Radical Cation and Dication Derived from 4,8-Diethylbenzo[1,2-*d*:4,5-*d*′]-bis[1,2,3]trithiole [DEBBT]: Change of Electronic State from Singlet-State Dication DEBBT(2+)-*S* to Triplet-State Dimer 2DEBBT(2+)-*T* in D_2SO_4 and CD_3CN Solutions

Takeshi Kimura,*[a] Takashi Sasaki,[b] Hiroaki Yamaki,[b] Eiichi Suzuki,[b] and Sigeya Niizuma[c]

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4,8-Diethylbenzo[1,2-*d*:4,5-*d*′]bis[1,2,3]trithiole [**DEBBT**] was oxidized using concentrated D_2SO_4, leading to the generation of the radical cation **DEBBT(·+)** which was verified by ESR spectroscopy. **DEBBT(·+)** in the solution was further oxidized to produce the dication **DEBBT(2+)**, as determined by ^1H and ^{13}C NMR spectroscopy. **DEBBT(2+)** was also prepared by treating **DEBBT** 1-oxide [**DEBBT 1-O]** with concentrated D_2SO_4, and was verified by ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts of **DEBBT(2+)**, calculated by the density functional theoretical (DFT) method at the B3LYP6-31G** level, correlated well with those obtained experimentally. The ESR signal of **DEBBT(2+)** generated from **DEBBT 1-O** was observed in solution, which implies that the singlet-state dication **DEBBT(2+)-*S*** isomerizes to the triplet-state dication **DEBBT(2+)-*T***, and that two molecules of **DEBBT(2+)-*T*** further form a spin pair at one trithiole ring with significant distance between the two radical centers. The oxidation of **DEBBT** with one or two equivalents of single-electron oxidizing reagents produced **DEBBT(·+)** and **DEBBT(2+)**, and the salts were isolated in a stable form. However, the **DEBBT(2+)** that was prepared by oxidation with $NOPF_6$ proved silent for NMR in CD_3CN, while ESR was active. The stability, electronic state, and NMR and ESR spectroscopy of the dication are affected by solvation with D_2SO_4 and CD_3CN. The optimized structures and the total energy of the singlet- and triplet-state dication were calculated using the DFT method at the B3LYP6-31G** level, which shows that the structures of the singlet- and triplet-state dications have a completely planar form with 1.7 kcal/mol as the total energy difference between them.

Introduction

The chemistry of the radical cation and dication that are derived from benzo-annelated five-membered heterocyclic molecules is of great interest from the viewpoint of their structures, electronic states, and electrochemical and magnetic properties. Much research has focused on applying these molecules to advanced materials.[1−5] Since Wolmershäuser reported on the isolation and structure determination of the benzo[1,2,3]triselenole radical cation (**1**) in 1992, which was the first benzo-annelated trichalcogenole radical cation,[6−8] several interesting radical cations (**2**) and (**3**) have been prepared by treating the corresponding benzotrichalcogenoles with single-electron oxidizing reagents such as nitrosonium hexafluorophosphate ($NOPF_6$) and pentachloroantimonate ($SbCl_5$), as shown in Figure 1.[9−12]

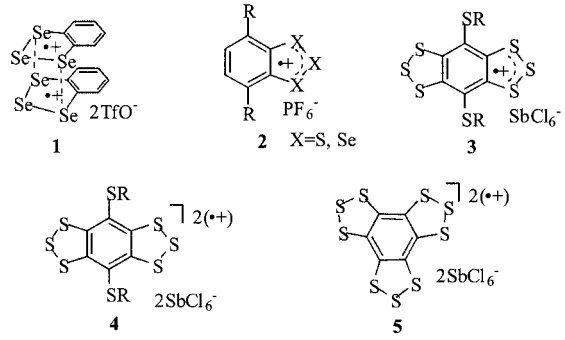

Figure 1. Benzotrichalcogenole radical cations and dications

The preparation and magnetic properties of the dications derived from hexathia-substituted benzene derivatives, 4,8-bis(alkylthio)benzo[1,2-*d*:4,5-*d*′]bis[1,2,3]trithiole dication

[a] Center for Instrumental Analysis, Iwate University, Morioka, Iwate 020−8551 Japan
[b] Department of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka, Iwate 020−8551 Japan
[c] Faculty of Humanities and Social Science, Iwate University, Morioka, Iwate 020−8550 Japan
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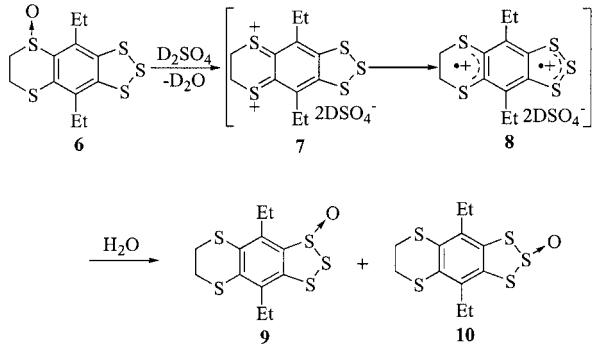
(**4**), and benzo[1,2-*d*:3,4-*d*′:5,6-*d*′′]tris[1,2,3]trithiole dication (**5**), were described by Fanghänel.[12] These dications could be stabilized by through-space σ-delocalization between the six spherical sulfur atoms.[13] However, no reports have been published on the dication derived from 4,8-diethylbenzo[1,2-*d*:4,5-*d*′]bis[1,2,3]trithiole [**DEBBT**], with two trithiole rings that are spherically separated by two ethyl groups, especially regarding the ^{1}H and ^{13}C NMR spectra and their electronic state in the solution. As a result of our studies into several cyclic oligosulfides,[14−17] we recently reported that the generation of the 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole dication (**7**) could be achieved by treating the corresponding monoxide (**6**) with concentrated D_2SO_4 (Scheme 1). In this molecule, the positive charges, initially generated on the dihydrodithiin ring, transferred to the trithiole ring as a result of conjugation with the π-electrons of the central benzene ring, which is also accompanied by a change in the electronic state from singlet to triplet. Compounds **7** and **8** were determined by ^{1}H NMR and ESR spectroscopic procedures, respectively.[18] After hydrolysis of the dication in the D_2SO_4 solution, trithiole monoxides (**9**) and (**10**) were obtained as major products.



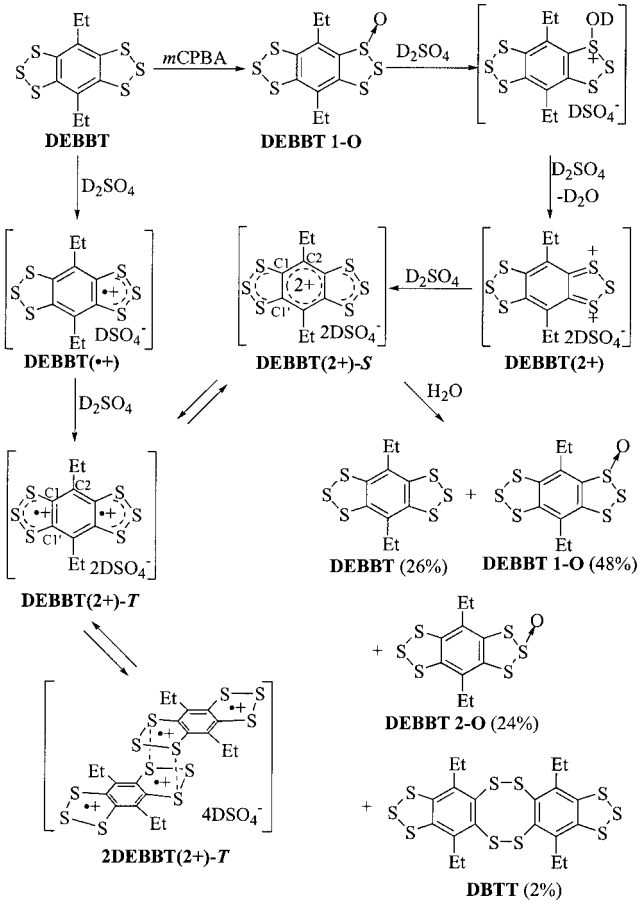
Scheme 1

Since **DEBBT** exhibits two reversible oxidation waves in the cyclic voltammetry measurement, and given that its two half-wave potentials are close to each other ($E_{1/2}$ = 0.83 and 0.95 V vs. Ag/AgNO$_3$),[16,17] it should be possible to generate the corresponding radical cation and dication by a suitable oxidation. To provide the radical cation and dication with two trithiole rings, and to examine the stability, electrochemical properties, electronic state, and π-conjugation between the two trithiole rings, **DEBBT** and **DEBBT** 1-oxide [**DEBBT 1-O**] were treated with concentrated D_2SO_4. The generation of **DEBBT(·+)** by the reaction of **DEBBT** with concentrated D_2SO_4 and the further oxidation of **DEBBT(·+)** to **DEBBT(2+)** were followed by ESR and ^{1}H and ^{13}C NMR spectroscopy. While **DEBBT(2+)** was also generated from **DEBBT 1-O** in D_2SO_4, which was determined by NMR spectroscopy, **DEBBT(2+)** was also found to be ESR-active in the solution. The oxidation of **DEBBT** with one or two equivalents of a single-electron oxidizing reagent produced **DEBBT(·+)** and **DEBBT(2+)** as stable forms, respectively. While the ESR spectra of **DEBBT(·+)** and **DEBBT(2+)** could be measured in CH_3CN, **DEBBT(2+)** was silent for ^{1}H and ^{13}C NMR in the solution. This paper reports on the preparation, detection, and isolation of the radical cation **DEBBT(·+)** and dication **DEBBT(2+)**, the change in electronic states between the singlet-state dication **DEBBT(2+)-*S*** and the triplet-state dimer **2DEBBT(2+)-*T*** in D_2SO_4 and CD_3CN solutions, and the computational examination of the dication regarding the NMR shielding constants and the energy difference between the singlet and triplet states.

Results and Discussion

Generation and Detection of the Radical Cation and Dication from DEBBT and DEBBT 1-O

To generate the radical cation and dication, **DEBBT** was dissolved in concentrated D_2SO_4 (Scheme 2). The resulting dark-blue solution was initially investigated by ^{1}H NMR spectroscopy but no spectrum was observed. In contrast, when the solution was followed by ESR spectroscopy, one strong signal was recorded; g = 2.018, ΔH_{pp} (peak-to-peak line width) = 0.3 mT (293 K), revealing that the radical cation **DEBBT(·+)** was generated by the oxidation of **DEBBT**



Scheme 2

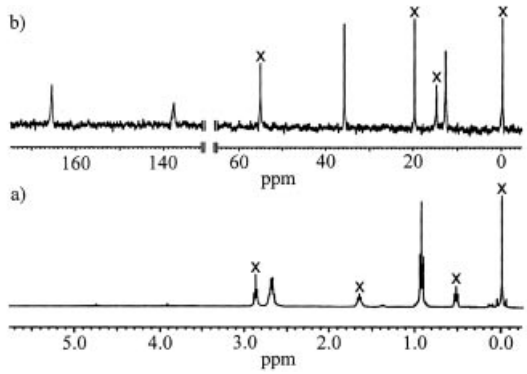


Figure 2. a) 400 MHz ^{1}H NMR spectrum of **DEBBT(2+)-*S*** measured in D_2SO_4; b) 101 MHz ^{13}C NMR spectrum of the same sample; x: DSS

with concentrated D_2SO_4. After several days, however, the solution became NMR active and hence we could determine the species present from the ^{1}H and ^{13}C NMR spectra (Figure 2). The ^{1}H NMR spectrum of the dark-blue species generated from **DEBBT** exhibited two relatively broad signals for the ethyl group (δ = 0.94 and 2.69), as shown in Figure 2(a). These signals were observed in a higher field than those of **DEBBT** measured in $CDCl_3$ (δ = 1.17 and 2.74 ppm). In the ^{13}C NMR spectrum of the species in the D_2SO_4 solution, two signals for the ethyl group (δ = 12.8 and 35.9 ppm) and two signals for the benzene ring (δ = 137.8 and 165.5 ppm) were observed (Figure 2, b), indicating that the species has a symmetrical structure. The chemical shifts in the benzene ring were found in a lower field than those of **DEBBT** measured in $CDCl_3$ (δ = 13.4, 33.2, 133.6, and 141.2 ppm), revealing that the positive charges partially delocalize on the benzene ring. The species in the D_2SO_4 solution remained stable at room temperature for several months. These results implied that the oxidation of **DEBBT** with concentrated D_2SO_4 initially produced **DEBBT(·+)**, which was gradually oxidized further in the solution to produce the singlet-state dication **DEBBT(2+)-*S*** via the triplet-state dication **DEBBT(2+)-*T***.

It has been reported that a molecule bearing both sulfinyl and sulfenyl groups in close proximity produces a corresponding dithia dication as a singlet state when treated with concentrated D_2SO_4, and the dithia dication, which was determined by ^{1}H NMR spectroscopy, was stabilized as a result of through-space interaction between two sulfur atoms.[19−22] To achieve the selective generation of two positive charges as a singlet-state dication, **DEBBT 1-O** was dissolved in concentrated D_2SO_4 at room temperature, after which the solution was examined by NMR spectroscopy. The ^{1}H NMR spectrum of **DEBBT 1-O** measured in $CDCl_3$ showed two pairs of triplet and two pairs of double-quadruplet signals for two ethyl groups,[23] while six signals for the benzene ring and four signals for two ethyl groups were observed in the ^{13}C NMR spectrum measured in the same solvent. The ^{1}H and ^{13}C NMR spectra of the dark-blue species generated from **DEBBT 1-O** in concentrated D_2SO_4 exhibit the same signals for the dication as those shown in Figure 2, which indicates that the species generated in the solution is a singlet-state dication **DEBBT(2+)-*S***, and the positive charges, initially generated on one trithiole ring, delocalized to the other trithiole ring by conjugation with the π-electrons of the central benzene ring.

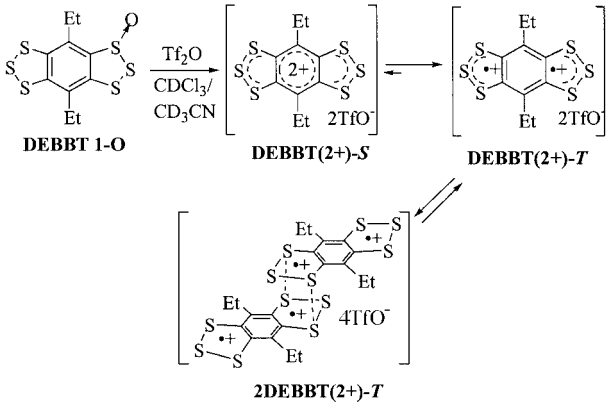
While the **DEBBT(2+)-*S*** derived from **DEBBT 1-O** could be observed by NMR spectroscopy in concentrated D_2SO_4 solution, when the solution was followed by ESR spectroscopy, one strong signal was recorded in the spectrum; g = 2.018, ΔH_{pp} = 0.2 mT (291 K). Based on these results, singlet-state dication **DEBBT(2+)-*S*** is expected to electronically isomerize into triplet-state dication **DEBBT(2+)-*T*** in the solution, while **DEBBT(2+)-*S*** and **DEBBT(2+)-*T*** are expected to be in equilibrium. Meanwhile, if **DEBBT(2+)-*T*** is in a triplet state as expected, **DEBBT(2+)-*T*** should further form a spin pair at one trithiole ring, and the ESR signal should be attributable to the partially associated structure **2DEBBT(2+)-*T*** and not to a free structure. The ESR signal of the dication resembles that of the radical cation, and hence, in the paired form, the two radical centers on the trithiole rings are expected to be effectively independent of each other.[4,5]

To estimate the quantity of the dication, **DEBBT 1-O** and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (an internal standard) were dissolved in concentrated D_2SO_4 (**DEBBT 1-O**/DSS = 1:1), after which the ^{1}H NMR spectrum of the solution was measured (Figure 2). The integral ratio of **DEBBT(2+)-*S*** (2 × CH_2) and DSS (CH_2SO$_3$Na) was determined from the spectrum as **DEBBT(2+)-*S***/DSS = 2.643:1.325. Based on this ratio, 97% of the dication is expected to be in the singlet state in the solution. Therefore, only 1.5% of the triplet-state dication dimer **2DEBBT(2+)-*T*** may exhibit the ESR signal.

The UV/Vis spectrum of **DEBBT(2+)-*S*** was measured in concentrated H_2SO_4 ($4.7\cdot10^{-5}$ mol/L). In the spectrum, one strong absorption was observed at λ_{max} = 714.0 nm (ε = 29000) together with three absorptions; λ_{max} = 564.5 nm (ε = 2900), 474.5 nm (ε = 3900), and 285.5 nm (ε = 24000). A change of the concentration to $9.4\cdot10^{-5}$ mol/L resulted in a change of the absorption intensity in the spectrum proportional to the concentration level.

When **DEBBT 1-O** was dissolved in concentrated D_2SO_4 and then treated with ice water, **DEBBT 1-O** and **DEBBT 2-O** were obtained in 48% and 24% yields, respectively, together with **DEBBT** (26%) and 1,4,7,10-tetraethyl[4,5-*b*:4′,5′-*i*]bis[1,2,3]trithiolodibenzo[*c*,*g*][1,2,5,6]tetrathiocin [**DBTT**] (2%) (Scheme 2). Based on the reaction giving **DEBBT 1-O** and **DEBBT 2-O** as major products and the ^{1}H and ^{13}C NMR spectra, the species generated from **DEBBT 1-O** when it is treated with D_2SO_4 should be the singlet-state dication **DEBBT(2+)-*S***. Meanwhile, since the reduced product **DEBBT** was produced by the treatment of **DEBBT 1-O** with D_2SO_4 and then with water, it is clear that a disproportionation reaction of **DEBBT(2+)** proceeds by this hydrolysis to produce **DEBBT** and **DEBB.** However, the mechanism leading to desulfurization of **DEBBT(2+)** is not clear.

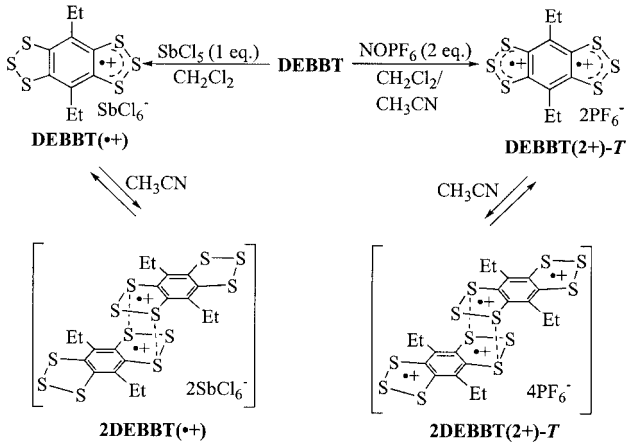
DEBBT 1-O was then treated with trifluoromethanesulfonic anhydride Tf_2O in $CDCl_3/CD_3CN$, to examine the effect of the solvent on the generation and stabilization of the dication (Scheme 3). The dark-blue species generated in the solution were examined by NMR spectroscopy but the solution proved to be NMR silent. We therefore used ESR spectroscopy to measure the species, and one signal was observed; $g = 2.018$, $\Delta H_{pp} = 0.1$ mT (293 K), suggesting that the initially generated **DEBBT(2+)-*S*** isomerizes to **DEBBT(2+)-*T*** in the $CDCl_3/CD_3CN$ solution and the triplet-state dication simultaneously forms a spin pair **2DEBBT(2+)-*T*** at the trithiole rings. The dication generated in $CDCl_3/CD_3CN$ was unstable at room temperature and decomposed in one hour, even though the dication generated in the D_2SO_4 solution was very stable. It appears that the stability and electronic structure of **DEBBT(2+)** are affected by solvation with D_2SO_4 and CD_3CN, and **DEBBT(2+)-*T*** is more likely to form a spin pair in $CDCl_3/CD_3CN$ than in concentrated D_2SO_4.



Scheme 3

Isolation of the Radical Cation and Dication from DEBBT

After the generation of the radical cation and dication by treating **DEBBT** and **DEBBT 1-O** with concentrated D_2SO_4 and with $Tf_2O/CDCl_3/CD_3CN$ had been confirmed by ESR and NMR spectroscopy, we examined the isolation of the radical cation and dication as stable forms (Scheme 4). To isolate the radical cation, **DEBBT** was treated with the equivalent of $NOPF_6$, in CH_2Cl_2/CH_3CN at −78 °C for 30 min to produce **DEBBT(·+)**·PF_6^- as a dark-blue solid. The radical cation salt was then dissolved in CD_3CN, and was measured by ^{31}P NMR spectroscopy because ^1H and ^{13}C NMR spectra were not measurable in the solution. The signal of PF_6^- was observed at $\delta = -147.4$ ppm (Sept, $J_{P\text{-}F} = 706$ Hz) in the spectrum. However, the radical cation remained thermally unstable even under a nitrogen atmosphere, so that a pure form of the salt could not be isolated.



Scheme 4

Instead of $NOPF_6$, **DEBBT** was treated with the equivalent of $SbCl_5$ in CH_2Cl_2 for 30 min at room temperature. As a result, radical cation **DEBBT(·+)**·$SbCl_6^-$ was obtained in 83% yield as a dark-blue solid (Scheme 4). A solution of the radical cation was then prepared by dissolving the solid in CH_3CN, which was followed by ESR spectroscopy. If **DEBBT(·+)**·$SbCl_6^-$ forms a strong spin pair at the trithiole ring in the solution, the ESR signal should be very weak and broad, and be solvent-dependent in the same way as the benzotriselenole radical cation (**1**) reported by Wolmershäuser. In the spectrum, one signal that had broadened considerably was recorded at 20 °C; $g = 2.018$, $\Delta H_{pp} = 5.1$ mT, revealing that **DEBBT(·+)** exists as a partially associated form in the solution. Equilibrium is expected between free-form radical cation **DEBBT(·+)** and its spin dimer **2DEBBT(·+)** in the solution, and the exchange rate of the species should be fast at this temperature. The ESR spectrum of **DEBBT(·+)** measured in D_2SO_4 differs from that measured in CH_3CN, so the signal for the radical cation depends on the solvent. In D_2SO_4, **DEBBT(·+)** exists in a predominantly free form relative to that in CH_3CN.

Meanwhile, the magnetic susceptibility measurement of radical cations is generally important in the fields regarding the magnetic properties of organic and inorganic materials, but the primary subject in this article is generation of **DEBBT(2+)-*S*** and its isomerization to **2DEBBT(2+)-*T***, and **DEBBT(·+)** is one of intermediates for preparation of the dications. We therefore did not examine the magnetic susceptibility of **DEBBT(·+)**.

We subsequently isolated the dication by means of a similar oxidation. When **DEBBT** was oxidized by two equivalents of $NOPF_6$ in CH_2Cl_2/CH_3CN at −78 °C for 30 min, the dication salt was obtained in 65% yield as a dark-blue solid after filtration (Scheme 4). **DEBBT(2+)** remained stable under a nitrogen atmosphere at room temperature, while it decomposed slowly when exposed to moisture. The dication seems to be stable relative to the radical cation. After purification, **DEBBT(2+)** was dissolved in CD_3CN, and ^1H and ^{13}C NMR spectra were measured. We could not, however, record any spectra at all, unlike the case of

the dication generated in concentrated D_2SO_4. The ^{31}P NMR spectrum of PF_6^-, on the other hand, was observed at $\delta = -143.7$ ppm (sept, $J_{P\text{-}F} = 706$ Hz). The solution was then examined by ESR spectroscopy, and the result is shown in Figure 3. One strong signal was recorded at 20 °C, specifically, $g = 2.018$, $\Delta H_{pp} = 0.3$ mT, which led us to anticipate that the dication generated by this procedure is triplet-state **DEBBT(2+)-*T*** in CH_3CN solution, and that the triplet state dication forms the spin pair **2DEBBT(2+)-*T***.

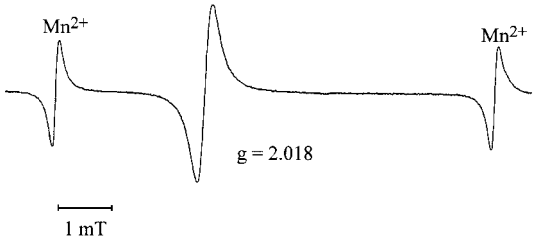


Figure 3. ESR spectrum of **2DEBBT(2+)-*S***·$4PF_6^-$ measured in CH_3CN

Meanwhile, when the obtained **DEBBT(2+)**·$2PF_6^-$ was dissolved in concentrated D_2SO_4, two very broad signals were initially observed in the ^1H NMR spectrum. After 15 h, the spectrum changed such that it was similar to that of **DEBBT(2+)-*S*** as shown in Figure 2(a), which suggests that solvation of the dication with D_2SO_4 occurs slowly at room temperature.

Theoretical Study

To obtain further evidence for the generation of singlet-state dication **DEBBT(2+)-*S***, the optimized structure and the NMR shielding constants of the dications were calculated using the DFT method.[24] The structure of **DEBBT(2+)-*S*** was optimized at the B3LYP/6-31G** level, which produced a completely planar form for **DEBBT(2+)-*S*** as the minimum-energy structure. The planar structure is shown to be minimum energy by vibrational analysis. In the structure, two ethyl groups exist anti to each other relative to the molecular plane. The shielding constants of the dications were then determined at the B3LYP/6-31G** level. The chemical shifts for the ^1H and ^{13}C NMR spectra were subsequently calculated from the difference between the shielding constants of the dication and those of tetramethylsilane. The calculated ^{13}C NMR chemical shifts of **DEBBT(2+)-*S*** correlated well with those obtained experimentally, but the difference between the ^1H NMR experimental and calculated chemical shifts was found to be relatively large (Table 1), which may result from the solvation in which the ethyl groups interact with the solvent more effectively than the benzene ring does. It appears that the downfield shift of the signals of the benzene ring in the ^{13}C NMR spectrum is caused by the delocalization of the positive charges from the trithiole ring to the benzene ring.

Table 1. ^1H and ^{13}C NMR chemical shifts of **DEBBT(2+)-*S***

^1H	δ	obsd.	0.94	2.69		
		calcd.	1.76	3.28		
^{13}C	δ	obsd.	12.8	35.9	137.8	165.5
		calcd.	11.7	39.2	131.0 (C2)	167.8(C1)

To examine the structure and chemical properties of **DEBBT(2+)**, we performed a molecular orbital calculation for the parent molecules related to **BBT(2+)-*S*** and **BBT(2+)-*T*** (with two hydrogen atoms instead of two ethyl groups) using the DFT method at the B3LYP/6-31G** level. The structures of **BBT(2+)-*S*** and **BBT(2+)-*T*** were optimized with no symmetry constraints. Vibrational analysis gave the minimum-energy structures. The optimized structures of **BBT(2+)-*S*** and **BBT(2+)-*T*** are both completely planar, and have similar structures. The optimized bond lengths (in Å) of **BBT(2+)-*S*** and **BBT(2+)-*T*** are shown in Table 2. The difference in the total energy between the singlet and triplet state of the dication was calculated with respect to the optimized structures. The results show that, while the singlet-state dication **BBT(2+)-*S*** is more stable than the triplet-state dication **BBT(2+)-*T***, the energy difference between **BBT(2+)-*S*** and **BBT(2+)-*T*** is only 1.7 kcal/mol, which suggests that isomerization of the dication between the singlet state and the triplet state occurs easily in a solution at room temperature.

Table 2. Optimized bond lengths (in Å) of **BBT(2+)-*S*** and **BBT(2+)-*T***

	S−S	S−C1	C1−C1′	C1−C2
BBT(2+)-*S*	2.084	1.732	1.445	1.396
BBT(2+)-*T*	2.074	1.763	1.417	1.400

Conclusion

DEBBT(·+) and **DEBBT(2+)** were prepared by oxidation of **DEBBT** with concentrated D_2SO_4, $NOPF_6$, and $SbCl_5$ and their generation was confirmed by ^1H and ^{13}C NMR and ESR spectroscopy. While the singlet-state dication **DEBBT(2+)-*S*** was prepared by treating **DEBBT 1-O** with concentrated D_2SO_4, **DEBBT(2+)-*S*** partially isomerized to the triplet-state dication **DEBBT(2+)-*T***, and **DEBBT(2+)-*T*** exists in a paired-form **2DEBBT(2+)-*T*** in the solution. The ^1H and ^{13}C NMR spectra of the dication are solvent-dependent, and the electronic state and the stability of the dications are strongly affected by solvation with concentrated D_2SO_4 and CD_3CN. It appears that the singlet-state dication **DEBBT(2+)-*S*** could exist in a free form in a concentrated D_2SO_4 solution owing to the strong solvation effect of this solvent relative to CD_3CN, while the dication in CD_3CN solution is the triplet-state

DEBBT(2+)-*T*, which exists as the paired form **2DEBBT(2+)-*T***. The ^{13}C NMR spectrum of **DEBBT(2+)-*S*** as measured in D_2SO_4 solution correlates well with the chemical shifts calculated by the DFT method at the B3LYP6-31G** level, even though the correlation of the ^1H NMR spectra obtained by experiment and calculation is relatively low. MO calculations for **BBT(2+)-*S*** and **BBT(2+)-*T*** using the DFT method at the B3LYP6-31G** level gave a small separation of the total energy between the singlet and triplet states, which suggests that the dication exchange between the singlet state and the triplet state occurs easily in the solution, and is affected by the degree of solvation.

Experimental Section

General: NMR spectra were measured using a Bruker AC-400 spectrometer at 298 K. ESR spectrum was recorded on a JEOL RE-2XG spectrometer. Elemental analyses were performed by a Yanako MT5 analyzer.

Computational Methods: All calculations were performed by the density functional theoretical method using Gaussian 98 program package. The structure optimization and the shielding constant calculation for **DEBBT(2+)-*S*** were carried out at the B3LYP/6-31G** level. The structure optimization for **BBT**, **BBT(2+)-*S***, and **BBT(2+)-*T*** was performed by a similar procedure.

Preparation of DEBBT and DEBBT 1-O

DEBBT and **DEBBT 1-O** were prepared by the reported methods.[23,25]

DEBBT(2+)-*S* Derived from DEBBT 1-O and Concentrated D_2SO_4

DEBBT 1-O (6.4 mg, 0.0189 mmol) and DSS (6.4 mg, 0.0183 mmol) were dissolved in concentrated D_2SO_4, and **DEBBT(2+)-*S*** was generated. The ^1H NMR spectrum of **DEBBT(2+)-*S*** was measured in the solution, and the integral ratio of **DEBBT(2+)-*S*** ($2 \times CH_2$) and DSS (CH_2SO_3Na) was determined from the spectrum; **DEBBT(2+)-*S***/DSS = 2.643:1.325. From this ratio, it was determined that 97% of **DEBBT(2+)** exists as the singlet-state; **DEBBT(2+)-*S***: ^1H NMR (400 MHz, D_2SO_4, DSS, ppm): δ = 0.94 (t, *J* = 7.6 Hz, 6 H), 2.69 (q, *J* = 7.6 Hz, 4 H). ^{13}C NMR (101 MHz, D_2SO_4, DSS, ppm): δ = 12.8, 35.9, 137.8, 165.5.

Treatment of DEBBT 1-O with Concentrated D_2SO_4 and Ice/Water

DEBBT 1-O (165 mg, 0.5 mmol) was dissolved in concentrated D_2SO_4 (5 mL) and the solution was stirred for 2 h. Then the solution was poured into ice/water and extracted with CH_2Cl_2 (3×40 mL). The extracts were combined, dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2/ethyl acetate, 5:1) to give **DEBBT 1-O** and **DEBBT 2-O** in 20% (33 mg) and 41% (67 mg) yields, respectively, together with **DEBBT** (26%) and **DBTT** (2%).[17]

Preparation of DEBBT(·+): To a solution of **DEBBT** (64 mg, 0.2 mmol) in CH_2Cl_2 (10 mL), $SbCl_5$ (35 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was added slowly and the solution was stirred for 30 min at room temperature. The solution was filtered under reduced pressure, and the dark-blue solid obtained was washed with CH_2Cl_2 and then dried under vacuum. Radical cation **DEBBT(·+)** was obtained in 83% yield (110 mg); **DEBBT(·+)**: m.p. 207 °C (decomp.). $C_{10}H_{10}Cl_5S_6Sb$ (%): calcd. C 18.28, H 1.53; found C 18.41, H 1.83.

Preparation of DEBBT(2+): To a solution of **DEBBT** (100 mg, 0.3 mmol) in CH_2Cl_2 (35 mL), $NOPF_6$ (120 mg, 0.7 mmol) in CH_3CN (1 mL) was added slowly at −78 °C and the solution was stirred for 30 min at this temperature. The solution was filtered under reduced pressure, and the dark-blue solid obtained was washed with Et_2O and then dried under vacuum. **DEBBT(2+)** was obtained in 65% yield (120 mg); **DEBBT(2+)**: 112−113 °C (decomp.). ^{31}P NMR (162 MHz, CD_3CN, H_3PO_4, ppm): δ = −143.7 (sept, $J_{P\text{-}F}$ = 706 Hz). $C_{10}H_{10}F_{12}P_2S_6$ (%): calcd. C 19.61, H 1.65; found C 19.91, H 1.71.

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