extremely large particles and accordingly very low specific surface area, which could not be even measured.

Thus, it can be concluded that materials for which a synthesis is reported here have a hydrotalcite-like structure, although its thermal stability is much lower than those of Ni-Al, Mg-Al, or Mg-Fe compounds with the same structure,[3,20,21] where no collapsing of the layered structure is observed below 523 and 573 K. It can be tentatively argued that this behavior is due to the presence of cations that can become oxidized during the hydrothermal treatment. Simultaneously, migration of the M(II) and/or M(III) cations from octahedral to tetrahedral sites of the lattice, leading to formation of spinel, may help the collapse of the HT-like structure. In fact, the Co(II) ions in spinel $Co_3O_4$ occupy tetrahedral sites and in its environment as $[CoO_4]$ species will give rise to electronic absorption bands around 400 nm, thus accounting for the increase in absorbance observed in the visible–UV/DR spectrum of sample M2 (Figure 3b).

**Acknowledgment.** We thank Mr. A. Montero (Universidad de Salamanca) and Unidad Estructural de Arcillas (IRNA-CSIC, Salamanca) for their assistance in obtaining some of the experimental data.

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# Synthesis and Physical Studies of a New Organic Donor: 2,3-Dimethyl-5,6:11,12-bis(dithio)tetracene[1,2]

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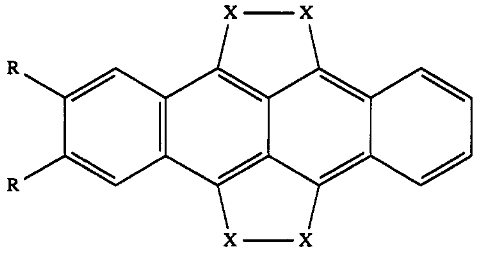
A new organic donor, 2,3-dimethyl-5,6:11,12-bis(dithio)tetracene (2,3-dimethyl-5,6,11,12-tetrathiotetracene, DMTTT), has been synthesized. Cyclic voltammetry of DMTTT in benzonitrile shows two reversible one-electron-transfer steps at 0.18 and 0.60 V vs the Ag/AgCl reference electrode. The electron spin resonance of $DMTTT^+$, generated in THF solution with trifluoroacetic acid, exhibits an 11-line hyperfine splitting spectrum with $g = 2.0078$. A single-crystal X-ray structure determination was carried out using crystals grown from chlorobenzene solution. The compound, $C_{20}H_{12}S_4\cdot[C_6H_5Cl]_{0.5}$, crystallizes in the triclinic space group $P\bar{1}$: $a = 7.635$ (1) Å, $b = 9.834$ (1) Å, $c = 13.214$ (2) Å, $\alpha = 100.39$ (1)°, $\beta = 101.46$ (1)°, $\gamma = 93.58$ (1)°, $V = 951.5$ (2) Å$^3$, and $Z = 2$. The structure involves linear chains of DMTTT molecules stacked along the $a$ axis, and the crystal lattice contains one solvent molecule per unit cell. Preliminary studies indicate the related donor DMTSeT can be prepared by using the reported synthetic scheme for DMTTT and that conducting charge-transfer salts of DMTTT can be prepared.

## Introduction

At room temperature, the electron donor 5,6,11,12-tetrathiotetracene (TTT, **1a**) and its selenium analogue (TSeT, **1b**) form charge-transfer salts that possess some of the highest electrical conductivities of any known synthetic metal.[3,4] A conductivity of ca. $10^3$ S/cm is observed for $(TTT)_2I_3$ at room temperature.[3] As the temperature of this salt is decreased, the conductivity increases, as does that of a metal, until ca. 35 K. At that point, it undergoes a metal-to-insulator (M–I) transition.



**1a** TTT: X = S, R = H

**1b** TSeT: X = Se, R = H

**2** DMTTT: X = S, R = $CH_3$

The introduction of a substituent or substituents into otherwise very symmetrical donors and acceptors (e.g., with original symmetry, $D_{2h}$) is known to suppress the temperature at which M–I transitions occur. A case in point is that of 2-fluorotetraselenotetracene (FTSeT), wherein the conductivity of the salt, $(FTSeT)_2Br$, increases smoothly from room temperature to 4.2 K.[5] Although the room-temperature conductivity of this salt is comparable to the other salts discussed above and the conductivity increases as the temperature is decreased, this salt never becomes superconducting.

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(1) Preliminary accounts of portions of this work have been presented at the March American Physical Society Meeting in St. Louis, MO, 20–24 Mar 1989 (*Bull. Am. Phys. Soc.* **1989**, *34*, 452), at the NATO Advanced Study Institute in Spetses Island, Greece, 21–23 June 1989 (*Lower Dimensional Systems and Molecular Devices*; Metzger, R. M., Day, P., Papavassiliou, G. C., Eds.; NATO ASI Series B: Physics; Plenum Publishing Co.: New York, 1991; p 205, in press), and at the Materials Research Society Meeting in Boston, MA, 27 Nov–2 Dec 1989 (*Electrical, Optical, and Magnetic Properties of Organic Solid State Materials*; Chiang, L. Y., Chaikin, P. M., Cowan, D. O., Eds.; Fall 1989, Materials Research Society Proceedings: Pittsburgh, 1990; Vol. 173, p 149).

(2) Maruo, T., Ph.D. Dissertation, University of Missouri—St. Louis, 1990.

(3) Shchegolev, I. F.; Yagubskii, E. B. In *Linear Extended Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 2, p 385 and references therein.

(4) Jones, M. T.; Jansen, S. A.; Acampora, L. A.; Sandman, D. J. *J. Phys. (France)* **1983**, *44*, C3-1159.

(5) Hilti, B.; Mayer, C. W.; Rihs, G.; Loeliger, H.; Paltzer, P. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 267.

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In light of the observation that the introduction of fluorine in the 2 position of TSeT suppresses the M–I transition, it was decided to introduce another substituent into the TTT family. For this purpose two methyl groups, one each in the 2 and 3 positions, respectively, were selected. The two methyl groups in DMTTT are placed in such a way that the symmetry of the donor is $C_{2v}$. The methyl group has the added advantage over fluorine substitution in that it is expected to introduce three dimensionality into the crystal structure of the charge-transfer complexes of DMTTT such that the complexes will resist the tendency to undergo metal-to-insulator transitions at lower temperatures.

Another problem in working with tetrathiotetracene and its tetrachalcogeno relatives is that their syntheses are complicated because of their relative insolubilities, which makes purification and handling of these materials difficult. The methyl group was selected as the substituent because it was expected to impart improved solubility to the parent compound because of its size. Moreover, it was expected to enhance the electron-donating ability of DMTTT, **2**, compared to TTT, **1a**.

Finally, as in the case of tetramethyltetraselenafulvalene (TMTSeF), the methyl group may weakly interact with the anion chain to prevent the potential phase transition that can arise from anion ordering.

## Experimental Section

**General Information.** Anhydrous solvents used in the reactions were prepared from reagent grade solvents (under Ar atmosphere) as indicated below. Benzene and toluene were distilled over sodium; hexane was distilled over sodium or calcium hydride, methanol over magnesium turnings, and methylene chloride over anhydrous calcium chloride; *N*,*N*-dimethylformamide (DMF), chlorobenzene, 1,2,4-trichlorobenzene (TCB), nitrobenzene, and benzonitrile were stored over molecular sieves or $P_2O_5$ and then distilled under reduced pressure.

**Preparation of 4,5-Dimethylphthalic Anhydride, 3.** 4,5-Dimethylphthalic anhydride, **3**, was prepared by the Diels–Alder reaction of maleic anhydride and 2,3-dimethyl-1,3-butadiene and subsequent aromatization of 4,5-dimethyltetrahydrophthalic anhydride by heating with sulfur. The removal of excess sulfur from the product by extraction with water gave 4,5-dimethylphthalic acid, which on dehydration with acetic anhydride and recrystallization from benzene afforded the sulfur-free anhydride, **3**, as colorless shiny flakes; mp 206 °C; IR (KBr, $cm^{-1}$) 1850, 1770, 1615, 1460, 1395, 1345, 1290, 1260, 1200, 1110, 1060, 1015, 910, 895, 740, 635, 530; $^1H$ NMR ($CDCl_3$) $\delta$ 2.43 (s, 6 H, 2 × $CH_3$), 7.40 (s, 2 H, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.81, 126.16, 129.23, 146.56, 163.1; MS (EI, 70 eV) 176 ($M^+$, 100) (calcd for $C_{10}H_8O_3$: 176.17).

**Preparation of 2,3-Dimethyl-6,11-dihydro-5,12-tetracenequinone, 5.** Boric oxide (6.5 g, 93 mmol), 4,5-dimethylphthalic anhydride (**3**, 14.5 g, 82.3 mmol), and 1,4-naphthalenediol (**4**, 13.6, 84.9 mmol), were mixed and ground to a fine powder and then heated to 200 °C for 2 h in a 300-mL round-bottom flask in an oil bath. The crude product, a red solid, was then scratched from the side of the flask. The solid was boiled with water (about 2000 mL) and filtered to remove any reacted boric oxide and 4,5-dimethylphthalic anhydride. The solid was ground to a fine powder in a mortar and then boiled again with water (about 1000 mL) and filtered. The red solid was washed several times with methanol, until the filtrate was almost colorless. The product was recrystallized from benzene to give an orange-red crystalline solid, 12.6 g, 48%; mp 322–4 °C; IR (KBr, $cm^{-1}$) 3450 (br, OH), 1630, 1585, 1512, 1470, 1275, 1020, 875, 740; $^1H$ NMR ($CDCl_3$) $\delta$ 2.46 (s, 6 H, 2 × $CH_3$), 7.80 (m, 2 H, Ar H), 8.28 (s, 2 H, Ar H), 8.45 (m, 2 H, Ar H); MS (EI, 70 eV) 318 ($M^+$, 100) (calcd for $C_{20}H_{14}O_4$: 318.31). Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.34; H, 4.42.

**2,3-Dimethyl-5,6,11,12-tetrachlorotetracene (DMTClT, 6).** 2,3-Dimethyl-6,11-dihydroxy-5,12-tetracenequinone (**5**, 12.4 g, 39.0 mmol), $PCl_5$ (48.7 g, 234 mmol), and $POCl_3$ (150 mL) were refluxed for 5 h. After cooling to room temperature, the resulting pale yellow solid[6] was filtered and washed with acetic acid, $H_2O$, and methanol, with a yield of 11.8 g. A mixture of the pale yellow solid (11.8 g), NaI (20.7 g, 138 mmol), and DMF (200 mL) was refluxed for 1 h. The red solution was filtered hot, and the filtrate was concentrated and cooled. The resulting red-purple needles were filtered and washed with $H_2O$ and methanol. Recrystallization from $CHCl_3$ gave dark red needles, 8.8 g, 57%; mp 212–3 °C; IR (KBr, $cm^{-1}$) 3075 (w), 2940 (w), 2920 (w), 1635 (w), 1460 (s), 1445 (w), 1385 (m), 1350 (m), 1278 (vs), 1200 (m), 1122 (s), 1030 (w), 1015 (m), 955 (m), 895 (m), 868 (w), 860 (m), 752 (s, C–Cl), 658 (s), 632 (w); $^1H$ NMR ($CDCl_3$) $\delta$ 2.52 (s, 6 H, 2 × $CH_3$), 7.58 (m, 2 H, Ar H), 8.32 (s, 2 H, Ar H), 8.58 (m, 2 H, Ar H); MS (EI, 70 eV) 396 (M + 2, 34), 394 ($M^+$, 69), 375 (50), 374 (12), 373 (50), 354 (100), 226 (45), 113 (13) (calcd for $C_{20}H_{14}Cl_4$: 394.31). Anal. Calcd for $C_{20}H_{14}Cl_4$: C, 60.95; H, 3.07. Found: C, 59.57; H, 2.96.

**2,3-Dimethyl-5,6,11,12-tetrathiotetracene,[7] 2.** Sulfur (1.60 g, 49.9 mmol) and HMPA[8] (15 mL) were introduced into a 250-mL three-neck boiling flask. The mixture was stirred and heated at 100 °C in an oil bath under Ar. Small pieces of sodium metal (1.10 g, 47.8 mmol) were added slowly. After the Na metal had reacted, DMTClT (**6**, 2.00 g, 5.1 mmol) suspended in HMPA (135 mL) was added, and the resulting solution was heated at 100 °C for 24 h under Ar. Excess solvent (HMPA) was distilled from the reaction flask at reduced pressure. The resulting solid was filtered and washed with water and MeOH until the washings became clear. About 2.0 g of crude product was obtained. The crude product was washed several times with hexane until the filtrate was no longer purple.[9] The hexane-washed crude product was sublimed two or more times (~250 °C at $10^{-5}$ Torr) and finally recrystallized from chlorobenzene to give very dark green needles of DMTTT, 600 mg, 31%; mp 300–5 °C (melt with decomposition); IR (KBr, $cm^{-1}$) 1622, 1605, 1470, 1440, 1315, 1300, 1232, 1150, 840, 735, 680; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.59 (s, 6 H, 2 × $CH_3$), 7.30 (m, 6 H, Ar H); MS (EI, 70 eV) 382 (M + 2, 20), 381 (M + 1, 26), 380 ($M^+$, 100), 347 (13), 190 (16) (calcd for $C_{20}H_{12}S_4$: 380.55). Anal. Calcd (sublimed sample) for $C_{20}H_{12}S_4$: C, 63.12; H, 3.18; S, 33.70. Found: C, 62.42; H, 3.33; S, 33.11.

**Physical Measurements.** Nuclear magnetic resonance (NMR) studies were conducted on a Varian XL FT 300 spectrometer. Proton ($^1H$) NMR spectra were measured at 300 MHz, and carbon ($^{13}C$) NMR spectra were measured at 75 MHz. Samples were dissolved in chloroform-*d* ($CDCl_3$) unless otherwise indicated. For $^1H$ NMR spectra, the 7.24 ppm resonance of residual chloroform was used as an internal standard. For $^{13}C$ NMR spectra, the $CDCl_3$ resonance at 77.00 ppm was used as an internal standard. The infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 grating spectrophotometer in KBr pellets, and only the principal bands are reported. Melting points

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(6) This pale yellow solid, which has not been fully characterized, is believed to be 2,3-dimethyl-5,5,6,11,12,12-hexachlorotetracene; $^1H$ NMR ($CDCl_3$) $\delta$ 2.56 (s, 6 H, 2 × $CH_3$), 7.77 (m, 2 H, Ar H), 8.29 (m, 2 H, Ar H), 8.47 (s, 2 H, Ar H).

(7) The selenium analogue, 2,3-dimethy-5,6,11,12-tetraselenotetracene (DMTSeT) was also synthesized by the reaction of **6** with $Na_2Se_2$ in DMF, however, in low yield. DMTSeT was recrystallized and sublimed several times to yield a dark green solid (chlorobenzene); IR (KBr, $cm^{-1}$) 1470, 1450, 1386, 1289, 1113, 1025, 955, 908, 887, 738, 472. Anal. Calcd for $C_{20}H_{12}Se_4$: C, 42.28; H, 2.13, Se, 55.59. Found: C, 42.89; H, 2.26; Se, 51.48.

(8) The use of HPMA as the solvent significantly improves the yield of DMTTT over DMF, which was used initially.

(9) The reaction of **6** with $Na_2S_2$ also yields 2,3-dimethyl-5,6-dithiotetracene (DMDTT) as a minor product. It was isolated from hexane washings as well as from sublimation of crude DMTTT at low temperature. Purification by resublimation and recrystallization from hexane yielded a purple microcrystalline solid; mp 208–9 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.38 (s, 3 H, $CH_3$), 2.39 (s, 3 H, $CH_3$), 7.30 (m, 3 H, Ar H), 7.56 (m, 1 H, Ar H), 7.58 (m, 1 H, Ar H), 7.83 (m, 1 H, Ar H), 7.89 (m, 1 H, Ar H), 7.98 (m, 1 H, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.42 ($CH_3$), 119.21, 119.48, 123.00, 123.55, 124.02, 124.81, 125.82, 127.46, 128.92, 131.23, 132.40, 132.72, 134.96, 136.58; MS (EI, 70 eV) 320 (M + 2, 10), 319 (M + 1, 24), 318 ($M^+$, 100) (calcd for $C_{20}H_{14}S_2$: 318.43). The isolation of DMDTT from the reaction of **6** with $Na_2S_2$ implies a reductive process as is observed, also, with $Na_2Se_2$ and $Na_2Te_2$. See: Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739. Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549. Stark, J. C.; Reed, R.; Acampora, L. A.; Sandman, D. J.; Jansen, S.; Jones, M. T.; Foxman, B. M. *Organometallics* **1984**, *4*, 732.

were measured on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Mass spectra (MS) were recorded on a Hewlett-Packard HP-5988A twin EI and CI quadrupole mass spectrometer at 70 eV by a direct probe and RTE data station. Pertinent peaks are reported as $m/z$ (relative intensity). Electronic absorption spectroscopy measurements were done on a Varian Cary-2200 spectrometer equipped with a DS-15 data station. Anhydrous benzene and chlorobenzene were used as solvents, and the cation radical was prepared by the addition of trifluoroacetic acid to the DMTTT and TTT solutions. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

**Cyclic Voltammetry.** Measurements were recorded with a Princeton Applied Research Model EG&G PARC 273 potentiostat/galvanostat. A single-compartment, three-electrode cell was employed with a platinum wire working electrode, a platinum disk (1.5-mm diameter) counter electrode, and an Ag/AgCl reference electrode. Measurements were performed in anhydrous benzonitrile solutions using 0.10 M of recrystallized and dried tetrabutylammonium hexafluorophosphate, ($(n\text{-}C_4H_9)_4NPF_6$) as the supporting electrolyte. The Ag/AgCl reference electrode is stable under these solutions. Concentrations of the solutions were $2.5 \times 10^{-4}$ M for both TTT and DMTTT. All solutions were purged with Ar for 10 min immediately prior to each scan. A blanks solution containing no TTT or DMTTT was scanned from −0.5 to +1.0 V vs Ag/AgCl and exhibited no redox current within these potential limits. The solutions of TTT and DMTTT were scanned from −0.5 to +1.0 V vs Ag/AgCl at a scan rate of 100 and 500 mV/s.

**Electron Spin Resonance.** ESR spectra were recorded on a Varian E-12 that has been described previously.[10] Anhydrous methylene chloride and tetrahydrofuran were used as the solvents for the DMTTT solutions to generate the cation radical by the addition of trifluoroacetic acid. The solutions were degassed by the freeze–pump–thaw technique.

**Crystallography.** Single crystals of DMTTT were obtained by slow cooling of a chlorobenzene solution. A single crystal was mounted in a random orientation on a glass fiber. Preliminary examination and data collection were carried out with Mo K radiation on a Siemens R3 diffractometer. Due to the small size of the crystal, data could be collected only up to $2\theta_{max} = 35°$. Data were collected by using the $2\theta$–$\theta$ technique in the triclinic crystal system. Out of a total 1345 reflections, 566 are observed ($F_o > 4.0\sigma F_o$). Intensities of three standard reflections were monitored every 50 reflections. No significant variation of intensity was observed for the standards during the data collection; hence, no decay correction was applied. No absorption correction was applied to the data. Summaries of the crystal data and intensity collection parameters are given in Table I.

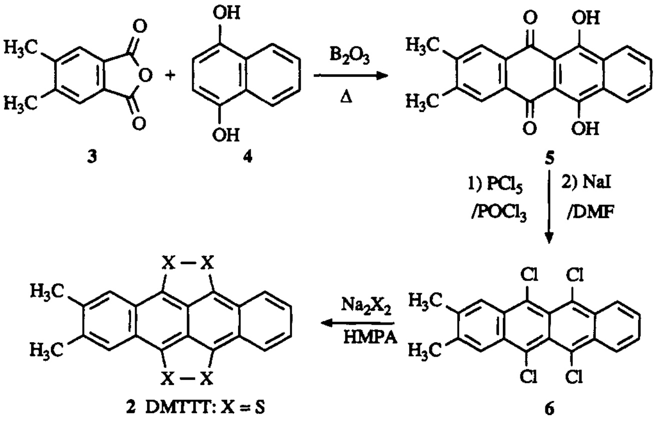
Data reduction, structure solution, and refinement were carried out by the SHELXTL-PLUS structure solution software package.[11] The structure was solved by direct methods and refined successfully in the space group $P\bar{1}$. The rest of the non-hydrogen atoms were located from subsequent difference Fourier syntheses. Full-matrix least-squares refinement was carried out by minimizing the function $w(F_o - F_c)^2$. Hydrogen atoms were calculated in their ideal geometry and were held fixed, whereas non-hydrogen atoms were refined anisotropically to convergence. All planar motifs were found to be within a deviation of 0.007 and 0.01 Å. The final refinement parameters are listed in Table I.

All calculations were performed on a VAX Station II GPX using SHELXTL-PLUS structure solution software.

**Table I. Structure Determination Summary**

| | |
|---|---|
| | Crystal Data |
| empirical formula | $C_{23}H_{14.5000}S_4Cl_{0.5000}$ |
| color, habit | dark green needles |
| cryst size | 0.4 × 0.1 × 0.1 mm |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| unit cell dimens | $a = 7.6350\ (10)$ Å<br>$b = 9.8340\ (10)$ Å<br>$c = 13.214\ (2)$ Å<br>$\alpha = 100.390\ (10)°$<br>$\beta = 101.460\ (10)°$<br>$\gamma = 93.580\ (10)°$ |
| volume | 951.5 (2) $Å^3$ |
| $Z$ | 2 |
| formula wt | 436.8 |
| density (calcd) | 1.525 $Mg/m^3$ |
| abs coeff | 0.556 $mm^{-1}$ |
| $F(000)$ | 450 |
| | Data Collection |
| diffractometer used | Siemens R3m/V |
| radiation | Mo K$\alpha$ ($\lambda = 0.71069$ Å) |
| temp | 293 K |
| monochromator | highly oriented graphite crystal |
| $2\theta$ range | 3.5–35.0° |
| scan type | $2\theta$–$\theta$ |
| scan speed | variable; 4.00–15.00°/min in $\omega$ |
| scan range ($\omega$) | 0.60° plus K$\alpha$ separation |
| background meas | stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time |
| std reflns | 3 measd every 50 reflns |
| index ranges | $0 \le h \le 6$, $-8 \le k \le 8$, $-11 \le l \le 10$ |
| reflns coll | 1345 |
| indep reflns | 1207 ($R_{int} = 0.98\%$) |
| obsd reflns | 566 ($F > 4.0\sigma(F)$) |
| abs corr | N/A |
| | Solution and Refinement |
| syst used | Siemens SHELXTL-PLUS (MicroVAX II) |
| solution | direct methods |
| refinement method | full-matrix least-squares |
| quantity minimized | $\sum w(F_o - F_c)^2$ |
| absolute configuration | N/A |
| extinction correction | N/A |
| hydrogen atoms | riding model, fixed isotropic $U$ |
| weighting scheme | unit weights |
| final $R$ indexes (obsd data) | $R = 4.69\%$, $R_w = 4.85\%$ |
| $R$ indexes (all data) | $R = 9.10\%$, $R_w = 7.43\%$ |
| goodness-of-fit | 1.72 |
| largest and mean $\Delta/\sigma$ | 0.002, 0.000 |
| data-to-parameter ratio | 4.3:1 |
| largest difference peak | 0.47 e $Å^{-3}$ |
| largest difference hole | −0.33 e $Å^{-3}$ |

**Scheme I**



## Results and Discussion

**Synthesis.** The synthesis of 2,3-dimethyl-5,6,11,12-tetrathiotetracene, 2, is summarized in Scheme I. Detailed procedures are given in the Experimental Section. 2,3-Dimethyl-5,6,11,12-tetrachlorotetracene, 6, synthesized from chlorination and dehydrochlorination of 2,3-dimethyl-6,11-dihydroxy-5,12-tetracenequinone, 5, was reacted with $Na_2S_2$ prepared in situ from sodium and sulfur in the aprotic solvent HMPA at 100 °C for 24 h to give

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[10] Rataiczak, R. D.; Jones, M. T.; Reeder, J. R.; Sandman, D. J. *Mol. Phys.* **1985**, *56*, 65.

[11] Sheldrick, G. M. Siemens Analytical X-ray Division; Madison, WI, 1989.

**Table II. Redox Potentials (volts) of DMTTT and TTT**[a,b]

| compd | $E_{pa}^1$ | $E_{pc}^1$ | $E_{pa}^2$ | $E_{pc}^2$ |
|---|---|---|---|---|
| TTT | 0.26 | 0.18 | 0.67 | 0.59 |
| DMTTT | 0.18 | 0.11 | 0.60 | 0.54 |

[a] Measured in benzonitrile solution. [b] 0.10 M $(n\text{-}C_4H_9)_4NPF_6$ was the supporting electrolyte, and the reference electrode was Ag/AgCl.

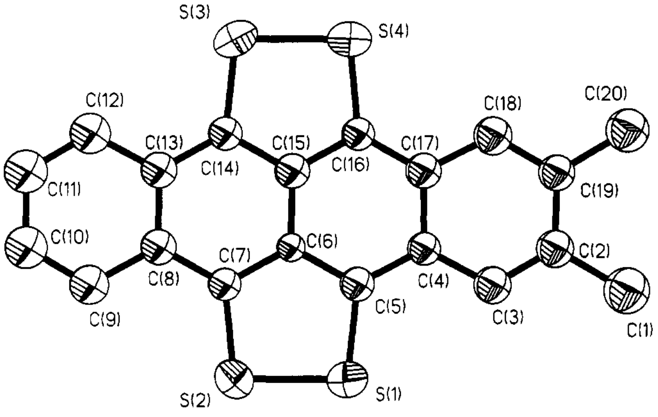

**Figure 1.** Projection view of DMTTT, showing atom-labeling scheme, with 50% probability ellipsoids.

DMTTT, 2. The purification of DMTTT was accomplished by repetitive sublimation. However, initial sublimation of the crude product gave a purple compound at low temperature (~200 °C at $10^{-5}$ Torr), which was characterized as 2,3-dimethyl-5,6-dithiotetracene (DMDTT).[10] DMTTT sublimed at a higher temperature (~250 °C at $10^{-5}$ Torr) as a dark green powder, which was recrystallized from chlorobenzene to give dark green needles of solvated DMTTT. The differences in physical properties between DMDTT and DMTTT are not unexpected (i.e., that DMDTT sublimes at a lower temperature than DMTTT and that the two materials have different colors in the solid state).

**Cyclic Voltammetry.** Cyclic voltammetry traces for TTT and DMTTT have been obtained, and the results are summarized in Table II. Two reversible one-electron steps are observed for each compound. As expected, the trace for DMTTT is shifted to more negative potentials relative to TTT. Thus, DMTTT transfers its electron more readily than TTT.

**Electronic Spectra.** The electronic absorption spectrum of DMTTT in benzene displays three absorption bands at 470, 635, and 693 nm, which compares with those observed at 472, 642, and 701 nm for TTT in benzene.

The molar absorptivity, or extinction coefficient, at the 696-nm peak for DMTTT and at the 701-nm peak for TTT were determined as 1.21 × $10^4$ and 1.02 × $10^4$ L/mol cm, respectively, in chlorobenzene. The extinction coefficient of TTT agrees with reported values of 1.1 × $10^4$ and 1.3 × $10^4$ L/mol cm, both in benzene.[12,13]

**Solubility.** Using the extinction coefficient at 696 nm for DMTTT and 701 for TTT, the solubilities of both compounds were determined. The DMTTT is ~20% more soluble in chlorobenzene on a molar basis than TTT. The solubilities are difficult to measure quantitatively because both TTT and DMTTT tend to form supersaturated solutions that return to equilibrium very slowly. Although this increase is not a major one, it does aid in the purification of DMTTT.

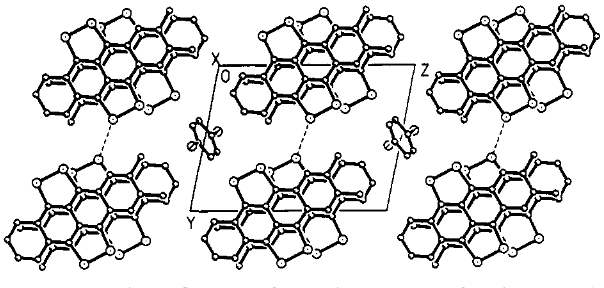

**Figure 2.** Packing diagram down the *a* axis with solvent molecules.

**Table III. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ × $10^3$)**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| S(1) | 2714 (7) | 2684 (5) | 6366 (4) | 64 (2) |
| S(2) | 1440 (7) | 3616 (5) | 5165 (4) | 64 (3) |
| S(3) | 786 (7) | −2024 (6) | 1931 (4) | 71 (3) |
| S(4) | 2045 (7) | −2969 (5) | 3135 (4) | 68 (3) |
| C(1) | 5730 (22) | −1094 (17) | 8478 (12) | 75 (6) |
| C(2) | 4811 (23) | −1199 (18) | 7318 (13) | 51 (6) |
| C(3) | 4208 (21) | −49 (17) | 7008 (12) | 46 (5) |
| C(4) | 3316 (25) | −114 (18) | 5935 (14) | 37 (5) |
| C(5) | 2615 (22) | 1017 (16) | 5559 (14) | 39 (5) |
| C(6) | 1733 (20) | 948 (18) | 4512 (13) | 30 (5) |
| C(7) | 1069 (21) | 2124 (16) | 4172 (12) | 36 (5) |
| C(8) | 258 (21) | 2048 (17) | 3129 (13) | 45 (5) |
| C(9) | −438 (21) | 3247 (17) | 2754 (13) | 58 (6) |
| C(10) | −1203 (22) | 3155 (19) | 1736 (14) | 63 (6) |
| C(11) | −1362 (24) | 1895 (19) | 1005 (14) | 66 (6) |
| c(12) | −747 (22) | 718 (17) | 1317 (13) | 59 (6) |
| c(13) | 89 (23) | 756 (18) | 2387 (14) | 47 (5) |
| C(14) | 762 (22) | −398 (16) | 2723 (13) | 43 (5) |
| C(15) | 1580 (22) | −340 (19) | 3793 (14) | 49 (6) |
| C(16) | 2303 (21) | −1478 (15) | 4135 (12) | 36 (5) |
| C(17) | 3145 (22) | −1404 (16) | 5181 (12) | 40 (5) |
| C(18) | 3883 (21) | −2547 (17) | 5572 (13) | 51 (6) |
| C(19) | 4691 (21) | −2467 (17) | 6617 (14) | 51 (5) |
| C(20) | 5356 (22) | −3784 (16) | 6958 (12) | 64 (6) |
| Cl | 1709 (15) | 4477 (11) | 573 (8) | 94 (4) |
| C(91) | 3724 (21) | 4865 (27) | 281 (18) | 115 (8) |
| C((2) | 3883 (32) | 3732 (23) | −486 (17) | 115 (8) |
| C(93) | 5456 (32) | 4029 (26) | −788 (17) | 117 (8) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Crystal Structure.** Figure 1 shows the molecular structure of DMTTT. The single-crystal X-ray diffraction studies of neutral DMTTT crystallized from chlorobenzene provide the final and definitive proof that DMTTT has been synthesized. The results of the single-crystal X-ray diffraction study show that the DMTTT molecules stack in a pancake fashion within the crystal lattice and that the orientation of the methyl groups alternates such that there is a local center of inversion symmetry between pairs of DMTTT molecules. In addition, one solvent molecule per unit cell is oriented approximately perpendicular to the planes of the DMTTT molecules. Due to the imposed crystallographic $\bar{1}$ symmetry, the solvent molecules are disordered (i.e., there are two 0.5 occupying Cl atoms related by the 1 center. A packing diagram looking down the *a* axis is shown in Figure 2 and along the *b* axis in Figure 3. A summary of the structure determination (atomic coordinates, bond distances, and bond angles) is given in Tables III–V, respectively.

The average intramolecular S–S distance of 2.084 Å is comparable to the reported S–S distance of 2.100 Å for TTT.[14] The average C–S distance of 1.758 Å also agrees

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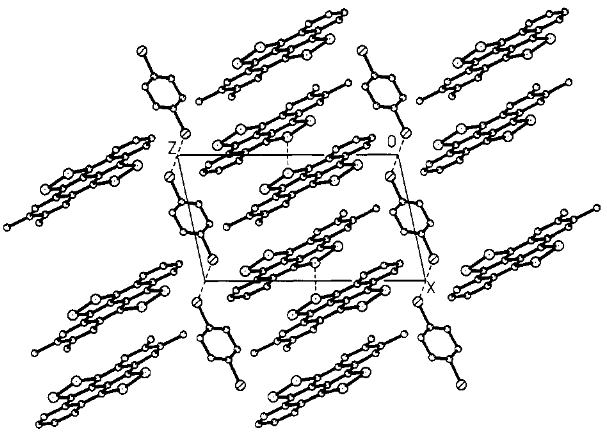

**Figure 3.** Packing diagram down the *b* axis with solvent molecules.

**Table IV. Bond Lengths (angstroms)**

| | | | |
|---|---|---|---|
| S(1)–S(2) | 2.080 (7) | S(1)–C(5) | 1.776 (16) |
| S(2)–C(7) | 1.749 (15) | S(3)–S(4) | 2.087 (7) |
| S(3)–C(14) | 1.749 (16) | S(4)–C(16) | 1.759 (15) |
| C(1)–C(2) | 1.537 (22) | C(2)–C(3) | 1.347 (25) |
| C(2)–C(19) | 1.399 (22) | C(3)–C(4) | 1.434 (23) |
| C(4)–C(5) | 1.393 (25) | C(4)–C(17) | 1.445 (22) |
| C(5)–C(6) | 1.400 (23) | C(6)–C(7) | 1.403 (24) |
| C(6)–C(15) | 1.423 (23) | C(7)–C(8) | 1.381 (22) |
| C(8)–C(9) | 1.450 (25) | C(8)–C(13) | 1.440 (23) |
| C(9)–C(10) | 1.339 (24) | C(10)–C(11) | 1.410 (24) |
| C(11)–C(12) | 1.375 (26) | C(12)–C(13) | 1.424 (24) |
| C(13)–C(14) | 1.383 (25) | C(14)–C(15) | 1.417 (24) |
| C(15)–C(16) | 1.386 (25) | C(16)–C(17) | 1.392 (21) |
| C(17)–C(18) | 1.421 (24) | C(18)–C(19) | 1.381 (23) |
| C(19)–C(20) | 1.530 (24) | Cl–C(91) | 1.697 (23) |
| C(91)–C(92) | 1.394 (32) | C(91)–C(93A) | 1.228 (31) |
| C(92)–C(93) | 1.370 (36) | C(93)–C(91A) | 1.228 (31) |

**Table V. Bond Angles (degrees)**

| | | | |
|---|---|---|---|
| S(2)–S(1)–C(5) | 95.5 (6) | S(1)–S(2)–C(7) | 96.3 (6) |
| S(4)–S(3)–C(14) | 96.5 (6) | S(3)–S(4)–C(16) | 95.3 (6) |
| C(1)–C(2)–C(3) | 118.5 (14) | C(1)–C(2)–C(19) | 118.9 (16) |
| C(3)–C(2)–C(19) | 122.5 (15) | C(2)–C(3)–C(4) | 120.0 (14) |
| C(3)–C(4)–C(5) | 123.6 (15) | C(3)–C(4)–C(17) | 119.5 (16) |
| C(5)–C(4)–C(17) | 117.0 (15) | S(1)–C(5)–C(4) | 123.3 (13) |
| S(1)–C(5)–C(6) | 113.3 (13) | C(4)–C(5)–C(6) | 123.4 (15) |
| C(5)–C(6)–C(7) | 121.1 (14) | C(5)–C(6)–C(15) | 118.1 (16) |
| C(7)–C(6)–C(15) | 120.8 (15) | S(2)–C(7)–C(6) | 113.8 (11) |
| S(2)–C(7)–C(8) | 125.9 (13) | C(6)–C(7)–C(8) | 120.3 (14) |
| C(7)–C(8)–C(9) | 121.6 (14) | C(7)–C(8)–C(13) | 119.9 (16) |
| C(9)–C(8)–C(13) | 118.5 (15) | C(8)–C(9)–C(10) | 120.6 (15) |
| C(9)–C(10)–C(11) | 121.1 (18) | C(10)–C(11)–C(12) | 121.0 (16) |
| C(11)–C(12)–C(13) | 120.4 (15) | C(8)–C(13)–C(12) | 118.3 (16) |
| C(8)–C(13)–C(14) | 119.6 (15) | C(12)–C(13)–C(14) | 122.0 (15) |
| S(3)–C(14)–C(13) | 126.2 (13) | S(3)–C(14)–C(15) | 112.6 (13) |
| C(13)–C(14)–C(15) | 121.1 (14) | C(6)–C(15)–C(14) | 118.3 (16) |
| C(16)–C(15)–C(16) | 120.0 (15) | C(14)–C(15)–C(16) | 121.6 (15) |
| S(4)–C(16)–C(15) | 113.9 (12) | S(4)–C(16)–C(17) | 124.7 (12) |
| C(15)–C(16)–C(17) | 121.4 (14) | C(4)–C(17)–C(16) | 120.1 (15) |
| C(4)–C(17)–C(18) | 116.4 (14) | C(16)–C(17)–C(18) | 123.4 (13) |
| C(17)–C(18)–C(19) | 122.9 (14) | C(2)–C(19)–C(18) | 118.5 (16) |
| C(2)–C(19)–C(20) | 123.1 (15) | C(18)–C(19)–C(20) | 118.4 (14) |
| C1–C(91)–C(92) | 103.9 (16) | C1–C(91)–C(93A) | 114.8 (20) |
| C(92)–C(91)–C(93A) | 141.3 (22) | C(91)–C(92)–C(93) | 106.1 (19) |
| C(92)–C(93)–C(91A) | 112.4 (22) | | |

well with the C–S distance of 1.781 Å for TTT. The C–C distances within the tetracene moiety of DMTTT are comparable to those of TTT and tetracene. The average intrastack molecular plane separation is calculated to be 3.55 Å. However, there may be a small dimerization between pairs of DMTTT molecules. One intrastack distance is calculated as 3.53 (2) Å and the other as 3.57 (3) Å. Since the difference between these two distances is approximately equal to the sum of the standard deviations, it is not possible to conclude with any certainty whether or not DMTTT is dimerized. Further, the shortest interstack (S)2···S(2) distance is 3.638 Å, and the shortest intrastack S(1)···S(4) distance is 3.838 Å.

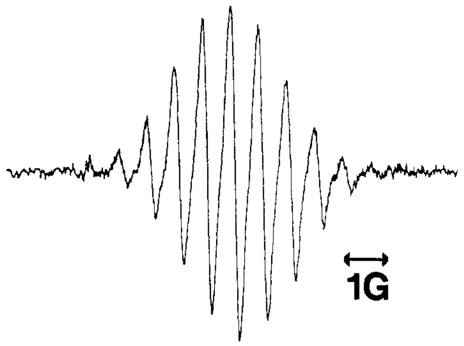

**Figure 4.** ESR spectrum of DMTTT$^+$ in THF.

**Electronic Spectra of DMTTT$^+$.** Reaction of dilute solutions of DMTTT with trifluoroacetic acid in solvents such as benzene, chlorobenzene, methylene chloride, and tetrahydrofuran (THF) yields the cation radical of DMTTT. The electronic absorption spectrum of DMTTT$^+$ in benzene displays three absorption bands at 463, 505, and 591 nm, which are shifted only slightly from those observed for TTT$^+$ in benzene.

**ESR Studies.** ESR spectra taken from dilute degassed solutions of DMTTT$^+$ in THF (Figure 4) or methylene chloride show 11 of the expected 13 approximately equally spaced absorption lines separated by 0.63 G and a *g* value equal to 2.007 78. It is expected that the methyl proton hyperfine splittings (hfs) are approximately equal to the aromatic proton hfs at the positions occupied by the methyl groups. Thus, the observed values fall within the range expected for the cation radical of DMTTT and agree quite well with those reported for the TTT cation radical in solution.[4]

**Solid-State Charge-Transfer Salts of DMTTT.** A number of charge-transfer salts of DMTTT have been isolated and are in the process of being characterized. Salts that have been prepared include as anions chloride, iodide, PF$_6$, tetracyanoquinodimethanide, and tetrafluorotetracyanoquinodimethanide. Preliminary electrical conductivity measurements show that conducting charge-transfer salts can be prepared from DMTTT. Studies of these systems and others will be discussed in a separate publication.

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**Registry No.** **2**, 130651-74-0; **2**$^+$ radical ion·F$_3$CCO$_2^-$, 134418-74-9; **2**·PhCl, 134391-83-6; **3**, 5999-20-2; **4**, 571-60-8; **5**, 76640-22-7; **6**, 134418-75-0; DMHCT, 134391-84-7; H$_2$C=C(CH$_3$)C(CH$_3$)=CH$_2$, 513-81-5; maleic anhydride, 108-31-6; 4,5-dimethyltetrahydrophthalic anhydride, 5438-24-4; 4,5-dimethylphthalic acid, 5680-10-4.

**Supplementary Material Available:** Tables of anisotropic thermal parameters and atomic coordinates for calculated H-atom positions (1 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.