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Generation and Structure Determination of 5,6-Bis(methylthio)-4,7-diethylbenzo[1,2,3]trithiole Dication MBT(2+)

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ABSTRACT: *5,6-Bis(methylthio)-4,7-diethylbenzo-[1,2,3]trithiole [MBT] was oxidized with two equivalents of* $SbCl_5$ *to produce a dication,* $MBT(2+) \cdot 2SbCl_6^-$*, as a stable, dark-brown solid. MBT(2+) was unexpectedly silent for* ^1H*-NMR in* CD_3CN*, whereas it was active for ESR, suggesting that MBT(2+) is a triplet-state dication MBT(2+)-T. Meanwhile, treatment of 5-methylsulfinyl-6-methylthio-4,7-diethylbenzo[1,2,3]-trithiole [MBTMO] with* D_2SO_4 *produced MBT(2+), whose* ^1H*-NMR gave no signals, whereas the solution is active for ESR. These results imply that MBT(2+) prepared from MBTMO is a triplet-state dication, and a singlet-state dication, MBT(2+)-S, initially generated by acidification of MBTMO, isomerized to the triplet-state dication, MBT(2+)-T. Since MBT(2+)-T is active for ESR at room temperature, two molecules of MBT(2+)-T should form a spin pair in the solution with a sufficient distance between the two radical centers. The structures of MBT(2+)-S and MBT(2+)-T were optimized with the DFT method at the B3LYP6-31G** level. The total energy difference between them was calculated to be 7.90 kcal/mol; MBT(2+)-T was shown to be more stable than MBT(2+)-S. A treatment of MBTMO with* $SbCl_5$ *gave a 1:1 complex. The structure of the complex was determined with X-ray crystallography, which showed that the complex is the corresponding sulfonium salt,* $MBTMO \cdot SbCl_5$*.*
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INTRODUCTION

It is well known that a dithia dication (**I**) can be prepared either by stepwise single-electron oxidation of sulfide (**II**) or by acidification of sulfoxide (**III**), and that the species is stabilized by intramolecular through-space interaction between the two sulfur atoms (Scheme 1) [1–5]. It was also reported that the dithia dication (**I**) gave the corresponding monoxide (**III**) quantitatively upon treatment with aqueous NaOH solution. When the sulfinyl and sulfenyl groups are separated from each other in a molecule, the tetrathia tetracation (**IV**), stabilized by intermolecular through-space interaction, was generated and characterized in detail [6]. In

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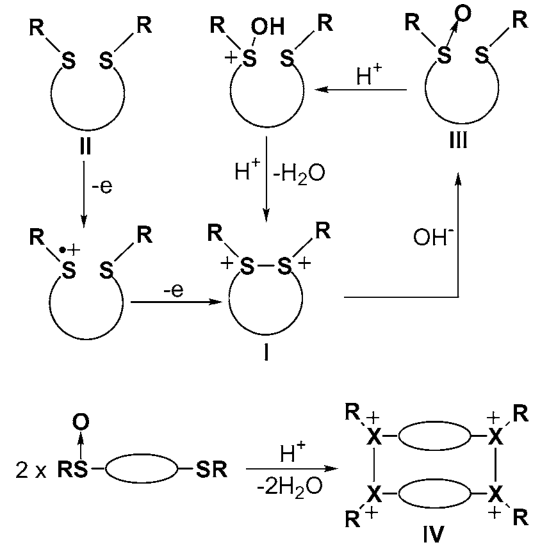
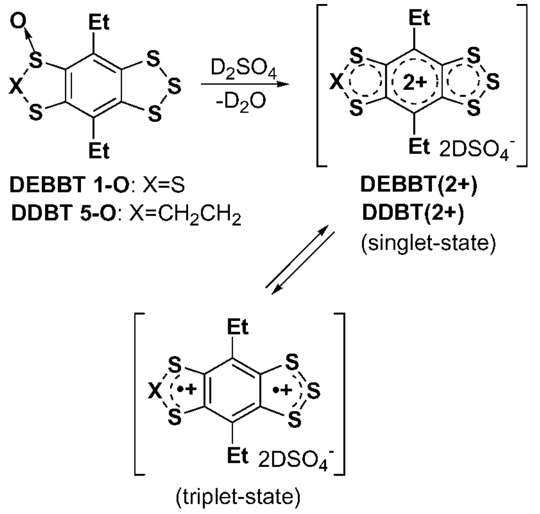
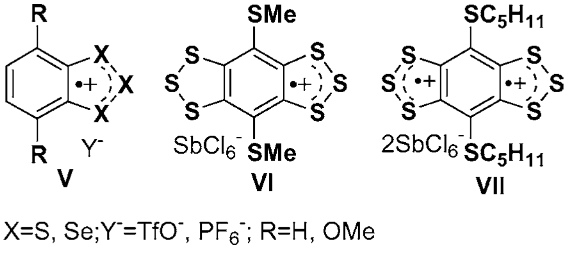


SCHEME 1



SCHEME 2

both cases, ^{1}H-NMR spectroscopy is useful for determining their structures. In contrast, radical cations and dications are prepared from benzoannelated five-membered heterocycles [7–11]. As shown in Fig. 1, a positive charge is generated on benzo[1,2,3]-trichalcogenoles (**V**) by oxidation, and benzo[1,2-*d*:4,5-*d*′]bis[1,2,3]trithioles can accept one or two positive charges on the trithiole rings (**VI** and **VII**). From our extensive studies on several cyclic oligosulfides [12–14], we recently reported that the dications can be prepared by the acidification of 4,8-diethylbenzo[1,2-*d*;4,5-*d*′]bis[1,2,3]trithiole 1-oxide [DEBBT 1-O] and 4,9-diethyl[1,4]dihydrodithiino-[5,6-*f*]benzo[1,2,3]trithiole 5-oxide [DDBT 5-O] with D_2SO_4 (Scheme 2) [15]. We also explained that the dications, which were detected by NMR spectroscopy, exist in both a singlet state and a triplet state in D_2SO_4 solution. To examine the interaction of two positive charges, initially generated on two methylthio groups, with a trithiole ring, 5,6-bis(methylthio)-4,7-diethylbenzo[1,2,3]trithiole [MBT] was oxidized with two equivalents of SbCl$_5$, and 5-methylsulfinyl-6-methylthio-4,7-diethylbenzo[1,2,3]trithiole [MBTMO] was treated with D_2SO_4 (Fig. 2). This paper reports (i) the generation, isolation, and characterization of the 5,6-bis(methylthio)-4,7-diethylbenzo[1,2,3]trithiole dication MBT(2+) derived from MBT and MBTMO and (ii) the calculations of the structures of the singlet-state and triplet-state dications, MBT(2+)-*S* and MBT(2+)-*T*, using the DFT (density functional theory) method at the B3LYP6-31G** level [16]. In addition, the preparation and structure determination of MBTMO · SbCl$_5$, an analog of a sulfonium salt, MBTOH, which is an intermediate to generate the dication from MBTMO by treatment with H_2SO_4, are also reported.



X=S, Se;Y$^-$=TfO$^-$, PF$_6^-$; R=H, OMe

FIGURE 1 The radical cations and dications derived from benzotrichalcogenoles.

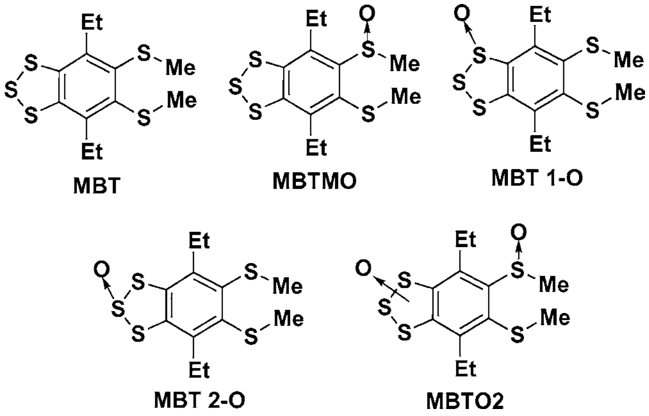


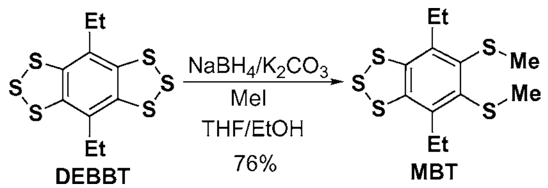
FIGURE 2

RESULTS AND DISCUSSION

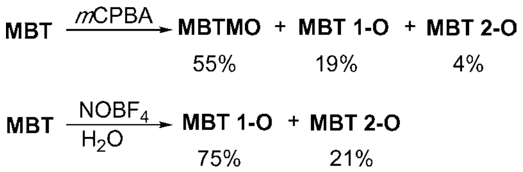
Generation and Isolation of Dication

MBT was prepared in 76% yield by treatment of DEBBT with $NaBH_4$ and then with methyl iodide (Scheme 3). MBT was subsequently oxidized by *m*CPBA in dichloromethane to produce MBTMO in 55% yield together with 5,6-bis(methylthio)-4,7-diethylbenzo[1,2,3]trithiole 1-oxide MBT 1-O (19%) and 2-oxide MBT 2-O (4%) (Fig. 2 and Scheme 4). Cyclic voltammetry of MBT showed two oxidation potentials; one is reversible and the other is irreversible ($E_{1/2} = 0.78$ V and $E\mathrm{p} = 1.14$ V vs. $Ag/AgNO_3$). It is presumed that if MBT is oxidized with two equivalents of a single-electron oxidizing agent, the reaction produces MBT(2+), whose generation can be observed by ^{1}H-NMR spectroscopy. As a preliminary experiment, MBT was treated with two equivalents of $NOBF_4$ at −30°C under an argon atmosphere for 2 h. The solution was then quenched with wet diethyl ether to produce MBT 1-O and MBT 2-O in 75% and 21% yields, respectively, clearly demonstrating that MBT(2+) is generated in solution. Interestingly, no MBTMO was detected during this oxidation reaction, which is different from the result obtained by the oxidation of MBT with *m*CPBA. The results suggest that the nucleophilicity of the methylthio group is higher than that of the trithiole ring, whereas the trithiole ring is more easily oxidized by the single-electron oxidizing reagent than the methylthio group.

Isolation of a stable form of MBT(2+) is an important subject. The MBT was oxidized with two equivalents of $NOBF_4$ or $NOPF_6$ in dichloromethane/acetonitrile at −30°C under an argon atmosphere for 1 h. While the color of the solution immediately became dark blue in both cases, no precipitation of the dication took place. The dication seems to be soluble in acetonitrile. In order to facilitate precipitation of the product, MBT was then treated with two equivalents of $SbCl_5$ in dichloromethane, instead of dichloromethane/acetonitrile, for 1 h (Scheme 5) [17]. A dark-brown precipitate produced by the oxidation was filtered under an argon atmosphere and washed with dichloromethane. The solid was dried under vacuum for 12 h to yield the desired product in 93% yield. The structure of the product was determined to be $\mathrm{MBT(2+)\cdot 2SbCl_6^-}$ by elemental analysis. To obtain further information about the product, ^{1}H-NMR was then measured in acetonitrile-d_3 but no signal was observed. In contrast, the ESR spectrum of MBT(2+) in acetonitrile showed one broad peak without a hyperfine splitting of $g = 2.007$. These results indicate that the compound prepared by this procedure is not a singlet-state dication MBT(2+)-*S*·$\mathrm{2SbCl_6^-}$ but a triplet-state dication MBT(2+)-*T*·$\mathrm{2SbCl_6^-}$. If MBT(2+) is a triplet-state dication as predicted, two molecules of MBT(2+)-*T* should further form a spin pair in the solution, and the ESR signal should be attributable to the partially associated structure 2MBT(2+)-*T* and not to free MBT(2+)-*T*. Interestingly, the *g* value of MBT(2+)-*T* is similar to that of the radical cation derived from 1,2,4,5-tetrakis(methylthio)benzene [7c]. Therefore, two molecules of MBT(2+)-*T* are expected to associate at the trithiole ring.



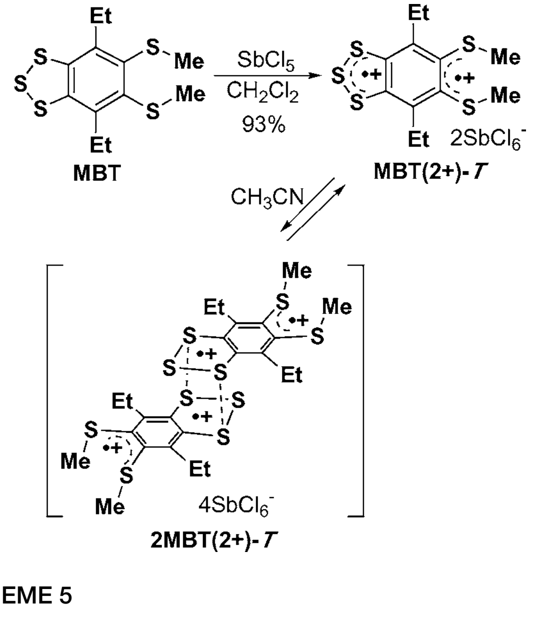
SCHEME 3



SCHEME 4

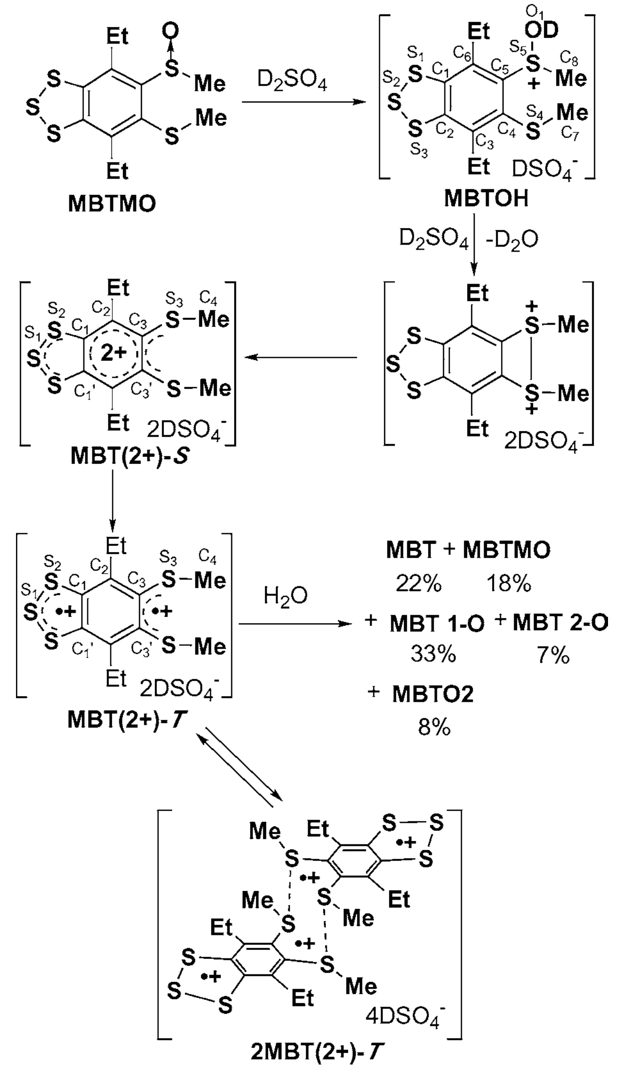
Generation of Dication from MBTMO

To generate the singlet-state dication MBT(2+)-*S* selectively, MBTMO was dissolved in D_2SO_4 at room



SCHEME 5

temperature (Scheme 6). It was expected that the dication generated from MBTMO via MBTOH is the singlet state and active for NMR spectroscopy. The solution was examined with ^{1}H-NMR. However, no signal was observed in the spectrum, which is different from the previous results obtained by treatment of DDBT 5-O or DEBBT 1-O with D_2SO_4 [15]. ESR of MBT(2+) generated from MBTMO in H_2SO_4 was then measured at room temperature. In the spectrum, one strong signal was recorded at $g = 2.016$ without hyperfine splitting. The value is similar to those of the paired triplet-state dications derived from DDBT 5-O or DEBBT 1-O by treatment with H_2SO_4. Based on these results, it was predicted that the initially generated singlet-state dication MBT(2+)-*S* electronically isomerizes into the triplet-state dication MBT(2+)-*T* in solution, and two molecules of MBT(2+)-*T* form a spin pair.



SCHEME 6

Similar to the result shown in Scheme 1, if the dication is generated in H_2SO_4, corresponding sulfoxide is obtained after the solution is treated with ice water. Therefore, MBTMO was dissolved in H_2SO_4, and the solution was quenched with ice water. By this reaction, MBT 1-O and MBT 2-O were obtained in 33% and 7% yields, respectively, together with MBTMO in 18% yield (Scheme 6). The result suggests that although the two positive charges initially generated on the methylthio groups interact with the trithiole ring through the benzene ring, the intramolecular charge transfer of MBT(2+) is less favorable than that of DDBT(2+) because of the free rotation of the two methylthio groups in MBT(2+). As a result, the hydrolysis of MBT(2+) might give MBT 1-O and MBT 2-O in low yields although that of DDBT(2+) produced 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzo[1,2,3]trithiole 1-oxide and 2-oxie in moderate yields [15a]. In contrast, since the reduced product MBT (22%) and further oxidized products MBTO2 (a mixture of bissulfoxides: 8%) were produced by this reaction, it is clear that a disproportionation of MBT(2+) proceeded by quenching with water.

It was reported that the Pummerer rearrangement proceeded in the molecules with both methylsulfinyl and methylsulfenyl groups by treatment with $(CF_3CO)_2O$, Tf_2O, and H_2SO_4 [6,18]. To examine the Pummerer reaction of the dication, MBTMO was treated with Tf_2O in dichloromethane/acetonitrile at −30°C under an argon atmosphere (Scheme 7). The resulting dark-blue solution was then quenched with water at room temperature to produce MBT (16%), MBTMO (32%), MBT 1-O (17%), and MBT 2-O (7%) together with a mixture of MBTO2 (8%). However, in this case, no rearranged product was observed. These results demonstrate that the positive charge, first generated on the methylsulfinyl group by treatment of MBTMO with Tf_2O, delocalizes to the trithiole ring via elimination of TfO^- before the Pummerer reaction proceeds.

Theoretical Study of MBT(2+)

To examine the structure and chemical properties of MBT(2+), we initially performed molecular

$$\text{MBTMO} \xrightarrow[H_2O]{Tf_2O} \underset{(16\%)}{\text{MBT}} + \underset{(32\%)}{\text{MBTMO}} + \underset{(17\%)}{\text{MBT 1-O}} + \underset{(7\%)}{\text{MBT 2-O}} + \underset{(8\%)}{\text{MBTO2}}$$

SCHEME 7

orbital (MO) calculations for the singlet-state dication MBTH(2+)-*S* and the triplet-state dication MBTH(2+)-*T* using the DFT method at the B3LYP/6-31G** level with no symmetry constraints; the simplified dications MBTH(2+)-*S* and MBTH(2+)-*T* have two hydrogen atoms instead of two ethyl groups [19]. Vibrational analyses showed that the calculated structures are the energy minimum. The optimized structure of MBTH(2+)-*S* is completely planar; the carbon atoms of two methylthio groups are also on the plane and directly outside (C2v) (Fig 3). While the trithiole ring of MBTH(2+)-*T* is completely planar, the C—S bonds of the two methylthio groups are roughly perpendicular to the molecular plane. For this reason, two forms of the triplet-state dication, *syn*- and *anti*-MBTH(2+)-*T*, exist (Cs for the syn form and C2 for the anti form; they are not shown). The structure of *anti*-MBTH(2+)-*T* is slightly more stable than that of *syn*-MBTH(2+)-*T*. Based on these results, the differences in the total energy between the singlet-state and triplet-state dications (ΔE) were calculated with respect to the optimized structures: $\Delta E_{[anti\text{-MBTH(2+)-}T\,-\,\text{MBTH(2+)-}S]} =$ 10.5 kcal/mol, suggesting that the singlet-state dication MBTH(2+)-*S* is more stable than the triplet-state dication MBTH(2+)-*T*. However, the calculation does not fit the experimental results described above.

It was predicted that the carbon atoms of two methylthio groups could not occupy the planar positions in MBT(2+)-*S* because of steric repulsion between the methylthio and ethyl groups. The structures of MBT(2+)-*S* and MBT(2+)-*T* were then optimized by the same method, respectively. The final vibrational analyses showed that the structures are the energy minimum (Fig. 3). Whereas the trithiole ring of MBT(2+)-*T* is completely planar, the C—S bonds of the two methylthio groups are roughly perpendicular to the plane, and the two ethyl groups are oriented in directions opposite that of the neighboring methylthio groups. As a result, two forms of triplet-state dications, *syn*- and *anti*-MBT(2+)-*T*, are obtained. In contrast, the optimized structure of MBT(2+)-*S* is not planar, and the trithiole and benzene rings are slightly twisted from the steric repulsion between the methylthio and ethyl groups. The partial bond distances (Å) of *anti*-MBT(2+)-*T* and MBT(2+)-*S* are listed in Table 1 (see also Scheme 6). To estimate the stability of the dications, the differences in the total energy between the singlet-state and the triplet-state dications (ΔE) were calculated with respect to the optimized structures: $\Delta E_{[syni\text{-MBT(2+)-}T\,-\,anti\text{-MBT(2+)-}T]} = 2.05$ kcal/mol and $\Delta E_{[\text{MBT(2+)-}S\,-\,anti\text{-MBT(2+)-}T]} = 7.90$ kcal/mol. These results reveal that the triplet-state dication *anti*-MBT(2+)-*T* is more stable than *syn*-MBT(2+)-*T* and the singlet-state dication MBT(2+)-*S*.

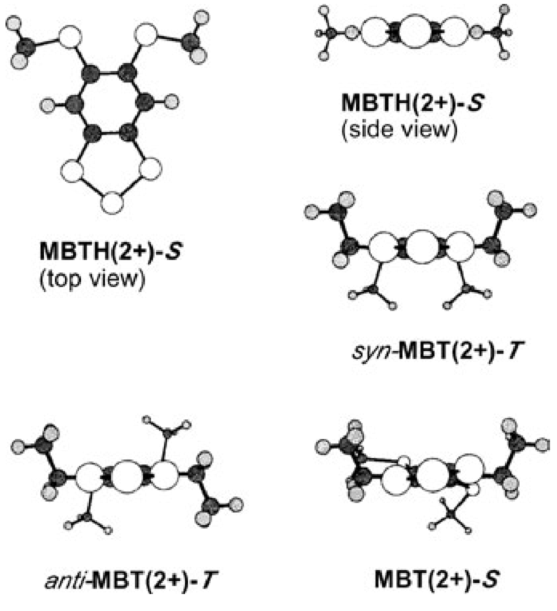
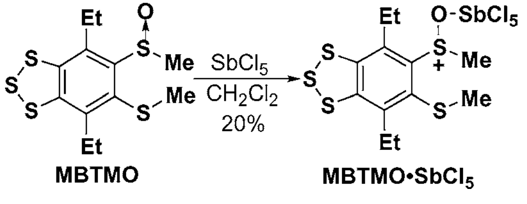


FIGURE 3 Optimized structure of dications.

Preparation and Structure of MBTMO · SbCl$_5$

It has been reported that dimethyl sulfoxide gives a 1:1 complex $Me_2SO \cdot SbCl_5$ by treatment with $SbCl_5$ [20]. To determine whether the complex MBTMO·$SbCl_5$ is a sulfonium salt, we treated MBTMO with $SbCl_5$ at room temperature under an argon atmosphere, and the reaction gave MBTMO·$SbCl_5$ in 20% yield (Scheme 8). The structure of MBTMO · $SbCl_5$ was determined with ^{1}H-NMR, IR, elemental analysis, and ultimately, X-ray crystallographic analysis. The result shows that MBTMO · $SbCl_5$ crystallizes in monoclinic form and the space group is $P2_1/c$ (#14). The unit cell consists of four molecules of the complex. The ORTEP drawing shows that (i) the structure of the Sb atom is a tetragonal bipyramid and (ii) the conformation of the trithiole ring is an envelope structure (Fig. 4). The bond lengths, bond angles, and



SCHEME 8

TABLE 1 Optimized Bond Distances (Å) of MBT(2+)-*S* and MBT(2+)-*T*

	S_1–S_2	S_2–C_1	C_1–C'_1	C_1–C_2	C_2–C_3	C_3–C'_3	S_3–C'_3	S_3–C_4
MBT(2+)-*S*	2.071	1.732	1.457	1.397	1.418	1.470	1.738	1.836
MBT(2+)-*T*	2.071	1.761	1.416	1.420	1.394	1.408	1.807	1.834

torsional angles are summarized in Tables 2, 3, and 4. In the molecule, the length of the Sb—O bond is 2.078(2) Å, which is shorter than the sum of the covalent radii of the Sb and O atoms (2.19 Å). The bond angle of Sb_1—O_1—S_5 is 119.97(14)°. The length of the S—O bond is 1.580(2) Å and the bond angles around the S_5 atom are 103.86(14)° (O_1—S_5—C_5), 102.62(18)° (O_1—S_5—C_8), and 102.44(18)° (C_5—S_5—C_8). It is important that the S—O bond of MBTMO·$SbCl_5$ is longer than that of sulfoxide, 1.502(4) Å [12], but shorter than that of ethoxy sulfonium salt, 1.612(2) Å [21]. Furthermore, in the IR spectrum, a signal for the S—O bond of the complex was observed at 847 cm^{-1} as a strong peak, which is a value similar to that of sodium 2-pyridinesulfenate (S—O: 870 cm^{-1}) [22]. These results suggest that the complex is sulfonium salt with zwitterions ($ArMeS^+$—O—$SbCl_5^-$).

In contrast, it is expected that the structure of MBTMO·$SbCl_5$ is similar to that of the sulfonium salt, MBTOH, which is an intermediate to generate the dication from MBTMO. To obtain information about the sulfonium salt with the OH group on the sulfur atom, the structure of MBTOH was optimized using the DFT method at the B3LYP/6-31G** level and compared with the structure of MBTMO·$SbCl_5$. Vibrational analysis gave the minimum energy structure; the bond lengths, bond angles, and torsional angles are summarized in Tables 2, 3, and 4 (see also Scheme 6). In the optimized structure, the length of the S—O bond is 1.663 Å, and the bond angles around the S_5 atom are 101.0° (O_1—S_5—C_5), 95.4° (O_1—S_5—C_8), and 105.0° (C_5—S_5—C_8). The conformation of the trithiole ring of the salt is an envelope structure. To compare the ^{1}H-NMR data of MBTMO·$SbCl_5$ with that of MBTOH, the chemical shifts of MBTOH were calculated from the differences between the shielding constants of MBTOH and those of tetramethylsilane. As shown in Table 5, the ^{1}H-NMR chemical shifts of MBTMO·$SbCl_5$ correlate well with the calculated chemical shifts of MBTOH. Although the calculated S—O bond length of MBTOH is longer than the S—O bond length of MBTMO · $SbCl_5$, it seems that the optimized structure of MBTOH resembles the structure of MBTMO · $SbCl_5$.

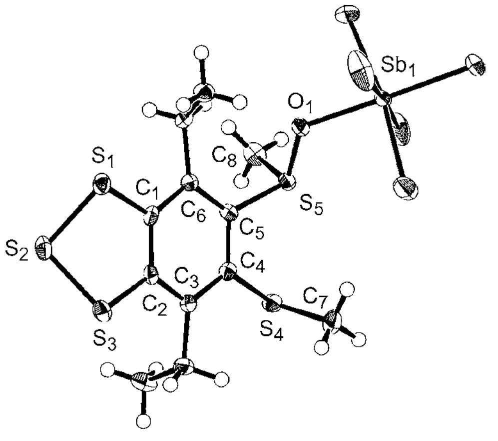


FIGURE 4 ORTEP drawing of MBTMO · $SbCl_5$.

CONCLUSION

MBT was oxidized with two equivalents of $SbCl_5$ to produce a triplet-state dication MBT(2+)-*T* · $2SbCl_6^-$, which was confirmed by elemental analysis and ESR spectroscopy. MBT(2+)-*T* was prepared by treatment of MBTMO with H_2SO_4 and Tf_2O. Hydrolysis

TABLE 2 Bond Lengths (Å) of MBTMO · $SbCl_5$ Determined by Crystallography and MBTOH Calculated by DFT

	Bond Lengths (Å)	
	MBTMO · $SbCl_5$	*MBTOH*
S_1–S_2	2.0596(14)	2.102
S_2–S_3	2.0605(14)	2.107
S_1–C_1	1.784(3)	1.798
S_3–C_2	1.786(3)	1.792
S_4–C_4	1.782(3)	1.799
S_4–C_7	1.814(4)	1.836
S_5–C_5	1.793(3)	1.809
S_5–C_8	1.790(4)	1.818
S_5–O_1	1.580(2)	1.668
C_1–C_2	1.405(5)	1.412
C_1–C_6	1.408(5)	1.408
C_2–C_3	1.393(5)	1.405
C_3–C_4	1.399(5)	1.404
C_4–C_5	1.403(5)	1.410
C_5–C_6	1.393(5)	1.411
O_1–Sb_1	2.078(2)	

TABLE 3 Bond Angles (deg) of MBTMO · $SbCl_5$ Determined by Crystallography and MBTOH Calculated by DFT

	Bond Angles (deg)	
	MBTMO·$SbCl_5$	*MBTOH*
S_1–S_2–S_3	94.68(5)	94.01
S_2–S_1–C_1	94.48(12)	94.60
S_2–S_3–C_2	94.27(12)	94.53
S_1–C_1–C_2	117.0(3)	117.3
S_3–C_2–C_1	117.1(3)	118.0
S_4–C_4–C_5	118.4(3)	116.6
C_4–S_4–C_7	101.21(18)	103.1
S_5–C_5–C_4	112.1(3)	110.7
C_5–S_5–C_8	102.44(18)	105.8
O_1–S_5–C_5	103.86(14)	105.3
O_1–S_5–C_8	102.62(18)	96.1
C_1–C_2–C_3	121.6(3)	121.9
C_2–C_3–C_4	117.0(3)	116.7
C_3–C_4–C_5	120.5(3)	120.8
C_4–C_5–C_6	123.4(3)	123.5
C_5–C_6–C_1	115.0(3)	114.8
C_6–C_1–C_2	122.2(3)	122.3

reactions of MBT(2+) gave MBTMO and related sulfoxides. The result suggests that the positive charges, initially generated on the methylthio group, transferred to the trithiole ring, and the reaction was accompanied with the disproportionation reaction. MO calculations for MBT(2+)-*S* and MBT(2+)-*T* using the DFT method at the B3LYP6-31G** level showed that the triplet-state dication MBT(2+)-*T* is more stable than the singlet-state dication MBT(2+)-*S*. Treatment of MBTMO with $SbCl_5$ in dichloromethane gave MBTMO·$SbCl_5$. The structure of MBTMO·$SbCl_5$correlates well with the calculated structure of MBTOH as an intermediate for the generation of the dication from MBTMO.

TABLE 4 Torsional Angles (deg) of MBTMO · $SbCl_5$ Determined by Crystallography and MBTOH Calculated by DFT

	Torsional Angles (deg)	
	MBTMO·$SbCl_5$	*MBTOH*
S_1–S_2–S_3–C_2	−40.87	−39.59
C_1–S_1–S_2–S_3	40.77	39.94
S_2–S_1–C_1–C_2	−29.55	−30.08
S_2–S_1–C_1–C_6	152.73	153.57
S_1–C_1–C_2–S_2	−0.42	0.78
S_2–S_3–C_2–C_1	30.13	28.94
S_2–S_3–C_2–C_3	−150.94	−153.48
S_4–C_4–C_5–S_5	−12.55	−12.51
O_1–S_5–C_5–C_4	−150.39	−157.45
O_1–S_5–C_5–C_6	28.61	20.77
C_8–S_5–C_5–C_4	103.06	101.49
C_8–S_5–C_5–C_6	−77.94	−80.31

TABLE 5 ^{1}H-NMR Chemical Shifts of MBTMO · $SbCl_5$ Determined Experimentally and MBTOH Calculated by DFT

MBTMO · $SbCl_5$	δ	1.26	1.41	2.59	3.02	3.31	3.54	–
MBTOH	δ	1.22	1.50	2.32	2.70	3.12	3.53	4.11(OH)

EXPERIMENTAL

General

The IR spectra were recorded using a JASCO FT-7300 spectrometer, and the NMR spectra were measured on a Bruker AC-400 spectrometer. The mass spectra were obtained using a Hitachi M-2000 mass spectrometer, while the UV spectrum was measured using a JASCO Ubest-30 spectrometer. The ESR spectra were recorded on a JEOL RE-2XG spectrometer. The elemental analysis was performed using a Yanako MT5 analyzer. X-ray data was collected using a Rigaku Mercury R-CCD/III diffractometer, while all calculations were performed using the Crystal Structure crystallographic software package. Oxidation potential was measured by cyclic voltammetry, using Ag/0.01 M $AgNO_3$ as a reference electrode.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 245678.

Computational Methods

All calculations were performed by the density functional theoretical (DFT) method using Gaussian 98 program package [19].

Preparation of MBT

To a solution of DEBBT (644 mg, 2.0 mmol, in 100 mL of THF and 10 mL of EtOH) was slowly added $NaBH_4$ (76 mg, 2.0 mmol), and the mixture was stirred for 30 min [23]. To this solution, K_2CO_3 (280 mg, 2.0 mmol) and CH_3I (13 mL, 48 mmol) was added slowly and the mixture was refluxed for 12 h. After treatment with water, the solvent was evaporated and the aqueous solution was extracted with CH_2Cl_2. The extract was dried with $MgSO_4$ and the solvent was evaporated. Then the product was purified by column chromatography (silica gel, hexane) to give MBT in 76% yield (487 mg); orange oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.21 (t, $J = 7.5$ Hz, 6H, CH_3), 2.42 (s, 6H, SCH_3), 3.05 (q, $J = 7.5$ Hz, 4H, CH_2); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 14.6, 21.7, 32.1, 141.7, 142.1, 142.7; MS (*m/z*) 320(M^+); anal. calcd for $C_{12}H_{16}S_5$: C, 44.95; H, 5.03%. Found: C, 44.96; H, 5.23%.

Oxidation of MBT with mCPBA

To a solution of MBT (320 mg, 1.0 mmol) in 100 mL CH_2Cl_2, *m*CPBA (191 mg, 1.0 mmol, assay $\geq$82%) in 100 mL CH_2Cl_2 was added gradually at −20°C. The solution was stirred for 12 h at −20°C, and treated with NH_3 gas. Then the solution was washed with aqueous NH_4Cl and H_2O, and was dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel; $CHCl_3$:hexane = 5:1, and then hexane:AcOEt = 2:1) to give MBTMO (184 mg, 55%) together with MBT 1-O (63 mg, 19%) and MBT 2-O (14 mg, 4%), and a mixture of bissulfoxides MBTO2 (trace); *MBTMO*: yellow plates; mp 138°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.4 Hz, 3H, —CH_3), 1.27 (t, *J* = 7.4 Hz, 3H, —CH_3), 2.36 (s, 3H, SCH_3), 2.97 (dq, *J* = 13.5, 7.4 Hz, 1H, —CH_2—), 3.04 (dq, *J* = 13.5, 7.4 Hz, 1H, —CH_2—), 3.06(s, 3H, SCH_3), 3.12 (dq, *J* = 13.5, 7.4 Hz, 1H, —CH_2—), 3.53 (dq, *J* = 13.5, 7.4 Hz, 1H, —CH_2—); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 14.4, 14.9, 21.4, 25.2, 29.3, 41.8, 132.1, 140.1, 142.5, 144.6, 145.9, 146.4; IR (KBr) 1060 cm^{-1}(SO); MS (*m*/*z*) 336(M^+); anal. calcd for $C_{12}H_{16}OS_5$: C, 42.82; H, 4.79%. Found: C, 42.50; H, 4.98%; *MBT 1-O*: yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.5 Hz, 3H, CH_3), 1.36 (t, *J* = 7.5 Hz, 3H, CH_3), 2.46 (s, 3H, SCH_3), 2.49 (s, 3H, SCH_3), 3.20 (dq, *J* = 14.2, 7.5 Hz, 1H, —CH_2—), 3.26 (dq, *J* = 14.2, 7.5 Hz, 1H, —CH_2—), 3.38 (dq, *J* = 13.8, 7.5 Hz, 1H, —CH_2—), 3.52 (dq, *J* = 13.8, 7.5 Hz, 1H, —CH_2—); IR (oil) 1096 cm^{-1}(SO); MS (*m*/*z*) 336 (M^+); anal. calcd for $C_{12}H_{16}OS_5$: C, 42.82; H, 4.79%. Found: C, 42.48; H, 4.90%; *MBT 2-O:* yellow crystal; mp 105°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.5 Hz, 6H, CH_3), 2.46 (s, 6H, SCH_3), 3.12 (dq, *J* = 13.5, 7.5 Hz, 2H, CH_2), 3.21 (dq, *J* = 13.5, 7.5 Hz, 1H, CH_2); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 14.3, 21.7, 32.2, 136.7, 142.2, 143.2; IR (KBr) 1135 cm^{-1}(SO); MS (*m*/*z*) 336 (M^+); anal. calcd for $C_{12}H_{16}OS_5$: C, 42.82; H, 4.79%. Found: C, 42.58; H, 4.63%; the mixture of MBTO2 are consisted of six bissulfoxides (5-methylsulfinyl-6-methylthio-4,7-diethylbenzo[1,2,3]trithiole 1-oxide, 2-oxide and 3-oxide), and the mixture was difficult to separate into each bissulfoxide. In this paper, ^{1}H-NMR, IR, and MS of MBTO2-A and MBTO2-B are shown although MBTO2-A and MBTO2-B contain a little amount of the isomer, respectively; *MBTO2-A*: yellow crystal; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H, —CH_3), 1.47 (t, *J* = 7.1 Hz, 3H, —CH_3), 2.41 (s, 3H, SCH_3), 3.11 (dq, *J* = 13.8, 7.1 Hz, 1H, —CH_2—), 3.14 (s, 3H, SCH_3), 3.28 (dq, *J* = 13.8, 7.1 Hz, 1H, —CH_2—), 3.31 (dq, *J* = 13.8, 7.1 Hz, 1H, —CH_2—), 4.02 (dq, *J* = 13.8, 7.1 Hz, 1H, —CH_2—); IR (KBr) 1060, 1084 cm^{-1} (SO); MS (*m*/*z*) 352(M^+); *MBTO2-B*: yellow needles; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3H, —CH_3), 1.41 (t, *J* = 7.2 Hz, 3H, —CH_3), 2.43 (s, 3H, SCH_3), 3.11 (s, 3H, SCH_3), 3.15 (dq, *J* = 14.3, 7.2 Hz, 1H, —CH_2—), 3.30 (dq, *J* = 14.3, 7.2 Hz, 1H, —CH_2—), 3.45 (dq, *J* = 14.3, 7.2 Hz, 1H, —CH_2—), 3.93 (dq, *J* = 14.3, 7.2 Hz, 1H, —CH_2—); IR (KBr) 1059, 1083 cm^{-1}(SO); MS (*m*/*z*) 352(M^+).

Treatment of MBTMO by H_2SO_4 and Then H_2O

MBTMO (168 mg, 0.5 mmol) was dissolved in H_2SO_4 (8 mL) and the solution was stirred for 24 h. The solution was poured into ice water and was stirred for 30 min. Then the solution was extracted with CH_2Cl_2. The extraction was dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography (silica gel; $CHCl_3$: hexane = 5:1, and then hexane: AcOEt = 2:1) to give MBT (36 mg, 22%), MBTMO (34 mg, 18%), MBT 1-O (55 mg, 33%), and MBT 2-O (12 mg, 7%), together with a mixture of bissulfoxide MBTO2 (10 mg, 8%).

UV-Vis Spectrum for MBT(2+)-T

The spectrum for MBT(2+)-*T* was measured in H_2SO_4 (7.55×10^{-5}mol/L); λ_{max} = 274 nm (ε 12300), 319 nm (ε 7750), 454 nm (ε 3510), and 725 nm (ε 2790).

Treatment of MBTMO by Tf_2O and Then H_2O in CH_3CN

To a solution of MBTMO (165 mg, 0.5 mmol) in 35 mL CH_2Cl_2, Tf_2O (0.1 mL, 0.6 mmol) in 10 mL CH_3CN was added gradually at −30°C under Ar, and the solution was stirred at −30°C for 24 h. Then the solution was treated with aqueous Et_2O, and was stirred until the dark-blue solution changed to yellow. The reaction mixture was extracted with CH_2Cl_2 and the solution was dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel; $CHCl_3$:hexane = 5:1, and then hexane:AcOEt = 2:1) to give MBT (32 mg, 20%), MBTMO (26 mg, 16%), MBT 1-O (28 mg, 17%), and MBT 2-O (13 mg, 8%), together with a mixture of bissulfoxide MBTO2 (5 mg, 3%).

Treatment of MBT with $NOBF_4$ and Then H_2O

To a solution of MBT (100 mg 0.3 mmol) in 10 mL CH_2Cl_2, $NOBF_4$ (70 mg, 0.6 mmol) in 1 mL CH_3CN was added gradually at −30°C under Ar, and the solution was stirred at −30°C for 2 h. Then the solution was treated with aqueous Et_2O, and was stirred until the dark-blue solution changed to yellow. The reaction mixture was extracted with CH_2Cl_2 and the solution was dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel; $CHCl_3$:hexane = 5:1, and then hexane:AcOEt = 2:1) to give MBT 1-O (75 mg, 75%) and MBT 2-O (20 mg, 21%).

Preparation of Dication upon Treatment of MBT with $SbCl_5$

To a solution of MBT (98 mg, 0.3 mmol) in 10 mL CH_2Cl_2, $SbCl_5$ (0.9 mL, 0.6 mmol) in 8 mL CH_2Cl_2 was added gradually under Ar, and the solution was stirred for 1 h. Then the dark-red solid was filtered and washed with CH_2Cl_2. The solid was dried under vacuum for 12 h to produce MBT(2+)-$T \cdot 2SbCl_6^-$ in 93% yield; mp 76–77°C; anal. calcd for $C_{12}H_{16}Cl_{12}S_5Sb_2$: C, 14.57; H, 1.63%. Found: C, 14.82; H, 1.88%.

Reaction of MBTMO with $SbCl_5$

To a solution of MBTMO (67 mg 0.2 mmol) in 10 mL CH_2Cl_2, $SbCl_5$ (0.6 mL, 0.4 mmol) in 10 mL CH_2Cl_2 was added under Ar, and the solution was stirred at room temperature for 2 h. Then the solution was treated with aqueous Et_2O. The reaction mixture was extracted with CH_2Cl_2 and the solution was dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel; $CHCl_3$:hexane = 5:1, and then hexane:AcOEt = 2:1) to give MBTMO · $SbCl_5$ (20%); orange prism; mp 166°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.26 (t, $J = 7.5$ Hz, 3H, $-CH_3$), 1.41 (t, $J = 7.5$ Hz, 3H, $-CH_3$), 2.59 (s, 3H, SCH_3), 3.02 (q, $J = 7.5$ Hz, 2H, $-CH_2-$), 3.31 (br, 2H, $-CH_2-$), 3.54 (s, 3H, SCH_3); IR (KBr) 847 cm^{-1}(SO); anal. calcd for $C_{12}H_{16}Cl_5OS_5Sb$: C, 22.68; H, 2.54%. Found: C, 22.79; H, 2.72%; The crystal data for MBTMO · $SbCl_5$: monoclinic, $P2_1/c$ (#14), $a = 13.305(1)$ Å, $b = 10.5945(9)$ Å, $c = 15.862(2)$ Å, $\beta = 95.2650(5)^\circ$, $V = 2226.6(3)$ Å^3, $Z = 4$, $D_{calc} = 1.896$ g/cm^{-3}, μ(Mo Kα) = 23.06 cm^{-1}, 25143 reflections collected: 4877 unique reflection ($R_{int} = 0.035$), 4330 [$I > 1.50\sigma(I)$] used in the refinement, reflection/parameter ratio = 15.41, $R = 0.034$ ($R_w = 0.091$), $GOF = 1.41$.

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