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Synthesis, structure, and electrochemical properties of [2.2]paracyclophane[4,5-*d*]trithiole

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

A novel five-membered trithiole with sulfur–sulfur linkages bound to a [2.2]paracyclophane framework with low-redox potential has been synthesized. Characterization of the new trithiole was performed by X-ray crystallographic analysis. The cyclic voltammogram of the trithiole showed well-defined reversible electrochemical redox coupled with low-oxidation potential. Novel radical cation salt was isolated in quantitative yield in the one-electron oxidation of the trithiole with one equivalent of $NOPF_6$ as a one-electron oxidant. The structure of the radical cation salt was analyzed by ^{31}P NMR and EPR spectroscopies and elemental analysis. The salt underwent one-electron reduction on treatment with one equivalent of samarium(II) iodide to give the neutral starting trithiole quantitatively.

Keywords: cyclophane; trithiole, electron transfer; redox property; radical cation

1. Introduction

Our study aimed at the design of a reversible one-electron redox system with a low-redox potential using neutral trithioles. In the past, such trithioles have received little attention due to their lower stability, as they are known to be readily converted to origomeric or polymeric forms (*1*). Recently, we reported a new efficient method for the synthesis of stable trithioles fused to a benzene ring. These trithioles showed well-defined chemical and electrochemical redox behavior (*2*). Here we provide synthesis, structural characterization, and electrochemical properties of a new type trithiole bound to [2.2]paracyclophane to stabilize the five-membered trithiole unit. Furthermore, novel radical cation salt was isolated in quantitative yield in the one-electron oxidation of the trithiole, and the desired salt underwent one-electron reduction to give the neutral starting trithiole quantitatively.

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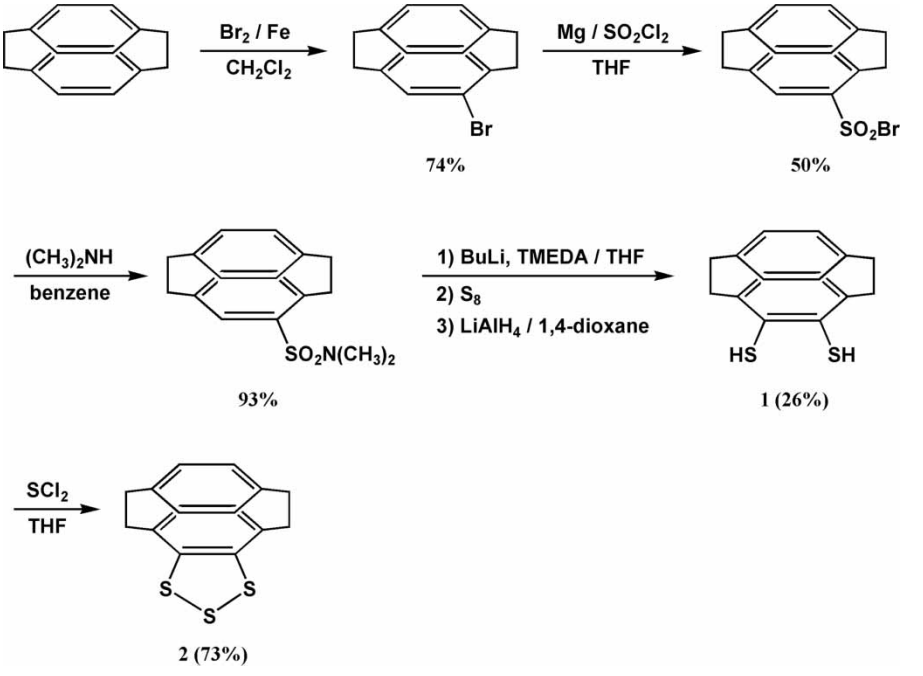
2. Results and discussion

2.1. *Synthesis of [2.2]paracyclophane-4,5-dithiol (1) and [2.2]paracyclophane[4,5-d]trithiole (2)*

The synthetic routes are shown in Scheme 1. [2.2]Paracyclophane-4,5-dithiol (**1**), a synthetic intermediate of the target [2.2]paracyclophane[4,5-*d*]trithiole (**2**), was prepared from commercially available [2.2]paracyclophane by adapting methods previously reported (*2*). 4-Bromo[2.2]paracyclophane, the precursor of the dithiol **1**, was prepared in 74% yield (*3*). Then a Grignard reaction and bromosulfonylation with sulfuryl chloride of the obtained bromo-derivative gave the corresponding 4-bromosulfonyl[2.2]paracyclophane as an isolated product in 50% yield. Treatment of 4-bromosulfonyl[2.2]paracyclophane with dimethylamine gave 4-(*N*,*N*-dimethylaminosulfonyl)[2.2]paracyclophane in 93% yield. Conversion into [2.2]paracyclophane-4,5-dithiol (**1**) was achieved in an overall 26% yield by ortho-lithiation (*4*) followed by reaction with elemental sulfur and reduction with LAH. Transformation into the trithiole **2** was successfully carried out by general method (*2*), namely by the reaction of the dithiol **1** with electrophile containing one sulfur unit, such as sulfur dichloride. Treatment of the dithiol **1** with sulfur dichloride afforded novel [2.2]paracyclophane[4,5-*d*]trithiole (**2**) in 73% yield.

2.2. *X-ray crystallographic analysis*

The crystal structure of the trithiole **2** was confirmed by X-ray crystallographic analysis (Figure 1, Table 1). The molecule has crystallographically imposed mirror symmetry. Two sulfur atoms at the 1 and 3-positions are almost coplanar with the fused benzene ring (S1–C3–C3*–S1* torsion angle is 0°), while the sulfur atom at the 2-position lie out of this plane (S1–S2–S1*–C3* torsion angle is 38.79(7)°). The distorted geometry of the 5-membered trithiole ring implies the presence



Scheme 1.

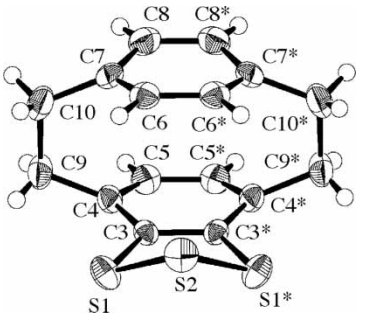
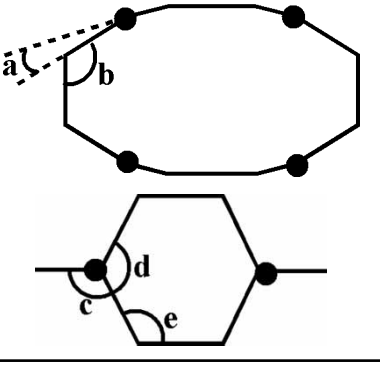


Figure 1. ORTEP drawing of compound **2**. Thermal ellipsoids are drawn at 50% probability. The atoms with an * in the atom label are at equivalent position (x, 1/2-y, z).

Table 1. Selected distance (Å) and angles (°) of 2 and [2,2]paracyclophane (PCP).

		PCP
Bond Length (Å)		
S1–S2	2.066(8)	
S1–C3	1.773(2)	
C3–C3*	1.402(4)	1.387
C5–C5*	1.380(4)	1.387
C9–C10	1.577(2)	1.562
Bond Angles (°)		
S1–S2–S1*	94.15(5)	
S2–C1–C3	95.50(7)	
S1–C3–C3*	117.27(7)	
C3–C4–C5	116.1(2)	118.8
C3–C4–C9	123.1(2)	120.4
Torsion Angles (°)		
S1–S2–S1*–C3*	38.79(7)	
S2–S1–C3–C3*	28.68(5)	
S1–C3–C3*–S1*	0	
Interatomic Distance (Å)		
C3–C6	3.086(3)	3.093
C5–C8	3.107(3)	3.093
Angles (°)		
a	9.9(2)	11.2
b	112.7(2)	113.7
c	123.1(2)	120.4
d	116.1(2)	118.8
e	120.9(2)	119.8



of lone pair–lone pair repulsion of the three divalent sulfur atoms. The sulfur–sulfur bond lengths of **2** are similar to those in S_8, and the sulfur–carbon(sp^2) bond lengths are marginally longer than those of the general sulfur–carbon(sp^2) single bond lengths (1.75 Å). The bond lengths, bond angles, and torsion angles are in good agreement with those of previously reported trithioles (*2*, *5*). In addition, as shown in Table 1, the structure of [2.2]paracyclophane framework of **2** arising from fused trithiole ring also marginally distorted, compared with the parent [2.2]paracyclophane (*6*).

2.3. *Electrochemical studies*

The solution redox property of the trithiole **2** was studied by the cyclic voltammetry technique. Cyclic voltammogram was measured in acetonitrile (MeCN) containing 0.1 M n-$Bu_4N^+ClO_4^-$ as a supporting electrolyte using a glassy carbon working electrode and Ag/0.01 M $AgNO_3$ couple in MeCN as a reference electrode at 20 °C under an argon atmosphere. Interestingly, the trithiole **2** exhibited one reversible one-electron step with low oxidation potential (Figure 2). The peak potentials of the oxidation peak (E_{pa}: 0.67 V), reduction peak (E_{pc}: 0.63 V), and half-wave ($E_{1/2}$: 0.60 V) have been found to be the lowest potentials among the trithioles of our previous system (*2*). Thus, the present result suggests that the desired stable one-electron oxidized species, trithiolium radical cation, may be generated during the electrochemical or chemical oxidation.

2.4. *One-electron redox reactions and EPR studies*

The result of the reversibility observed in cyclic voltammetry described above clearly indicates that the trithiole **2** provide the stable radical cation $\mathbf{2}^{\cdot+}$ even at room temperature. Indeed, the trithiolium radical cation salt $\mathbf{2}^{\cdot+}$ was readily isolated in the one-electron oxidation of the trithiole **2** with one equivalent of $NOPF_6$ in ether-MeCN (Scheme 2). The dark-blue salt was stable, and the structure of the radical ion in solution was analyzed by ^{31}P NMR and EPR (Figure 3) spectroscopies. The salt dissolved readily in THF or MeCN to give a dark-blue solution. The EPR spectrum of the solution showed the presence of a triplet peak ($g = 2.017$, aH = 0.120 mT) attributable to a

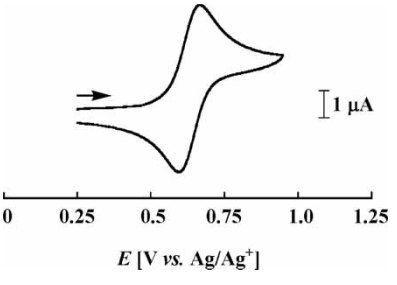
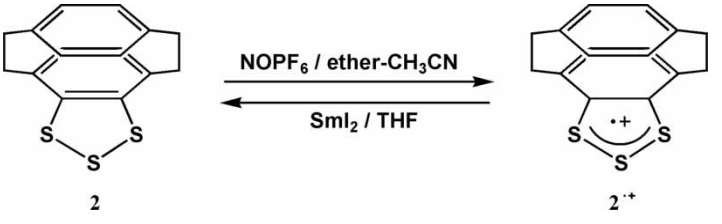


Figure 2. Cyclic voltammogram (scan rate: 100 mV s^{-1}) of compound **2**.



2 $\quad$ $\mathbf{2}^{\cdot+}$

Scheme 2.

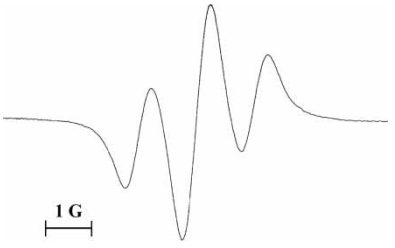


Figure 3. EPR spectrum of $\mathbf{2}^{\cdot+}$ in CH_3CN at $-30\,^{\circ}C$.

trithiolium radical cation. The aH splitting (triplet) suggests a partially spin delocalized system over both the trithiole and its fused benzene ring of [2.2]paracyclophane. Interestingly, the radical cation salt undergoes one-electron reduction to give trithiole quantitatively on treatment with samarium(II) iodide (Scheme 2) (*7*).

3. Conclusion

We have succeeded in the synthesis and structural characterization of a new type trithiole, [2.2]paracyclophane[4,5-*d*]trithiole, and its radical cation. Their facile interconversion in the one-electron redox reaction of the trithiole and its radical cation is ascribed to the destabilization of the distorted neutral trithiole framework by lone pair–lone pair repulsion and the unusual stabilization of the oxidized radical cation by the 7π electron framework.

4. Experimental

General melting points were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H (400 MHz), ^{13}C (101 MHz), and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker AC-400 instrument. Mass spectra were recorded on a Hitachi M-2000 spectrometer. IR spectra were obtained on a JASCO FT-7300 spectrometer. Elemental analyses were obtained using Yanaco MT-5 apparatus at the Elemental Analysis Division of Iwate University. Cyclic voltammetric experiments were performed by employing a Cypress Systems CS-1090. A three-electrode system was used, consisting of a glassy-carbon working electrode, a platinum wire auxiliary electrode and $Ag/0.01\,M\,AgNO_3$ reference electrode. The measurements were carried out in MeCN solution with 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte with scan rates 50–500 mV s^{-1} at 20 °C under an argon atmosphere. EPR data was taken in a JEOL RE 2X spectrometer working in the X-band with DPPH and Mn^{2+} on MgO as field markers. All solvents used in the reactions were purified by the general methods. The silica gel used for column chromatography was Wakogel C-200.

4.1. *Synthesis of 4-bromo[2.2]paracyclophane (6)*

To a refluxed solution of [2.2]paracyclophane (2.91 g, 14.0 mmol) and iron (38.0 mg, 0.68 mmol) in dichloromethane (CH_2Cl_2) (300 ml) was slowly added Br_2 (1.70 ml, 14.0 mmol) in CH_2Cl_2 (60 ml). After 19 h under reflux, aqueous sodium thiosulfate was added to the reaction mixture. The organic layer was extracted with CH_2Cl_2 and dried over anhydrous sodium sulfate (Na_2SO_4) and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with hexane/$CHCl_3$ (2:1 v/v) mixed solvent as an eluent to give 2.96 g (74%) of 4-bromo[2.2]paracyclophane as colorless crystals: mp 136 °C ((*6d*) mp 136–138 °C); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 2.78–3.23 (m, 7H, CH_2), 3.42–3.49 (m, 1H, CH_2), 6.43–6.57 (m, 7H, ArH), 7.16 (dd, $J = 8.8$ Hz, 1.9 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 33.5, 34.8, 35.4, 35.8, 126.9, 128.7, 131.4, 132.2, 132.9, 133.3, 135.0, 137.2, 139.1(2C), 139.3, 141.6; IR (KBr) ν 2926, 2851, 1586, 1543, 1497, 1476, 1391, 1036, 896, 795, 710, 641, 515 cm^{-1}.

4.2. *Synthesis of 4-bromosulfonyl[2.2]paracyclophane*

To a stirred solution of 4-bromo[2.2]paracyclophane (3.46 g, 12.0 mmol) and magnesium (0.365 g, 15.0 mmol) in anhydrous THF (48 ml) was added ethylene dibromide (0.50 ml). The mixture was stirred at room temperature for 2 h under an argon atmosphere. Sulfuryl chloride (1.92 ml, 24.0 mmol) was added to the mixture and stirred for 30 min at 0 °C. To the mixture was added water, which was then extracted with CH_2Cl_2, dried over anhydrous magnesium sulfate ($MgSO_4$) and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with hexane/$CHCl_3$ (2:1 v/v) mixed solvent as an eluent to give 2.13 g (50%) of 4-bromosulfonyl[2.2]paracyclophane as pale yellow crystals: mp 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03–3.11 (m, 3H, CH_2), 3.17–3.37 (m, 4H, CH_2), 4.02–4.08 (m, 1H, CH_2), 6.42 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.56 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.62 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.64 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.70 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.79 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 7.19 (d, $J = 1.7$ Hz, 1H ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 34.4, 34.8, 35.0, 35.2, 130.6, 132.5, 132.6, 132.75, 132.83, 138.2, 138.6, 139.3, 139.4, 139.9, 141.9, 145.6; IR (KBr) ν 2932, 2851, 1351, 1157, 913 cm^{-1}. MS m/z 350 (M^+); Anal. Calcd for $C_{16}H_{15}BrO_2S$: C, 54.71; H, 4.30%. Found C, 54.87; H, 4.28%.

4.3. *Synthesis of 4-(N,N-dimethylaminosulfonyl)[2.2]paracyclophane*

To a stirred solution of 4-bromosulfonyl[2.2]paracyclophane (208 mg, 0.60 mmol) in anhydrous benzene (5 ml) was added 50% aqueous solution of dimethylamine (0.15 ml, 1.50 mmol). After stirring for 1 h at room temperature, water was added to the reaction mixture, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give 175 mg (93%) of 4-(*N*,*N*-dimethylaminosulfonyl)[2.2]paracyclophane as colorless crystals: mp 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 6H, CH_3), 2.87–2.94 (m, 1H, CH_2), 2.94–3.24 (m, 5H, CH_2), 3.31–3.38 (m, 1H, CH_2), 3.92–3.98 (m, 1H, CH_2), 6.50–6.53 (m, 2H, ArH), 6.42 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.56 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H, ArH), 6.61 (d, $J = 7.9$ Hz, 1H, ArH), 6.68 (dd, $J = 7.9$ Hz, 1.7 Hz, 1H, ArH), 6.78–6.81 (m, 1H, ArH), 7.11 (d, $J = 7.9$ Hz, 1H, ArH) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 35.0, 35.2, 36.2, 35.5, 131.8, 132.3, 132.6, 132.7, 133.3, 133.9, 137.2, 137.3, 139.2, 139.5, 139.7, 140.9; IR (KBr) ν 2933, 1586, 1501, 1459, 1395, 1331, 1157, 1057, 946, 885, 852, 793, 710, 641, 589 cm^{-1}. MS m/z 315 (M^+); Anal. Calcd for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44%. Found C, 68.58; H, 6.65, N, 4.32%.

4.4. *Synthesis of [2.2]paracyclophane-4,5-dithiol (1)*

Butyllithium (1.92 ml of 1.54 M solution in hexane, 2.90 mmol) was added to a stirred solution of 4-(*N*,*N*-dimethylaminosulfonyl)[2.2]paracyclophane (315 mg, 1.00 mmol) and *N*, *N*, *N*′, *N*′-tetramethylethylenediamine (8.00 ml, 52.2 mmol) in THF (15 ml) at 0 °C. After 3 h at room temperature under an argon atmosphere, elemental sulfur (64.0 mg, 2.00 mmol) was added at 0 °C, and the reaction mixture was stirred for 17 h at room temperature. The reaction mixture was acidified with diluted hydrochloric acid solution, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on

silica gel with $CHCl_3$ as an eluent. Then, the obtained solution was concentrated *in vacuo* and the residue was dissolved in 1,4-dioxane (40 ml). The mixture was treated with lithium aluminum hydride (55.0 mg, 1.45 mmol) at 0 °C, and was stirred under reflux for 4 h. The reaction mixture was neutralized with diluted hydrochloric acid solution, extracted with ether, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with hexane/$CHCl_3$ (2:1 v/v) mixed solvent as an eluent to give 71.0 mg (26%) of [2.2]paracyclophane-4,5-dithiol (**1**) as pale yellow crystals: mp 166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79–2.86 (m, 1H, CH_2), 2.98–3.17 (m, 5H, CH_2), 3.36–3.42 (m, 1H, CH_2), 3.53 (s, 2H, SH), 6.43 (s, 2H, ArH), 6.52 (d, J = 1.1 Hz, 2H, ArH), 6.89 (d, J = 1.1 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.9, 35.6, 126.9, 131.6, 132.8, 132.9, 138.7, 140.1; IR (KBr) ν 2922, 1436, 1373, 1096, 852, 717, 519 cm^{-1}. MS m/z 272 (M^+); Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92%. Found C, 70.38; H, 5.89%.

4.5. *Synthesis of [2.2]paracyclophane[4,5-d]trithiole (2)*

To a solution of [2.2]paracyclophane-4,5-dithiol (430 mg, 1.58 mmol) in THF (15 ml) was added sulfur dichloride (0.152 ml, 2.40 mmol) in THF at −78 °C under a nitrogen atmosphere. After stirring for 30 min at −78 °C water was added to the reaction mixture, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with hexane/$CHCl_3$ (2:1 v/v) mixed solvent as an eluent to give 347 mg (73%) of [2.2]paracyclophane[4,5-*d*]trithiole (**2**) as orange crystals: mp 216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96–3.16 (m, 8H, CH_2), 6.26 (s, 2H, ArH), 6.61 (d, J=2.0 Hz, 2H, ArH), 7.13 (d, J=2.0 Hz, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 34.0, 36.3, 129.4, 132.7, 132.8, 136.7, 139.0, 141.9; IR (KBr) ν 2927, 1491, 1452, 1410, 1362, 851, 796, 717, 660, 575, 525 cm^{-1}. MS m/z 302 (M^+); Anal. Calcd for $C_{16}H_{14}S_3$: C, 63.53; H, 4.67%. Found C, 63.14; H, 4.46%.

4.6. *Synthesis of [2.2]paracyclophane[4,5-d]trithiolium hexafluorophosphate ($2^{\cdot+}PF_6^-$)*

A solution of [2.2]paracyclophane[4,5-*d*]trithiole (**2**) (151 mg, 0.500 mmol) in acetnitrile (2 ml) under argon was treated with nitrosonium hexafluorophosphate (263 mg, 1.50 mmol) in acetnitrile (3 ml) at −78 °C. The solution immediately changed from orange to dark blue. After stirring for 45 min at −78 °C, dry Et_2O (20 ml) was added to the mixture. The dark blue product was separated from the solution by filtration. The product was washed with Et_2O and dried under reduced pressure to give 156 mg (70%) of [2.2]paracyclophane[4,5-*d*]trithiolium hexafluorophosphate ($\mathbf{2}^{\cdot+}\mathbf{PF}_6^-$) as dark blue powder: mp 120 °C (decomp.); ^{31}P NMR (161 MHz, CD_3CN, relative to H_3PO_4) δ-143.7 (sept, J_{P-F} = 707 Hz); Anal. Calcd for $C_{16}H_{14}S_3PF_6$: C, 42.95; H, 3.15%. Found: C, 43.27; H, 3.48 %; X-band EPR (CH_3CN, 243 K) g = 2.017 (aH = 0.120 mT).

4.7. *The reduction with samarium(II) iodide of [2.2]paracyclophane[4,5-d]trithiolium hexafluorophosphate ($2^{\cdot+}PF_6^-$)*

A solution of [2.2]paracyclophane[4,5-*d*]trithiolium hexafluorophosphate ($\mathbf{2}^{\cdot+}\mathbf{PF}_6^-$) (44.7 mg, 0.100 mmol) in THF (5 ml) under argon was treated with 0.1 M samarium(II) iodide THF solution (1.0 ml; 0.100 mmol). The solution was stirred for 30 min at −78 °C and then poured into water. The organic layer was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and purified by column chromatography on silica gel with hexane/$CHCl_3$ (2:1 v/v) mixed solvent as an eluent to give 30.0 mg (quant.) of [2.2]paracyclophane[4,5-*d*]trithiole (**2**) as orange crystals.

5. X-ray crystallographic analysis of 2

The intensity data of **2** was collected on a Rigaku AFC7R diffractometer employing Cu-$K\alpha$(λ = 1.54178 Å) radiation using the $\omega/2\theta$ scan technique. The structures were determined by direct methods (SIR92) (*8*) and expanded using Fourier technique (DIRDIF94) (*9*). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically. The refinement was on Fobs. All calculations were performed using the teXsan (*10*) crystallographic software package of the Molecular Structure Corporation.

Crystal data for **2**: $M = 302.47$, $C_{16}H_{14}S_3$, orthorhombic, space group Pnma (#62), a = 17.796(2) Å, b = 9.258(1) Å, c = 8.028(1) Å, V = 1322.6(3) Å^3, $Z = 4$, $D_{calc} = 1.519\,g\,cm^{-3}$, $T = 293 \pm 1$ K, $\mu(CuK_\alpha) = 49.44\,cm^{-1}$. The final cycle of full-matrix least-squares refinement was based on 1181 observed reflections ($I > 1.50\sigma(I)$) and 117 variable parameters with $R = 0.046$, $wR = 0.076$.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: Deposition number CCDC-721900 for compound **2**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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