Synthesis and Unique Packing Structure by X-Ray Analysis of New Types of Stable Trithioles Bound to Fused Aromatic Systems

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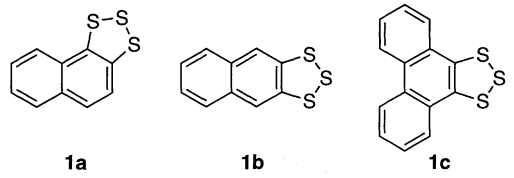
New types of stable trithioles bound to fused aromatic systems have been synthesized and one of them, phenanthro[9,10-d][1,2,3]trithiole, has been characterized by X-ray crystallographic analysis, which has a unique helical packing arrangement.

Alkene trithioles may form planar 7π radical cation frameworks by oxidation.[1] However, benzotrithiole is an unstable molecule, which has never been isolated, and readily forms oligomeric or polymeric mixture.[2] Recently, we have succeeded in the stabilization and isolation of benzotrithiole derivatives by introduction of bulky substituents onto benzene ring.[3] As further search for the finding of new stabilization systems we have employed fused aromatic rings to prepare new types of stable trithioles. This paper presents the synthesis of the trithioles bound to fused aromatic rings, e.g., naphthalene and phenanthrene, and the characterization of a unique stacked structure of phenanthro[9,10-d][1,2,3]trithiole by X-ray crystallographic analysis.



Scheme 1.

By semiempirical PM3 calculations of naphtho[1,2-d][1,2,3]-trithiole (**1a**), naphtho[2,3-d][1,2,3]trithiole (**1b**), and phenanthro[9,10-d][1,2,3]trithiole (**1c**), we found that the density gradient of virtual HOMOs of **1a-c** was dispersed on both the aromatic and the trithiole rings in comparison with that of simple benzotrithiole.[4] These results suggested that trithioles having distorted geometry caused by the lone pair-lone pair repulsion of neighboring divalent sulfur atoms could be stabilized thermodynamically by polyaromatics. Therefore, we have tried to synthesize the above three trithioles (Scheme 1) by employing the corresponding dithiastannoles, which were easily obtained by our methods previously reported.[5] The stannoles were readily transferred to trithioles **1a-c** by two steps upon treating with thionyl chloride and then NaI/HClO4 in quantitative yields.[6]

Expectedly, phenanthrotrithiole **1c** was obtained as stable orange crystals, whereas naphthotrithioles **1a** and **1b** were obtained as relatively unstable yellow crystals which gradually changed to oligomeric forms under air after several hours. The crystal structure of trithiole **1c** was confirmed by X-ray crystallographic analysis (Figure 1).[7] Two sulfur atoms bound to carbon are almost coplanar with the phenanthrene ring, while the sulfur at 2-position lies out of this plane. Interestingly, the distorted trithiole **1c** has a unique packing structure. While solid-state naphthalene, phenanthrene, and triphenylene may be classified into herringbone packing type,[8] the phenanthrene rings in **1c** are stacked one another of their naphthalene unit to form helical packing arrangement by six molecules.

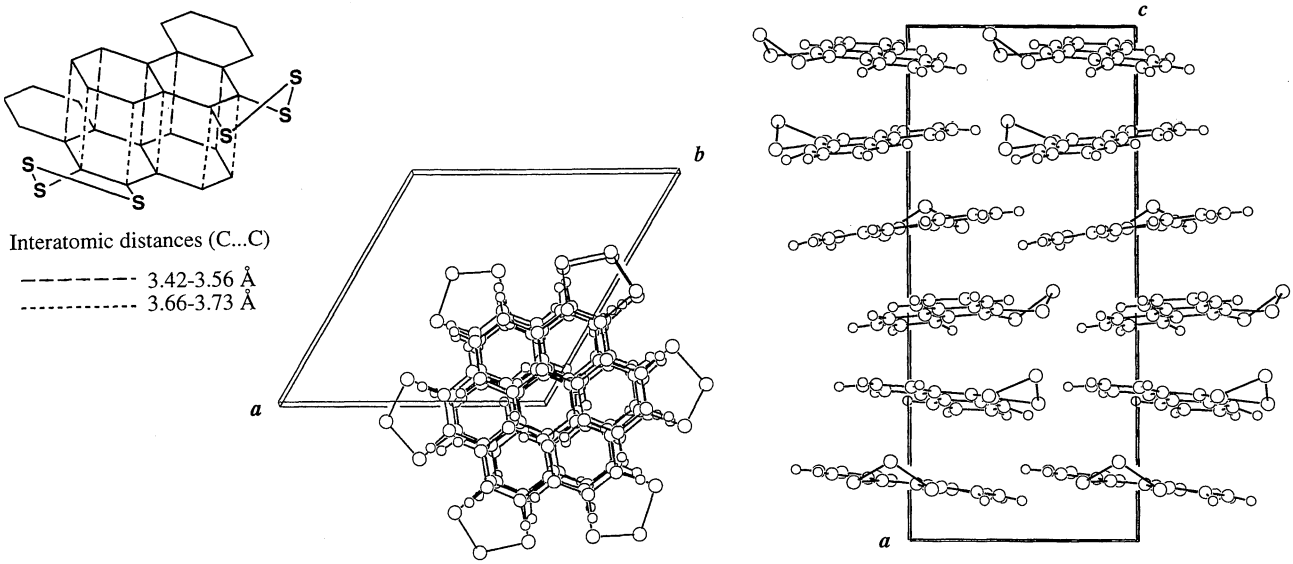
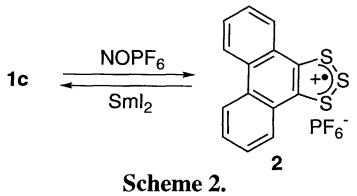


Figure 1. The crystal packing of trithiole **1c**. Selected bond lengths (Å), bond angles(°), and torsion angles(°) are as follows: S-C 1.789(5), 1.778(5); S-S 2.063(2), 2.052(2); S-S-C 93.0(2), 93.4(2); S-S-S 94.92(9); S-S-S-C 40.0(2), -40.8(2). Intermolecular C---C contacts are shown in Figure.

These interesting findings prompted us to prepare the planar heterocyclic tetracycline, phenanthro[9,10-d][1,2,3]trithiolium radical cation salt (**2**), by oxidation of trithiole **1c**. To evaluate the stability of the radical cation, cyclic voltammetry was measured in acetonitrile (MeCN) under an Ar atmosphere containing 0.1M $Bu_4N^+ClO_4^-$ as a supporting electrolyte using a glassy carbon working electrode and Ag/0.01M $AgNO_3$ couple in MeCN as a reference electrode. The voltammograms of **1c** showed reversible one-electron redox waves at E_{pa}=0.69 V and E_{pc}=0.62 V. Indeed, although it has not yet been succeeded in growing single crystals suitable for X-ray diffraction, new trithiolium radical cation salt **2** was obtained quantitatively as stable dark blue powder under air by one-electron oxidation of **1c** with 1 equiv. of $NOPF_6$ in THF-MeCN.[9] The salt **2** underwent one-electron reduction to give **1c** quantitatively by treatment with 1 equiv. of samarium(II) iodide in THF (Scheme 2).



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Scheme 2.

Consequently, now we have succeeded in isolating of new trithioles by adopting polyaromatics as thermodynamic stabilization units and found the new packing structure of the polyaromatics. Further studies on redox reactions of trithioles bound to fused aromatic systems are in progress.

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References and Notes

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4 PM3 calculations were carried out on a HITAC M680/160E computer by the MOPAC Ver. 6.02 [(QCPE No. P015), J. J. P. Stewart, *QCPE Bull.*, **9**, 10 (1989); Revised as Ver. 6.01 by T. Hirano, University of Tokyo, for HITAC and UNIX machines, *JCPE Newsletter*, **1**, 10 (1989); Revised as Ver. 6.02 by present authors]. The structures of **1a-c** were optimized by Allinger's MM2(77) molecular mechanics force field.

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6 Compound **1a**: Yellow crystals; mp 140.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J=8.0 Hz, 1H, ArH), 7.74 (d, J=8.0 Hz, 1H, ArH), 7.62 (d, J=8.5 Hz, 1H, ArH), 7.54 (t, J=8.0 Hz, 1H, ArH), 7.48 (d, J=8.5 Hz, 1H, ArH), 7.46 (t, J=8.0 Hz, 1H, ArH); $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 138.3, 137.6, 132.4, 129.5, 128.3, 127.8, 127.4, 127.0, 126.2, 120.8; Found: m/z 221.9611. Calcd for $C_{10}H_6S_3$: M, 221.9632. Compound **1b**: Yellow crystals; mp 145.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 2H, ArH), 7.67 (dd, J=6.2, 3.3 Hz, 2H, ArH), 7.45 (dd, J=6.2, 3.3 Hz, 2H, ArH); $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 139.3, 132.2, 127.4, 127.3, 122.4; Found: m/z 221.9629. Calcd for $C_{10}H_6S_3$: M, 221.9632. Compound **1c**: Orange crystals; mp 164.0-165.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.61 (m, 2H, ArH), 7.85-7.83 (m, 2H, ArH), 7.66-7.62 (m, 4H, ArH); $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 136.8, 129.9, 128.1, 128.0, 127.7, 127.1, 132.2; MS m/z 272 (M^+). Found: C, 61.36; H, 2.83%. Calcd for $C_{14}H_8S_3$: C, 61.72; H, 2.97%.

7 Crystal data for **1c**: An orange prismatic crystal of $C_{14}H_8S_3$, M=272.40, crystal size 0.27 x 0.20 x 0.18 mm, hexagonal space group $P6_1$, a=10.106(2) Å, c=19.667(3) Å, α=90.0000 °, V=1739.7(3) Å^3, Z=6, D_c=1.560 gcm^{-3}. The intensity data ($2\theta_{max}$=140.2 °) were collected on a Rigaku AFC7R diffractometer at 20.0 °C with ω-2θ scan technique, scan speed=8.0 °min^{-1} (in ω), scan width=(1.42 + 0.30 tanθ) °, and CuKα radiation (λ=1.54178 Å). The structure was solved by direct methods (SAPI91) and expanded using Fourier techniques (DIRDIF92). All calculations were performed using the teXsan crystallographic software package. The final cycle of full-matrix least-square refinement was based on 1005 observed reflections (I>3.00σ(I)) and 186 variable parameters with R=0.036, R_w=0.039.

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9 Compound **2**: Dark blue powder; mp 134.0 °C (decomp.); Found: C, 40.58; H, 2.00. Calcd for $C_{14}H_8S_3PF_6$: C, 40.28; H, 1.93. $\{^1H\}^{31}P$ NMR (162 MHz, CD_3CN, relative to H_3PO_4) δ -143.6 (sept, $J_{^{31}P^{19}F}$ =707 Hz); X-band ESR (THF, 10 °C) g=2.011.