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Generation and Detection of the Radical Cation and the Dication Derived from 4,9-Diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole and Its 5-Oxide

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ABSTRACT: *4,9-Diethyl[1,4]dihydrodithiino[5,6-f]benzotrithiole (DTBT) gave a radical cation, DTBT(•+), and a dication, DTBT(2+), on treatment with a single-electron oxidizing reagent. Both compounds showed an ESR signal, whereas the dication, generated by this procedure, was silent for ^{1}H NMR. Hydrolysis of DTBT(2+) gave DTBT 1-oxide (DTBT 1-O) and 2-oxide (DTBT 2-O) together with DTBT and a mixture of several dioxides. A singlet-state dication, DTBT(2+)-S, which was generated upon treatment of DTBT 5-oxide (DTBT 5-O) with concentrated D_2SO_4, was detected by ^{1}H and ^{13}C NMR. After 20 h, the NMR signals disappeared while the solution was active for ESR. The results suggest that (i) a species generated from DTBT by oxidation with the single-electron oxidizing reagent is a triplet-state dication, DTBT(2+)-T, and (ii) DTBT(2+)-S, initially generated, gradually isomerizes to DTBT(2+)-T in the solution, and DTBT(2+)-T forms a partial spin pair.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:394–401, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20445

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INTRODUCTION

Five-membered heterocycles, consisting of an unsaturated C—C bond and nitrogen, sulfur, and/or selenium atoms, have been good candidates for studying radical cations and related species [1,2]. The molecules bearing such two heterocycles, linked to each other or fused to a benzene ring, are able to accept one or two positive charges by oxidation procedures, and the charged species can be stabilized by enlarged π-conjugation. Cameron and coworkers isolated the simple trithiole derivative (**1**) (Chart 1) [6,7], as the first stable radical cation with a cyclic trisulfide bond, whereas the chemistry of the benzotriselenole radical cation (**2**) was started by Wolmershäuser and Heckmann [8]. The radical cation and dication, in which two or three trithioles are annelated to the one common benzene ring, were prepared by Fanghänel et al.; one of those compounds is the benzotristrithiole dication (**3**) [12].

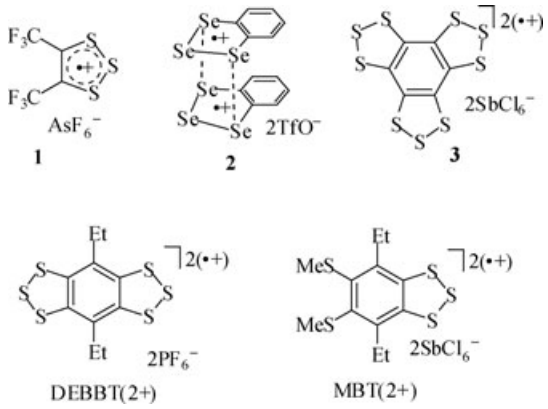
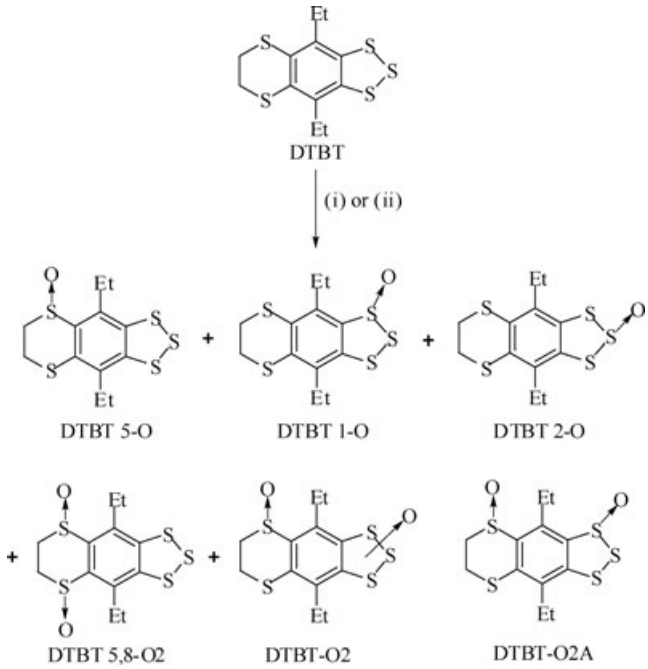


CHART 1 Radical cations and dications.

If two positive charges are generated on one molecule, the electronic state and the spin distribution are important subjects for consideration. Namely, the molecule can exist as a singlet state, a triplet state, or a mixture of them, and the magnetic property is strongly affected by the electronic states. Recently, we reported that 4,8-diethylbenzo[1,2-*d*;4,5-*d*′]bis[1,2,3]trithiole (DEBBT) can accept two positive charges on the two trithiole rings in a singlet or triplet state to produce the dication, DEBBT(2+), which was verified by ^{1}H NMR, ^{13}C NMR, and ESR spectroscopic methods [13]. In contrast, the unsymmetrically substituted dication, MBT(2+), generated from 5-methylsulfinyl-6-methylthio-4,7-diethylbenzo[1,2,3]-trithiole (MBT oxide) on treatment with D_2SO_4, was active for ESR, while silent for NMR [14]. To examine the stability and the electronic state of unsymmetrically substituted cyclic dications, 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole (DTBT) was oxidized by single-electron oxidizing reagents, and 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 5-oxide (DTBT 5-O) was treated with concentrated D_2SO_4 [15]. This paper reports the generation of the dication, DTBT(2+), and its characterization with ^{1}H NMR, ^{13}C NMR, ESR, and the DFT (density functional theory) calculations.

RESULTS AND DISCUSSION

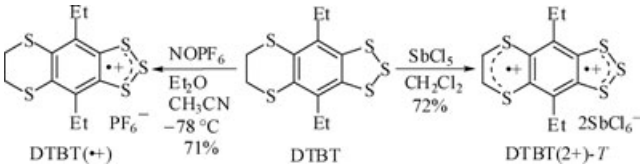
DTBT was oxidized by *m*CPBA in CH_2Cl_2 at room temperature to produce DTBT 5-O in 67% yield together with a small amount of 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 1-oxide (DTBT 1-O), 2-oxide (DTBT 2-O), 5,8-dioxide (DTBT 5,8-O2), and *n*,8-dioxides ($n = 1, 2, 3$) (DTBT-O2) (Scheme 1), which reveals that the reactivity of the dihydrodithiin ring is higher than that of



SCHEME 1 Oxidation of DTBT with *m*CPBA and $NOPF_6$, (i) *m*CPBA/CH_2Cl_2: DTBT 5-O (67%), DTBT 1-O (7%), DTBT 2-O (trace), DTBT 5,8-O2 (trace), DTBT-O2 (trace); (ii) $NOPF_6/CH_2Cl_2/CH_3CN$, H_2O, −78°C: DTBT 1-O (70%), DTBT 2-O (13%), DTBT-O2 (trace).

the trithiole ring in this oxidation [16]. The positions of the sulfinyl sulfur atom of DTBT 5-O, DTBT 1-O, and DTBT 2-O were determined by their ^{1}H NMR, ^{13}C NMR, and IR spectra; DTBT 5-O: IR (KBr): 1020 cm^{-1}, DTBT 2-O: 1114 cm^{-1}, and DTBT 1-O: 1074 cm^{-1}. The structure of 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 5,8-dioxide (DTBT 5,8-O2) has already been determined by X-ray crystallography. In contrast, oxidation of DTBT with 2 equivalents of $NOPF_6$ in CH_2Cl_2/CH_3CN at −78°C and subsequent hydrolysis gave DTBT 1-O and DTBT 2-O in 70% and 13% yields, respectively, but no DTBT 5-O was detected in this reaction. These results imply that (i) the positive charges, initially generated on the dihydrodithiin ring by oxidation via electron transfer, are able to delocalize to the trithiole ring through the central benzene ring, (ii) the intermediate is a dication, DTBT(2+), and (iii) the trithiole ring can exclusively undergo the nucleophilic addition of water, whereas the dihydrodithiin ring cannot.

It is well known that dithia dication derivatives can be prepared by stepwise single-electron oxidation of a substance having two or more sulfide groups appropriately arranged in space or by treatment of sulfoxide, bearing a sulfide moiety in close proximity, with a strong acid, and their formation



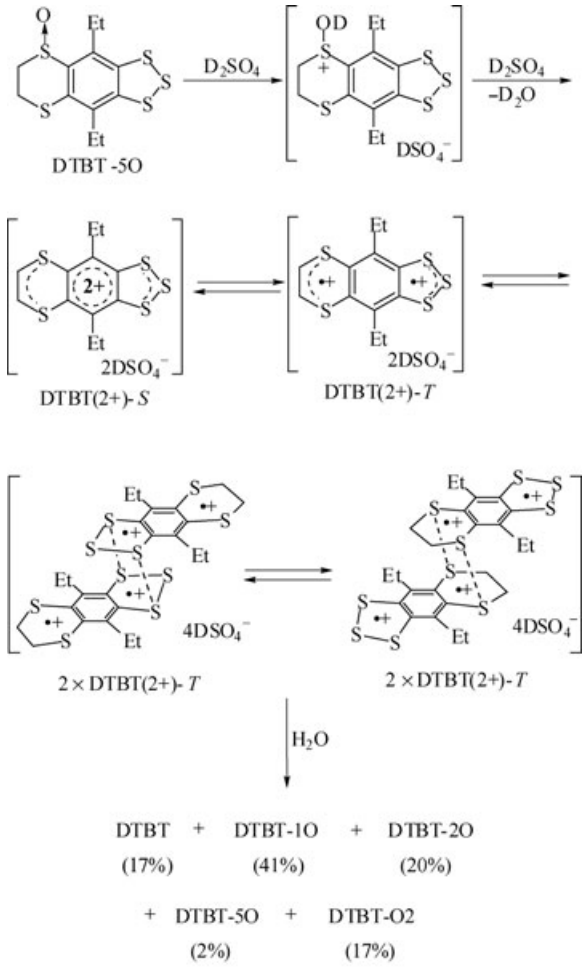
SCHEME 2 Oxidation of DTBT with $NOPF_6$ or $SbCl_5$.

can be determined by ^{1}H NMR spectroscopy [17–20]. To prepare a radical cation, DTBT(•+), and the dication, DTBT(2+), as stable compounds, DTBT was treated with single-electron oxidizing reagents. When DTBT was treated with 1 equivalent of $NOPF_6$ in Et_2O/CH_3CN at −78°C for 30 min, DTBT(•+)•PF_6^- was obtained in 71% yield as a black-green solid (Scheme 2). DTBT(•+)•PF_6^- was decomposed slowly by moisture to produce DTBT, DTBT 1-O, and DTBT 2-O, whereas it was stable under N_2 at room temperature. Purified DTBT(•+)•PF_6^- showed the signal for PF_6^- at $\delta = -148.7$ ppm (sept, $J_{P-F} = 706$ Hz) for the ^{31}P NMR measured in CD_3CN and the ESR signal for DTBT(•+) in CH_3CN was observed as one broad singlet peak at $g = 2.011$ at −30°C.

DTBT was then oxidized with 2 equivalents of $NOPF_6$ in Et_2O/CH_3CN at −78°C. The solid product was collected by filtration, and it was shown to be DTBT(2+)•$2PF_6^-$ by ^{31}P NMR. However, it was less stable than the radical cation and could not be isolated in a pure form. The use of 2 equivalents of $SbCl_5$ instead of $NOPF_6$ gave DTBT(2+) in 72% yield (Scheme 2). The dication dissolved in CH_3CN was followed by ESR spectroscopy, which showed one broadened signal at $g = 2.013$. Therefore, the species generated by this procedure could be a triplet-state dication, DTBT(2+)-*T*, which should exist as a partially associated form in the solution, and the two radical centers should be sufficiently separated from each other.

DEBBT and DTBT show two reversible redox potentials, respectively (vs. $Ag/AgNO_3$ as a reference): DEBBT ($E_{1/2} = 0.83$, 0.95 V) and DTBT ($E_{1/2} = 0.78$, 1.12 V) [21,22]. DTBT has the largest potential difference between the first and second oxidation potentials compared to DEBBT, which should be a reason that DTBT(2+) is unstable compared to DTBT(•+) and DEBBT(2+).

If the positive charge can be generated selectively on the dihydrodithiin ring, the charge transfer will take place from the dihydrodithiin ring to the trithiole ring. Therefore, to obtain evidence for the generation of the dication by ^{1}H NMR spectroscopy, DTBT 5-O was dissolved in D_2SO_4 (Scheme 3). Initially, the solution became dark purple, and then changed to dark green in a few minutes. The UV–vis spectrum of DTBT 5-O was measured in H_2SO_4 (7.95×10^{-5} mol/L), which showed one broadened strong absorption at $\lambda_{max} = 721.0$ nm (ε 17,900) together with an absorption at $\lambda_{max} = 487.5$ nm (ε 2930). In the ^{1}H NMR spectrum measured in $CDCl_3$, DTBT 5-O showed two triplets, a quartet, and a double quartet signals for the two ethyl groups, and four ddd signals for the methylene protons on the dihydrodithiin ring (Fig. 1a). DTBT 5-O has α-sulfinyl protons. However, Pummerer rearrangement was not observed under the reaction conditions, which suggests that DTBT(2+) was stabilized by the transannular interaction of the dithiin ring and the charge delocalization to the trithiole ring through the central benzene ring. In contrast, the spectrum measured in D_2SO_4 exhibited three somewhat broad signals for the ethyl group and the dihydrodithiin ring (Fig. 1b), which suggests that the species generated in the solution has a symmetrical structure. In the ^{13}C NMR spectrum measured in D_2SO_4, three signals for the ethyl group and the dihydrodithiin ring ($\delta = 12.6$,



SCHEME 3 Generation of DTBT(2+) from DTBT 5-O.

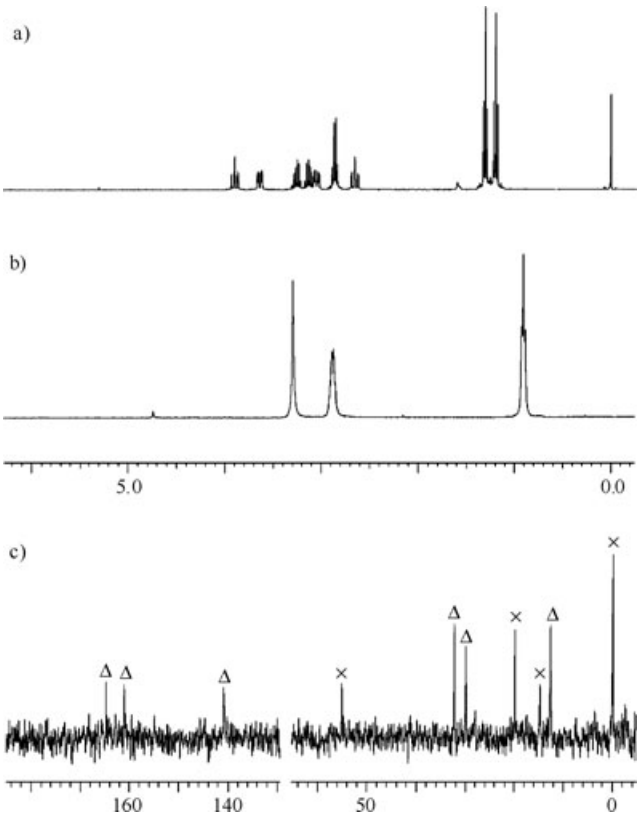


FIGURE 1 (a) 400 MHz ^{1}H NMR spectrum of DTBT 5-O measured in $CDCl_3$; (b) 400 MHz ^{1}H NMR spectrum of DTBT(2+)-*S* measured in D_2SO_4; (c) 101 MHz ^{13}C NMR spectrum of DTBT(2+)-*S* measured in D_2SO_4; ×: DSS, △: sample.

30.0, and 32.3 ppm) and three signals for the benzene ring ($\delta = 140.8$, 161.0, and 164.7 ppm) were observed (Fig. 1c). The signals for the benzene ring were found at fields lower than those of DTBT measured in $CDCl_3$ (δ = 13.3, 29.7, 30.8, 133.1, 137.0, and 137.9 ppm), revealing that the positive charges partially delocalize on the benzene ring. In the ^{1}H and ^{13}C NMR spectra, the signal of the product became broad slowly and disappeared after 20 h. Fast atom bombardment mass spectrometry (FABMS) for DTBT 5-O was measured using H_2SO_4 as a matrix. In the spectrum, the signals corresponding to [DTBT(2+), (318)], [DTBT(2+)•HSO_4^-, (415)], and [DTBT(2+)•HSO_4^-•H_2SO_4, (513)] were observed together with the signals for H_2SO_4. These results demonstrate that the species generated in the solution is a singlet-state dication, DTBT(2+)-*S*, which was produced in $H(D)_2SO_4$ by way of protonation of the oxygen atom of the sulfinyl group and then further protonation and elimination of water.

It was reported that the dithia dications, generated in H_2SO_4, were hydrolyzed with ice water to afford several sulfoxides in good yields. To determine the hydrolysis products of the dication, DTBT 5-O was dissolved in H_2SO_4. After 1 h, the solution was treated with ice water to produce DTBT 1-O and DTBT 2-O in 41% and 20% yields, respectively, together with DTBT (17%), DTBT-O2 (17%), and recovered DTBT 5-O (2%,) (Scheme 3). DTBT and DTBT-O2 would be produced by disproportionation of DTBT(2+) on the hydrolysis of the H_2SO_4 solution.

DTBT-O2 consisted of a mixture of several dioxides, but only DTBT-O2A could be isolated from other isomers by column chromatography and repeated recrystallization. DTBT-O2A was subjected to spectroscopic and elemental analyses, and IR signals for the sulfinyl groups were observed at 1083 and 1023 cm^{-1}. The structure of DTBT-O2A was finally determined by X-ray crystallography [15], which reveals that DTBT-O2A has one oxygen atom on each of the trithiole and dihydrodithiin rings. The crystal structure has been deposited at the Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk).

Although DTBT(2+)-*S*, derived from DTBT 5-O in the D_2SO_4 solution, could be observed by NMR spectroscopy, one strong signal for ESR was also recorded in the spectrum ($g = 2.013$) suggesting that DTBT(2+)-*S* isomerizes into DTBT(2+)-*T* in the solution. The ESR spectrum of a H_2SO_4 solution of DTBT 5-O showed one strong signal at room temperature, which changed to complex broad one at −170°C. However, the signal for the corresponding triplet-state dication, which is anticipated to appear at around $g = 4.000$, could not be observed under the measurement conditions. Therefore, if DTBT(2+)-*T* is a triplet state as expected, DTBT(2+)-*T* should further form a spin pair at the trithiole ring or the dihydrodithiin ring, and the ESR signal should be attributable to the partially associated structure 2DTBT(2+)-*T* with sufficient distance between two radical centers and not to a free structure.

In the previous paper, it was reported that when DEBBT was dissolved in D_2SO_4, the resulting dark blue solution was not initially active for ^{1}H and ^{13}C NMR spectroscopies but became active after several days [13]. The dication generated in the solution is the same as that derived from DEBBT 5-O upon treatment with D_2SO_4. These results reveal that DEBBT(2+) is produced by stepwise oxidation of DEBBT with D_2SO_4. DTBT was then dissolved in D_2SO_4, and the solution was examined by ^{1}H NMR. However, the solution was not NMR-active even after several days. Thus, seemingly the stepwise single-electron oxidation of DTBT gave no dication as the singlet state.

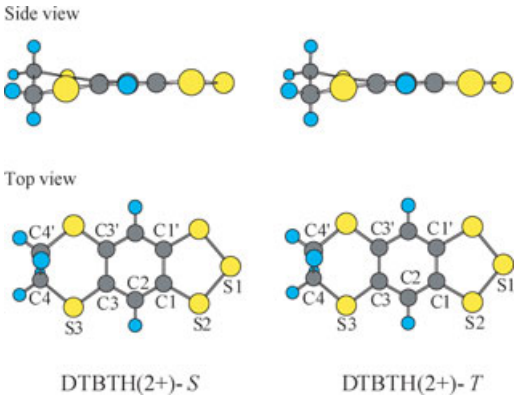


FIGURE 2 Optimized structure of dications.

Furthermore, when DTBT 1-O was dissolved in D_2SO_4, no signal was observed in the ^1H NMR spectrum whereas one strong signal was recorded by ESR spectroscopy: $g = 2.013$. Treatment of DTBT 1-O with H_2SO_4 and then with ice water gave DTBT (25%), DTBT 1-O (9%), DTBT 2-O (33%), and DTBT O2 (9%), but DTBT 5-O was not formed in this reaction. The product distribution of the hydrolysis of the H_2SO_4 solution derived from DTBT 1-O is different from that of the H_2SO_4 solution derived from DTBT 5-O. On the basis of the results, it is supposed that the higher reactivity of the dihydrodithiin ring of DTBT 1-O than that of DTBT 5-O affected the spectroscopy and the product distribution.

To characterize the singlet-state and the triplet-state dications, the optimized structures of DTBTH(2+)-*S* and DTBTH(2+)-*T* having two hydrogen atoms instead of two ethyl groups were calculated by using the DFT method. The calculations produced the energy minimum structures for the dications, which were examined by vibrational analysis (Fig. 2 and Table 1) [23]. In the optimized structures, the trithiole rings of DTBTH(2+)-*S* and DTBTH(2+)-*T* are completely planar. In contrast, the dihydrodithiin ring has a slightly distorted structure from the plane of the benzene ring. As shown in Table 1, the structure of DTBTH(2+)-*S* is slightly different from that of DTBTH(2+)-*T*. To estimate the stability of the dication, the total energy difference (ΔE) between DTBTH(2+)-*S* and DTBTH(2+)-*T* was determined with respect to the optimized structures: $\Delta E_{[\text{DTBTH(2+)-}T-\text{DTBTH(2+)-}S]} = -8.2$ kcal/mol. The results suggest that DTBTH(2+)-*S* is slightly more stable than DTBTH(2+)-*T* which is in a monomeric state. Hence, the NMR spectra for DTBT(2+)-*S* can be measured in the D_2SO_4 solution as shown in Fig. 1. On the other hand, the NMR signal for DTBT(2+)-*S* gradually disappeared in the D_2SO_4 solution, where ESR was active. Therefore, although the stability of DTBTH(2+)-*S* in monomeric state is greater than is DTBTH(2+)-*T* in the calculated structures, the dimerization of the triplet-state dication in the solution should produce stabilization energy that is expected to be greater than ΔE.

The structure of DTBT(2+)-*S* was then optimized at the B3LYP/6–31G** level calculations, which led to a structure similar to DTBTH(2+)-*S* as the energy minimum with respect to the dihydrodithiino[5,6-*f*]benzotrithiole skeleton. In contrast, two ethyl groups exist on the *anti* side with respect to each other on the molecular plane. The shielding constants of the dications were then calculated by the B3LYP/6-31G** level, and the chemical shifts about the ^1H and ^{13}C NMR spectra were subsequently calculated from the differences between the shielding constants of the dication and those of tetramethylsilane. The calculated ^{13}C NMR chemical shifts of DTBT(2+)-*S* correlated well with those obtained experimentally, but the difference in the ^1H NMR chemical shifts was relatively large (Table 2). 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 to the benzene ring.

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

	S1–S2	S2–C1	S3–C3	S3–C4	C1–C1′	C1–C2	C2–C3	C3–C3′	C4–C4′
DTBTH(2+)-*S*	2.075	1.727	1.723	1.835	1.456	1.388	1.406	1.467	1.514
DTBTH(2+)-*T*	2.071	1.770	1.737	1.833	1.425	1.385	1.418	1.438	1.515

TABLE 2 ^1H and ^{13}C-NMR Chemical Shifts of DTBT(2+)-*S*

^1H	δ	Obs.	0.93	2.89	3.32			
		Calcd.	1.74	3.49	3.99			
^{13}C	δ	Obs.	12.6	30.0	32.3	140.8	161.0	164.7
		Calcd.	12.5	32.3	35.4	135.6	162.9	164.6

CONCLUSION

The radical cation, DTBT(•+), and the triplet-state dication, DTBT(2+)-*T*, were prepared by oxidation of DTBT with single-electron oxidizing reagents. The singlet-state dication, DTBT(2+)-*S*, was prepared by treating DTBT 5-O with concentrated D_2SO_4, and its structure was determined by ^1H and ^{13}C NMR spectroscopy. Disappearance of the NMR signal for DTBT(2+)-*S* suggests the isomerization of DTBT(2+)-*S* to DTBT(2+)-*T*, and the construction of the paired dication, 2DTBT(2+)-*T*. Furthermore, monomeric DTBT(2+)-*T* and paired 2DTBT(2+)-*T* should be in the equilibrium. MO calculations for DTBTH(2+)-*S* and DTBTH(2+)-*T* by using the DFT method show that DTBTH(2+)-*S* is more stable in monomeric form than is DTBTH(2+)-*T*. However, since the isomerization of the singlet-state dication proceeded in the solution, it is expected that the dimerization of the triplet-state dication should produce greater stabilization energy in the solution than the total energy difference between DTBTH(2+)-*S* and DTBTH(2+)-*T*.

EXPERIMENTAL

General

The NMR spectra were measured on a Bruker AC-400 spectrometer. The IR spectra were recorded using a JASCO FT-7300 spectrometer. The mass spectra were obtained using a JEOL JMS-700 mass spectrometer, a Hitachi M-2000 mass spectrometer, and a Shimadzu QP-2010 mass spectrometer. The UV spectra were measured using a JASCO V-570 spectrometer. The ESR spectra were recorded on a JEOL JES-SA100 spectrometer. The elemental analyses were performed using a Yanako MT5 analyzer. For X-ray crystallographic analysis, the data collection was made on a Rigaku AFC7R diffractometer with Cu $K\alpha$ and all calculations were performed using teXsan Structure Analysis Package, Molecular Structure Corp. (1985 and 1992). Concentrated D_2SO_4 was purchased from Kanto Chemical Co., Tokyo, Japan.

Computational Methods

All calculations were performed by the DFT method using Gaussian 98 program package. The structure optimization and the shielding constant calculation for DTBT(2+)-*S* were carried out at the B3LYP/6–31G** level. The structure optimization for DTBTH(2+)-*S* and DTBTH(2+)-*T* was performed by the similar procedure.

Oxidation of DTBT with mCPBA

DTBT (321 mg, 1.0 mmol) was treated with *m*CPBA (196 mg, 1.0 mmol, assay ≥88%) in CH_2Cl_2 (100 mL). After usual work-up, the products were purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:AcOEt = 1:1) to give DTBT 5-O in 67% (226 mg) together with DTBT 1-O (25 mg, 7%), DTBT 2-O (trace), DTBT 5,8-O2 (trace), and a mixture of bissulfoxides DTBT-O2 (trace).

DTBT 5-O: mp 158.0–159.0°C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, $J = 7.5$ Hz, 3H), 1.30 (t, $J = 7.5$ Hz, 3H), 2.65 (ddd, $J = 13.8$, 13.8, 2.7 Hz, 1H), 2.68 (q, $J = 7.5$ Hz, 2H), 3.05 (ddd, $J = 13.8$, 4.7, 2.7 Hz, 1H), 3.14 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.21 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.64 (ddd, $J = 13.8$, 4.7, 2.7 Hz, 1H), 3.89 (ddd, $J = 13.8$, 13.8, 2.7 Hz, 1H); ^{13}C NMR(101 MHz, $CDCl_3$) δ: 11.9, 14.4, 15.1, 28.0, 28.7, 41.9, 131.3, 131.6, 135.5, 137.3, 140.6, 146.2; IR (KBr): 1020 cm^{-1} (SO); MS (*m*/*z*) 334 (M^+); anal. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22. Found: C, 42.71; H, 4.44.

DTBT 1-O: mp 140–141°C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, $J = 7.5$ Hz, 3H), 1.32 (t, $J = 7.5$ Hz, 3H), 3.01 (dq, $J = 14.4$, 7.5 Hz, 1H), 3.07 (dq, $J = 14.4$, 7.5 Hz, 1H), 3.11–3.37 (m, 4H); ^{13}C NMR(101 MHz, $CDCl_3$) δ: 12.4, 14.8, 28.2, 29.7, 29.9, 30.8, 132.3, 136.1, 138.3, 139.1, 141.2, 147.3; IR (KBr): 1074 cm^{-1} (SO); MS (*m*/*z*): 334 (M^+); anal. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22. Found: C, 43.04; H, 4.20.

DTBT 2-O: mp 180–183°C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, $J = 7.5$ Hz, 6H), 2.94 (dq, $J = 14.2$, 7.5 Hz, 2H), 3.04 (dq, $J = 14.2$, 7.5 Hz, 2H), 3.10–3.33 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 13.0, 29.7, 30.9, 132.7, 134.2, 137.1; IR (KBr): 1116 cm^{-1} (SO); MS (*m*/*z*): 334 (M^+); anal. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22. Found: C, 43.07; H, 4.08.

Oxidation of DTBT with $NOPF_6$

When DTBT (64 mg, 0.2 mmol) was treated with $NOPF_6$ (70 mg, 0.4 mmol) in a mixed solvent of CH_2Cl_2 (20 mL) and CH_3CN (1 mL) at −78°C for 30 min and then with H_2O, DTBT 1-O and DTBT 2-O was obtained in 70% (47 mg) and 13% (9 mg) yields, respectively, together with recovery of DTBT in 14% (9 mg) yield.

Treatment of DTBT 5-O with Concentrated H_2SO_4

Compound DTBT 5-O (165 mg, 0.5 mmol) was dissolved in concentrated H_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 combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:AcOEt = 5:1) to give DTBT 1-O and DTBT 2-O in 41% (67 mg) and 20% (33 mg) yields, respectively [13].

DTBT-O2A: mp 180.5–182.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, $J = 7.6$ Hz, 3H), 1.50 (t, $J = 7.5$ Hz, 3H), 2.70 (dt, $J = 14.0$, 2.9 Hz, 1H), 3.01 (q, $J = 7.6$ Hz, 2H), 3.14 (ddd, $J = 13.5$, 4.5, 2.9 Hz, 2H), 3.56 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.64 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.71 (ddd, $J = 14.0$, 4.5, 2.4 Hz, 1H), 3.96 (dt, $J = 13.5$, 2.4 Hz, 1H); IR (KBr): 1083, 1023 cm^{-1} (SO); MS (m/z): 350 (M^+); anal. Calcd for $C_{12}H_{14}O_2S_5$: C, 41.11; H, 4.03. Found: C, 41.11; H, 4.01.

The crystal data for DTBT-O2A: monoclinic, $P2_1/c$ (#14), $a = 8.7569(8)$ Å, $b = 9.569(2)$ Å, $c = 18.2457(8)$ Å, $\beta = 101.368(5)°$, $V = 1498.9(3)$ Å^3, $Z = 4$, $D_{calc} = 1.553$ g/cm^3, μ(Cu Kα) = 70.81 cm^{-1}, 3118 reflections collected: 2920 unique reflection ($R_{int} = 0.051$), 2163 [$I > 1.50\sigma(I)$] used in the refinement, $R = 0.066$ ($R_w = 0.090$), GOF = 1.02.

Preparation of DTBT(•+)•PF_6^-

To a solution of DTBT (64 mg, 0.2 mmol) in Et_2O (10 mL), NOPF6 (35 mg, 0.2 mmol) in CH_3CN (1 mL) was added slowly at −78°C and the solution was stirred for 30 min at this temperature. After addition of a small amount of Et_2O, the solution was filtered under reduced pressure. A black green solid obtained was washed with Et_2O and then dried under vacuum. The radical cation DTBT(•+)•PF_6^- was obtained in 71% yield (66 mg); DTBT(•+)•PF_6^-: mp 92–93°C; ^{31}P NMR (162 MHz, CD_3CN, H_3PO_4) δ: −148.7 (sept, $J_{P-F} = 706$ Hz); ESR $g = 2.011$; anal. Calcd for $C_{12}H_{14}S_5PF_6$: C, 31.09; H, 3.04. Found: C, 31.42; H, 3.11.

Preparation of DTBT(2+)•2$SbCl_6^-$

To a solution of DTBT (63 mg, 0.2 mmol) in CH_2Cl_2 (10 mL), $SbCl_5$ (52 μL 0.4 mmol) in CH_2Cl_2 (10 mL) was added slowly at room temperature and the solution was stirred for 30 min at this temperature. A dark solid product precipitated was corrected by filtration, washed with CH_2Cl_2 (50 mL), and then dried under vacuum. DTBT(2+)•2$SbCl_6^-$ was obtained in 72% yield (142 mg); DTBT(2+)•2$SbCl_6^-$; mp 138°C; ESR $g = 2.013$; anal. Calcd for $C_{12}H_{14}S_5Sb_2Cl_{12}$: C, 14.59; H, 1.43. Found: C, 14.08; H, 1.79.

REFERENCES

[1] Williams, K. A.; Nowak, M. J.; Dormann, E.; Wudl, F. Synth Met 1986, 14, 233–238.
[2] Wolmershäuser, G.; Schnauber, M.; Wiltelm, T. Synth Met 1986, 14, 239–244.
[3] Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O. F., Jr.; Wudl, F. J Am Chem Soc 1987, 109, 2594–2599.
[4] Barclay, T. M.; Cordes, A. W.; de Laat, R. H.; Goddard, J. D.; Haddon, R. C.; Jeter, D. Y.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Patenaude, G. W.; Reed, R. W.; Westwood, N. P. C. J Am Chem Soc 1997, 119, 2633–2641.
[5] Barclay, T. M.; Cordes, A. W.; Goddard, J. D.; Mawhinney, R. C.; Oakley, R. T.; Preuss, K. E.; Reed, R. W. J Am Chem Soc 1997, 119, 12136–12141.
[6] Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. J Chem Soc, Chem Commun 1991, 358–360.
[7] Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. J Chem Soc, Dalton Trans 1992, 1563–1572.
[8] Wolmershäuser, G.; Heckmann, G. Angew Chem, Int Ed Engl 1992, 31, 779–780.
[9] Ogawa, S.; Kikuchi, T.; Niizuma, S.; Sato, R. J Chem Soc, Chem Commun 1994, 1593–1954.
[10] Ogawa, S.; Saito, S.; Kikuchi, T.; Kawai, Y.; Niizuma, S.; Sato, R. Chem Lett 1995, 321–324.
[11] Ogawa, S.; Ohmiya, T.; Kikuchi, T.; Kawaguchi, A.; Saito, S.; Sai, A.; Ohyama, N.; Kawai, Y.; Niizuma, S.; Nakajo, S.; Kimura, T.; Sato, R. J Organomet Chem 2000, 611, 136–145.
[12] Fanghänel, E.; Herrmann, R.; Narmann H. Tetrahedron 1995, 51, 2533–2542.
[13] Kimura, T.; Sasaki, T.; Yamaki, H.; Suzuki, E.; Niizuma, S. Eur J Org Chem 2003, 4902–4908.
[14] Kimura, T.; Ito, K.; Ogawa, S.; Sato, R.; Kawai, Y. Heteroatom Chem 2005, 16, 111–120.
[15] Kimura, T.; Ito, S.; Sasaki, T.; Niizuma, S.; Ogawa, S.; Sato, R.; Kawai, Y. Chem Lett 2002, 540–541.
[16] Kimura, T.; Hanzawa, M.; Ogawa, S.; Sato, R.; Fujii, T.; Kawai, Y. Heteroatom Chem 2003, 14, 88–94.
[17] Musker, W. K. Ace Chem Res 1980, 13, 200–206.
[18] Fujihara, H.; Furukawa, N. J Mol Struct (Theochem) 1988, 186, 261–272.
[19] Kimura, T.; Horie, Y.; Ogawa, S.; Fujihara, H.; Iwasaki, F.; Furukawa, N. Heterocycle 1992, 33, 101–104.
[20] Furukawa, N.; Kimura, T.; Horie, Y; Ogawa, S.; Fujihara, H. Tetrahedron Lett 1992, 33, 1489–1490.
[21] Kimura, T.; Tsujimura, T.; Mizusawa, S.; Ito, S.; Kawai, Y.; Ogawa, S.; Sato, R.; Tetrahedron Lett 2000, 41, 1801–1805.
[22] Kimura, T.; Mizusawa, S.; Yoneshima, A.; Ito, S.; Tsujimura, K.; Yamashita, T.; Kawai, Y.; Ogawa, S.; Sato, R. Bull Chem Soc Jpn 2002, 75, 2647–2653.
[23] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, Y. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.;

Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A. 11.1; Gaussian, Inc., Pittsburgh, PA, 2001.