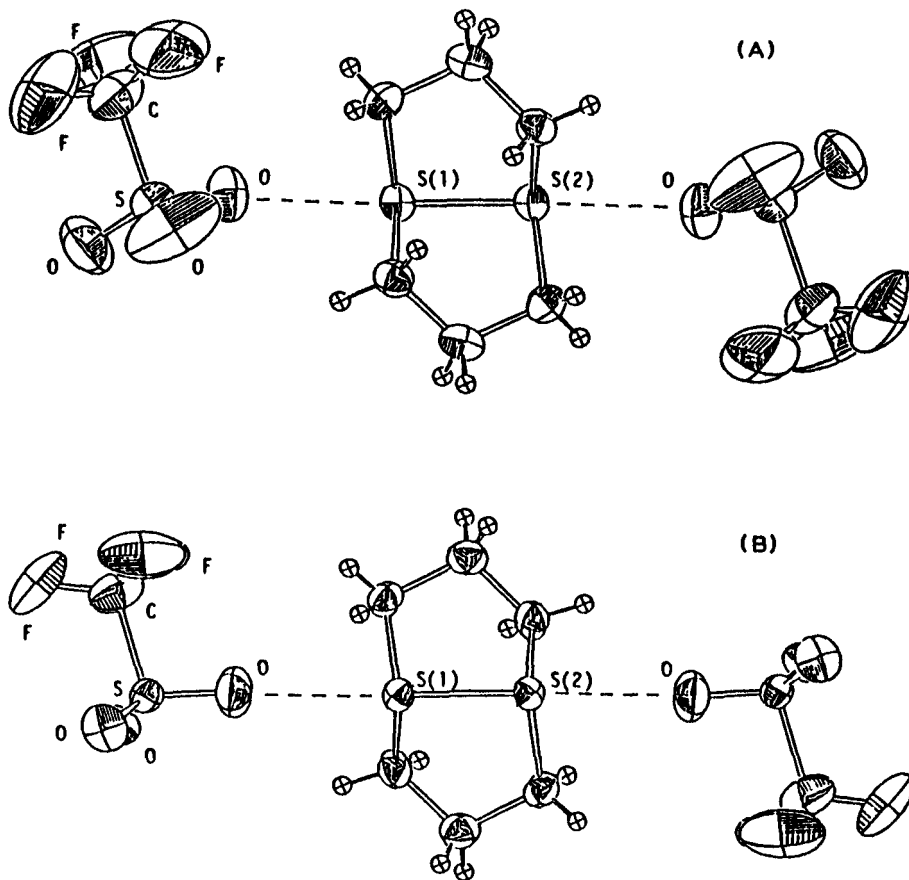


Fig 2 Collinear O S-S O interactions between cations and anions (A) dication A (B) dication B

plate The distance of $S^+ \cdots O$ is 2.682 and 2.766 Å for A and B, respectively which are remarkably shorter than the van der Waals' contact of 3.35 Å. The angles of $S-S \cdots O$ are 176.3 and 166.8°, for A and B, respectively. Nearly collinear interactions of $O \cdots S-S \cdots O$, especially in A, are formed with the central two fold symmetry as shown in Fig 2. This strong interaction between the cation and anion are also an attribute to the stabilization of the crystals.

The optimized transannular sulfur-sulfur distance (S-S) is 3.307 Å for 1,5 DFCO and 2.140 Å for 1,5 DTCCO²⁺ by ab initio molecular orbital calculation based on the STO-3G basis set [13]. The S^+-S^+ distance by ab initio calculation is consistent with that of the X-ray analysis.

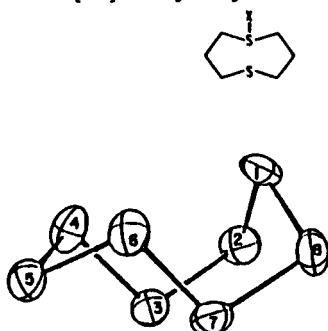
Gillespie and co workers [14] reported the crystal structure of elemental sulfur dication, S_8^{2+} which was obtained by oxidation of S_8 with AsF_5 in HF (Fig 3). They showed that the structure of S_8^{2+} consists of a cis fused bicyclic

TABLE 1

Comparison of transannular S-S interaction in 1,5 dithiacyclooctane derivatives

X	S-S (Å)	X-S (Å)	Ring conformation
NTs ^a	3.143	1.778	boat-chair
CH ₂ COCH ₃ ^b	3.121	1.789	boat-chair
CH ₃	3.259	1.740	chair-chair
O ^d	3.175	1.769	boat-chair
O	3.135	1.754	boat-chair

^a 1-Tosylimino-1,5-dithiacyclooctane [9] ^b 1-Acetyl-1-thio-5-thiacyclooctane perchlorate [10] ^c 1-Methyl-5-thia-1-thionacyclooctane iodide [11] ^d 3-Methoxy-1,5-dithiacyclooctane-1-oxide [12] ^e 3-Hydroxy-1,5-dithiacyclooctane-1-oxide [12]

Fig. 3 The configuration of the S₈²⁺ ring in S₈(AsF₆)₂ [14]

clo[3.3.0] ring system. The cross ring S(3)-S(7) distance is only 2.86 Å compared with 4.68 Å in the S₈ ring.

Since solutions containing the S₈²⁺ ion as well as crystals obtained from such solutions are always blue and exhibit a broad absorption band at 590 nm, it has first been concluded that S₈²⁺ itself is responsible for the blue color [15-19]. However, Giggensbach presented evidence that the blue species is a radical anion of type S_n^{•+} which can be detected by ESR spectroscopy and is believed to be S₄^{•+} [20]. Later it was shown that S₈^{•+} is responsible for the blue color and part of the ESR spectrum [21], indicating that an equilibrium exists between S₈²⁺ and S₈^{•+}. In fact, even a solid S₈(AsF₆)₂ at higher temperature exhibits a small paramagnetism [15], at either room temperature or 77 K the ESR lines of S₈^{•+} can be detected in solid S₈(AsF₆)₂ [22].

REACTIONS VIA DITHIA DICATION

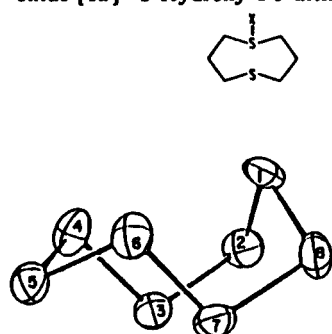
Musker and Doi [23] found that the reduction of 1,5-DTCO-1-oxide (3) with aqueous HI proceeds 10⁶ times more rapidly than simple sulfoxides and suggested the intermediary formation of dithia dication (Scheme 4).

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H_2SO_4 solution of **3** was followed by the ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of the D_2SO_4 solution of **3** showed the signals at δ 4.32–3.40 and 3.32–2.10 in a 2:1 ratio (Fig. 4).

Musker et al. [2] have reported that the dication (BF_4) salt has broad ^1H NMR signals at δ 4–2 in CD_3CN , while their ^{13}C NMR spectra agreed roughly with ours. The ESR spectrum of the H_2SO_4 solution of **3** showed signals due to the cation radical of 1,5-DTCO and was consistent with that reported by Musker [1]. On the other hand, the UV spectra of H_2SO_4 solution of **3** showed absorption maxima of the dication at 230 nm (233 and 212 [2]) but no absorption due to a cation radical of 1,5-DTCO at 420 nm. We have assumed that the intermediate in this reaction is mainly the dithia dication in equilibrium with a low concentration of the cation radical of 1,5-DTCO. Glass and Wilson [4] have suggested from electrochemical studies that it is easier to remove an electron from 1,5-DTCO cation radical than from 1,5-DTCO itself, hence the cation radical of 1,5-DTCO should be oxidized easily to the dication. Similarly, 1,5-DTCO *N*-tosylsulfonamide (**9**) was treated with concentrated H_2SO_4 to afford the dithia dication, although in general *N*-tosylsulfonamides undergo cleav-

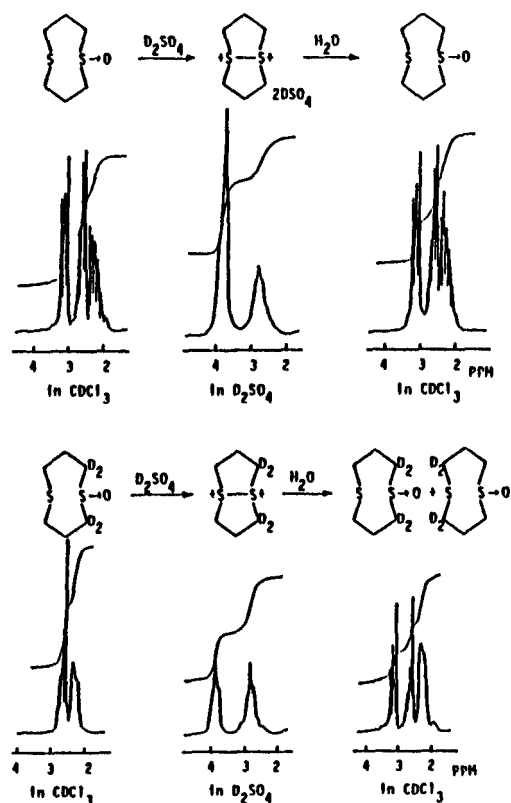
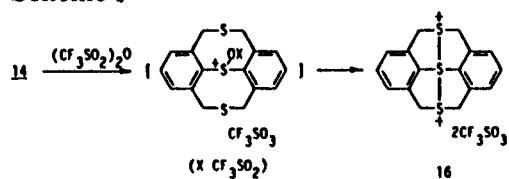


Fig. 4 ^1H NMR spectra of the D_2SO_4 solution of **3** and **3a**

A new type of oxygen transfer reaction via the dication of **12** was found by the hydrolysis of the H_2SO_4 solutions of **12**–**14**. These results reveal that the oxygen migration from the benzylic sulfur to the aryl one in **13** in concentrated H_2SO_4 proceeds via the initial formation of dication **15** on which the H_2O molecule attacks the central aryl sulfur atom. It is a previously unknown type of reaction, since in the previous experiments involving the acid catalyzed oxygen transfer from sulfoxides to sulfides, the migration takes place solely from the aryl sulfur atom to the alkyl sulfur atom [26–29]. This unusual behavior of the dication **15** as compared with the other acyclic system or even dibenzodithiocin [26,28,29] can be explained in terms of the rigidity of the dication **15**. The S–S–S bond in dication **15** forms a sulfurane structure under the present reaction conditions to give a hypervalent bond. This hypervalent bond as shown in Scheme 8 is orthogonal to the π orbitals of the two phenyl rings in **15**. Therefore, the positive charge on the central sulfur atom cannot be stabilized by resonance with the two phenyl rings. Thus, the positive charge should be concentrated preferentially on the central aryl sulfur atom rather than the benzylic sulfur atoms.

The reaction of the sulfoxide **14** with trifluoromethanesulfonic anhydride gave the dicationic salt **16** [m.p. 134–135°C (decomp), ^1H NMR (CD_3CN) δ 4.65, 5.20 (ABq, $J=17$ Hz, 8H), 7.39–7.98 (m, 6H), ^{13}C NMR (CD_3CN) δ 42.5, 131.4, 137.2, 139.8, field desorption (FD) mass spectrum, m/z 601 (MH^+), 451 (M OTf^+), 302 (M 2OTf^+), 151 (doubly charged cation)] as shown in Scheme 9.



Scheme 9

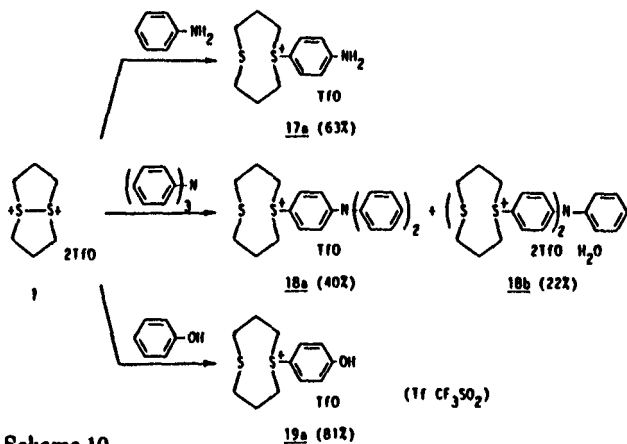
This is the first example for the dication with hypervalent bond of the central sulfur atom.

REACTIVITY OF DITHIA DICATION

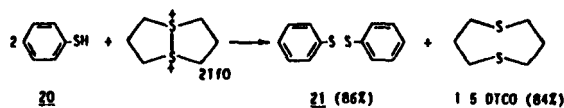
The reactivities of the dithia dication with the adjacent two positively charged sulfur atoms are of considerable interest. However, the reactions using the dithia dication have not been well explored because of the difficulties in obtaining stable compounds.

Our investigations indicate that the dithia dication **1** acts both as an electrophile and an oxidant towards aromatics [7,30]. The reaction of dithia dication **1** with aniline (**17**), triphenylamine (**18**), and phenol (**19**) gave the corresponding para substituted sulfonium salts **17a**, **18a**, **18b**, and **19a**, re

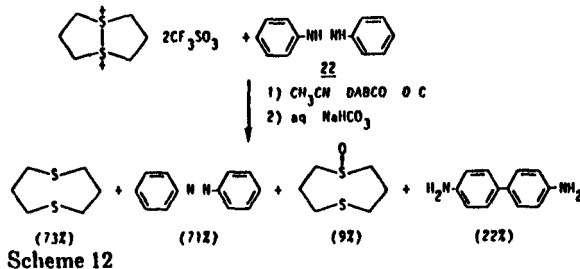
spectively (Scheme 10) In contrast to 17-19, treatment of thiophenol (20)



with dication 1 afforded diphenyl disulfide (21) as the oxidation product and 1,5 DTCO as the reduction product (Scheme 11) Several thiols can be oxidized to the disulfides by dication 1



The redox reaction was found in the reaction of 1,2 diphenylhydrazine (22) with dication 1 [7] (Scheme 12) These reaction modes depend on the oxidation potential of the aromatics



In summary, we succeeded in preparation of the dithia dication, 1,5 dithionabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (1) as a remarkably stable crystalline salt by the reaction of 1,5 dithiacyclooctane 1 oxide with trifluoromethanesulfonic anhydride. The crystal structure of dithia dication 1 was first determined by X ray crystallographic analysis. There are two independent dications, A and B, in the crystals, each of which has an exact twofold axis coincident with the crystal symmetry. The S⁺-S⁺ distances of 1 are 2.126

and 2.122 Å for the dications A and B, respectively. The conformation of the eight-membered ring is a distorted chair-chair form. Interestingly, very strong interactions were observed between the S⁺ of the dication and the oxygen atoms of the triflate anions. This new sulfur species is of particular interest and would become attractive if one could prepare the analogous derivatives bearing multithia centers. Until now there have been no clear-cut examples of the transannular interaction between more than three sulfur atoms in multithia compounds. However, more recently, the transannular bond formation between the three sulfur atoms of trithia compound, 1,11-(methanothiome-thano)-5H,7H-dibenzo[b,g][1,5]dithiocin (**12**) was characterized by high-field ¹H and ¹³C NMR spectroscopy and the corresponding dithia dication salt with hypervalent bond of the central sulfur atom was isolated. The investigations on the crystal structure of new type of dithia dication in trithia compound **12** and the reactivity of dithia dication **1** are underway in this laboratory.

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