
Methyl and Dimethyl Derivatives of Tetrathionaphthalene and Tetraselenonaphthalene as Novel Electron Donors

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ABSTRACT: *Monomethyl and dimethyl tetrathionaphthalenes and tetraselenonaphthalenes have been developed as modified electron donors. Introduction of methyl groups is very helpful in enhancing the inherent low solubilities of the parent compounds. In the cyclic voltammograms, they show two reversible redox waves, whose first and second oxidation potentials are gradually lowered with the increasing number of the introduced methyl groups. They all are able to form charge-transfer complexes with tetracyanoquinodimethane. Irrespective of the chalcogen kind of the donor, the complexes of the dimethyl derivatives are conductive, while those of the monomethyl derivatives are insulating. The different conductivities are explained by the difference of their crystal structures, which are studied by infrared spectroscopy. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:287–292, 2001*

INTRODUCTION

Naphtho[1,8-*c,d*:4,5-*c'd'*]bis[1,2]dithiole (common name, tetrathionaphthalene [TTN]) is a prototype of peridichalcogen bridged arenes, which can form a conductive charge-transfer complex with tetracyanoquinodimethane (TCNQ) [1]. However, it has a disadvantage of inherent low solubilities in organic solvents, which hampers its wide complexation study. In addition, its selenium counterpart, naphtho[1,8-*c,d*:4,5-*c'd'*]bis[1,2]diselenole (TSN) is nearly insoluble, and therefore, has not been used as an electron donor at all [2,3]. In order to make the best use of their donor properties, we previously studied their tetramethyl derivatives TMTTN and TMTSN, which showed considerably improved solubilities [4,5]. Furthermore, the tellurium bridged compound TMTTeN was obtained [4,5] and successfully used for the formation of metallic radical cation salts [6]. However, their TCNQ complexes showed conductivities of 10^{-3} Scm^{-1} , which is much lower by four orders of magnitude than that of the original TTN·TCNQ complex. The decline in conductivity is considered to be caused by a sterical hindrance of additionally introduced methyl groups. This has prompted us to study the analogous derivatives with fewer methyl groups. Here, we would like to report

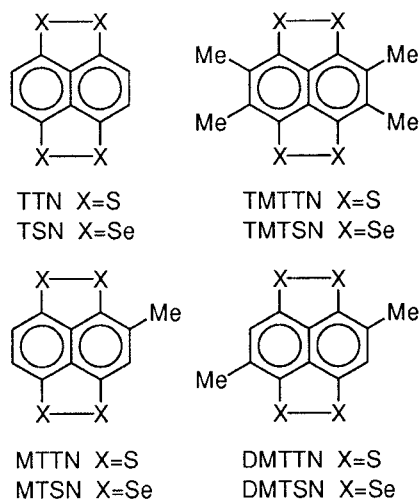
Dedicated to Professor Naoki Inamoto on the occasion of his 72nd birthday.

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the synthesis and properties of methyl and dimethyl derivatives of tetrathionaphthalene, MTTN and DMTTN, and of tetraselenonaphthalene, MTSN and DMTSN.



RESULTS AND DISCUSSION

Generally peridichalcogen arenes are accessible from treatments of the corresponding tetrachloro ones with sodium dichalcogenide in an aprotic polar solvent [7]. Thus 1,4,5,8-tetrachloro-2-methylnaphthalene (2), the precursor for MTTN and MTSN, was prepared in 68% yield by lithiation of 1,4,5,8-tetrachloronaphthalene (1) with butyllithium in tetrahydrofuran (THF) at -78°C , followed by treatment with iodomethane (Scheme 1). A repeated treatment of 2 with the same reagents gave the dimethyl derivative (3) in 57% yield, which was, however, found to comprise a mixture of the 2,6-dimethyl isomer and the 2,7-dimethyl isomer in a 1:1.3 ratio based on ^1H NMR spectroscopy. Both isomers were not isolable from each other by conventional purification procedures. Instead, as the precursor for DMTTN and DMTSN, 1,4,5,8-tetrachloro-2,6-dimethylnaphthalene (5) was prepared in 37% yield by electrophilic chlorination of 2,6-dimethylnaphthalene (4) with excess sulfuryl chloride and silica gel in tetrachloromethane (Scheme 1).

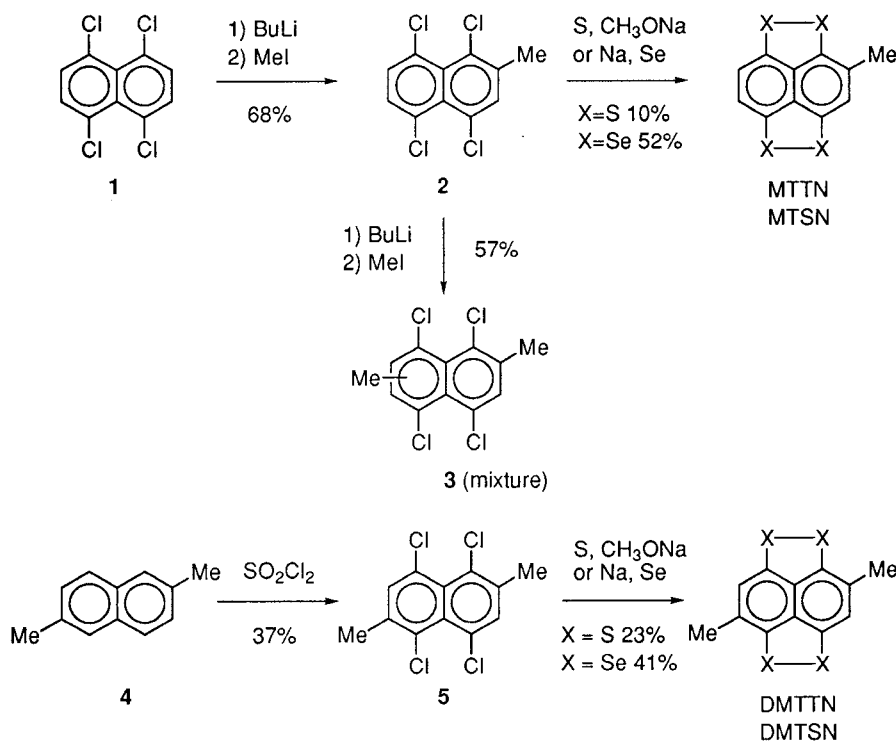
Conventional substitution reactions of 2 with sodium disulfide, in situ generated from sodium and sulfur in 1,3-dimethyl-2-imidazolidinone (DMI), gave the desired MTTN but in a very low yield (2%). This is also the case for the synthesis of DMTTN from 5 and sodium disulfide (8% yield). Alternative treatments with a similar reagent generated from sodium methylate and sulfur in *N,N*-dimethylacetamide (DMA) [8] gave appreciably improved yields,

MTTN (10%) and DMTTN (23%). On the other hand, conventional substitution reactions of 2 and 5 with sodium diselenide in *N,N*-dimethylformamide (DMF) smoothly occurred to give MTSN (52%) and DMTSN (41%) in reasonable yields, respectively.

All new TTN and TSN derivatives were characterized by both spectroscopic analyses and elemental analyses. Their cyclic voltammetry showed two reversible redox waves at low potentials. As summarized in Table 1, the first and second oxidation potentials are gradually lowered with the increasing number of the introduced methyl groups. Table 1 also includes the solubilities in chloroform, indicating that introduction of methyl groups is very helpful to the enhancement of low solubilities of the parent TTN and TSN. Interestingly, in the case of the TTN series, monomethylation is more effective for enhanced solubilities than dimethylation or tetramethylation. Evidently, unsymmetrical substitution of methyl groups in TTN weakens intermolecular forces rather than multimethylation. On the other hand, in the case of the TSN series, the solubility increases with the increasing substitution number. Probably nonbonded Se–Se contacts are dominant in the intermolecular forces of the selenium system, and weakening them requires multimethylation.

Figure 1 shows the X-ray crystallographic structure of DMTSN, which is of a typical herringbone type and isostructural with that of TSN [3]. There are two crystallographically independent stacking columns, and the dihedral angle between the component molecules in the different columns is 126° . The face-to-face molecular distance in one column is 3.552 Å, whereas that in the other column is 3.881 Å. The stacking columns adopt a warped arrangement in such a way as to avoid the mutual contacts of the methyl groups. As shown in the *b*-axis projection of Figure 2, there are some nonbonded Se–Se contacts between the adjacent molecules; those marked *a* (3.531 Å), *b* (3.525 Å), and *d* (3.488 Å) are smaller than the shortest contacts (3.534 and 3.626 Å) of TSN. This suggests that DMTSN is able to complex without sterical hindrance of the methyl groups.

All TTN and TSN derivatives formed charge-transfer complexes with TCNQ, whose properties are summarized in Table 2. Almost all the complexes have the 1:1 stoichiometry of donor to acceptor. Their conductivities are very varied, deeply depending on the substitution number of the donor species; the complexes of DMTTN and DMTSN, like TTN, are highly conductive with 10^0 – 10^1 Scm^{-1} , whereas those of MTTN and MTSN are nearly insulating with 10^{-8} – 10^{-9} Scm^{-1} , and those of TMTTN and TMTSN are semiconductive with 10^{-3} Scm^{-1} . The infrared spectra of the complexes show nitrile vibration frequencies around 2200 cm^{-1} , which means incom-



SCHEME 1

TABLE 1 Half-Wave Oxidation Potentials^a and Solubilities of Peri-dichalcogen Naphthalenes

Compound	$E_{1/2}(1)/V$	$E_{1/2}(2)/V$	Solubility in Chloroform (mol dm ⁻³)
TTN	0.53	0.99	1.5×10^{-4}
MTTN	0.52	0.97	5.4×10^{-3}
DMTTN	0.49	0.98	1.5×10^{-3}
TMTTN	0.45	0.94	1.5×10^{-3}
TSN	0.51	0.92	$<10^{-6}$
MTSN	0.49	0.92	3.2×10^{-5}
DMTSN	0.48	0.93	4.4×10^{-4}
TMTSN	0.45	0.98	8.8×10^{-4}

^aV vs. Ag/AgCl in benzonitrile containing 0.1 M Bu₄NPF₆; scan rate 100 mV s⁻¹; WE and CE: Pt.

plete degrees of charge transfer, when compared to those of TCNQ (2223 cm⁻¹) and its potassium radical anion salt (2168 cm⁻¹). Apparently the conductivities are independent of the degree of charge transfer calculated according to the method of Chappell et al. [9]. However, only the conductive complexes demonstrate a broad strong absorption band in the infrared region: TTN·TCNQ 3.2×10^3 cm⁻¹; DMTTN·TCNQ 2.8×10^3 cm⁻¹; DMTSN 2.8×10^3 cm⁻¹. This band is ascribable to electron-transfer transition characteristic of a segregated stacked

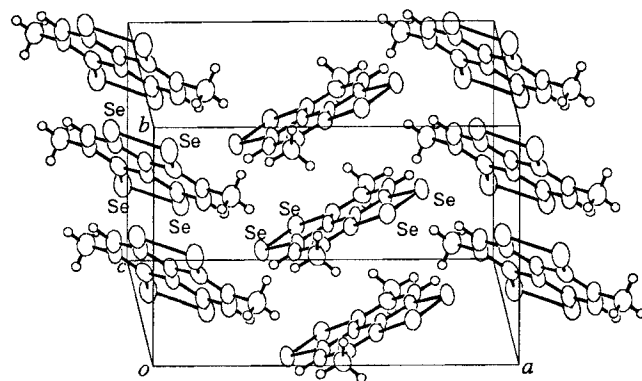


FIGURE 1 Crystal structure of DMTSN.

structure of donors and acceptors in mixed valence states [10]. This result clearly indicates that the two methyl groups of DMTTN and DMTSN do not sterically interfere with the formation of the segregated stacking structure favorable for high conduction, as suggested by the crystal structure of DMTSN. On the other hand, all the TCNQ complexes of monomethyl and tetramethyl derivatives are considered to adopt mixed stacking structures unfavorable for conduction. Probably the four methyl groups of TMTTN and TMTSN sterically interfere with the formation of the segregated columns. The reason why MTTN and

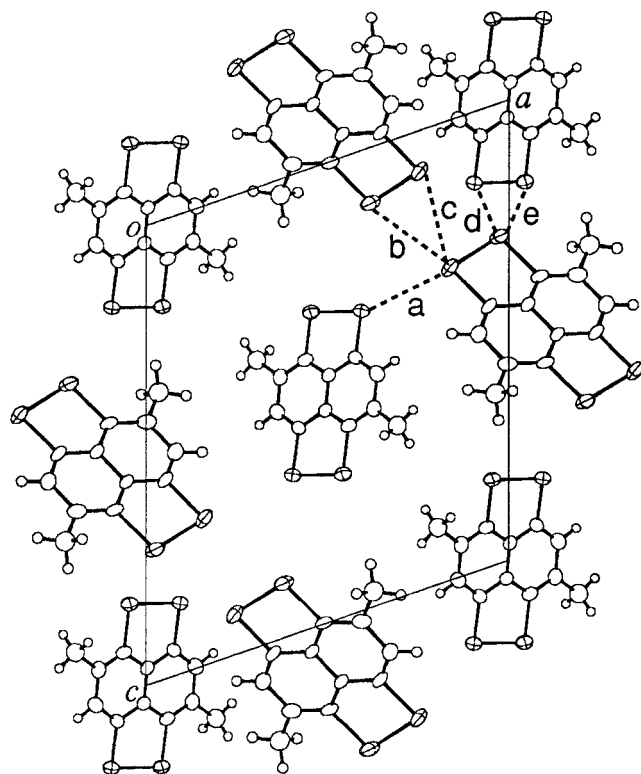


FIGURE 2 Crystal structure of DMTSN viewed along the *b*-axis; Se–Se contacts: *a*, 3.531(3); *b*, 3.525(2); *c*, 4.078(3); *d*, 3.488(3); *e*, 3.744(3) Å.

TABLE 2 Properties of Charge-Transfer Complexes of Peridichalcogen Naphthalenes

Complex	<i>D:A</i> ^a	Appearance	σ^b/Scm^{-1}	$\nu_{\text{CN}}^c/\text{cm}^{-1}$
TTN · TCNQ	1:1	Black needles	3.8	2197 (0.47)
MTTN · TCNQ	1.2:1	Brown powder	1.5×10^{-8}	2215 (0.14)
DMTTN · TCNQ	1:1	Black powder	2.8	2199 (0.43)
TMTTN · TCNQ	1:1	Black powder	5.8×10^{-3}	2194 (0.52)
MTSN · TCNQ	1:1	Black powder	8.9×10^{-9}	2195 (0.50)
DMTSN · TCNQ	1:1	Black powder	14.4	2190 (0.61)
TMTSN · TCNQ	1:0.77	Black needles	2.4×10^{-3}	2198 (0.45)

^aCalculated on the basis of elemental analyses.

^bMeasured on a compressed pellet by a two-probe method for low conductivity samples or by a four-probe method for high conductive samples.

^cValues in parentheses indicate degrees of charge transfer calculated from ν_{CN} values.

MTSN favor mixed stacking structures still remains incomprehensible. It might be related to the molecular unsymmetry unsuitable for crystal packing.

In summary, we have developed monomethyl and dimethyl peridichalcogen naphthalenes, MTTN, DMTTN, MTSN, and DMTSN as new electron donors. They all have some advantageous properties, such as low oxidation potentials and high solubili-

ties. Of these, however, with TCNQ only the dimethyl derivatives DMTTN and DMTSN can form conductive charge-transfer complexes whose crystal structures are of a segregated stacking type.

EXPERIMENTAL SECTION

General

All chemicals and solvents are of reagent grade. Melting points are uncorrected. All reactions were carried out under a nitrogen atmosphere. NMR spectra were recorded on a JEOL Lambda 400 spectrometer (400 MHz) in CDCl_3 or $\text{CDCl}_3\text{-CS}_2$ solution using tetramethylsilane as an internal standard. IR spectra were taken on a Shimadzu FTIR-8100A spectrometer with a KBr disk. 1,4,5,8-Tetrachloronaphthalene (**1**) was prepared according to the literature [11]. 2,6-Dimethylnaphthalene (**4**) is commercially available on a 1 g scale but is expensive, and it was prepared on a large scale by the usual reduction of inexpensive dimethyl naphthalenedicarboxylate with LAH (62% yield), bromination with PBr_3 (quantitative yield), and again reduction with LAH (73% yield).

1,4,5,8-Tetrachloro-2-methylnaphthalene (**2**)

Into a solution of 1,4,5,8-tetrachloronaphthalene (**1**) (0.40 g, 1.5 mmol) in THF (30 mL) cooled at -70 to -80°C was added a hexane solution of butyllithium (1.6 M, 1.0 mL, 1.6 mmol), and the mixture was stirred for 5 minutes. After iodomethane (0.11 mL, 1.7 mmol) had been added, the mixture was stirred for a further 30 minutes at the same temperature and then warmed to room temperature (RT) over a period of 6 hours. After water (ca. 30 mL) was added, most of THF was evaporated, and the residue was extracted with dichloromethane (20 mL \times 3). The extract was washed with brine and dried (MgSO_4). After evaporation of the solvent, the residue was purified by column chromatography on silica gel with hexane and then by gel-permeation liquid chromatography, and finally recrystallized from hexane to give colorless needles of **2** (0.284 g, 68%); m.p. $148\text{--}149^\circ\text{C}$; MS m/z 278 (M^+ based on ^{35}Cl) with the isotopic pattern of four Cl atoms; $^1\text{H NMR}$ δ 2.52 (s, 3H, CH_3), 7.46 (d, $J = 8.2$ Hz, 1H, ArH), 7.51 (d, $J = 8.2$ Hz, 1H, ArH), 7.55 (s, 1H, ArH); Anal. Calcd for $\text{C}_{11}\text{H}_6\text{Cl}_4$: C, 47.19; H, 2.16%. Found: C, 47.45; H, 2.20%.

1,4,5,8-Tetrachloro-2,6-dimethylnaphthalene (**5**)

Sulfuryl chloride (3.1 mL, 38.6 mmol) was slowly added into an ice-cooled suspension of 2,6-dimethylnaphthalene (**4**) (0.5 g, 3.2 mmol) and silica gel (2.55 g) in tetrachloromethane (30 mL), and the mix-

ture was stirred for 80 hours at RT. After water (20 mL) was added, the insoluble silica gel was removed by filtration and washed with dichloromethane, and the filtrate was extracted with dichloromethane (30 mL). The washings and the extracts were combined, washed with brine, and dried (MgSO_4). After evaporation of the solvent, the residue was purified by column chromatography on silica gel using hexane as eluant, followed by recrystallization from 1:3 benzene-methanol to give colorless needles of **5** (0.35 g, 37%); MS m/z 292 (M^+ based on ^{35}Cl) with the isotopic pattern of four Cl atoms; $^1\text{H NMR}$ δ 2.48 (s, 6H, CH_3), 7.46 (s, 2H, ArH); Anal. Calcd for $\text{C}_{12}\text{H}_8\text{Cl}_4$: C, 49.02; H, 2.74%. Found: C, 49.10; H, 2.62%.

3-Methylnaphtho[1,8-c,d:4,5-c'd']bis[1,2]dithiole (MTTN) and 3,7-Dimethylnaphtho[1,8-c,d:4,5-c'd']bis[1,2]dithiole (DMTTN)

A mixture of sulfur powder (137 mg, 4.3 mmol) and sodium methylate (231 mg, 4.3 mmol) in DMA (7 mL) was heated in an oil bath, the temperature rising from 100°C to 150°C over a period of 30 minutes, and then maintained at 120°C for 6 hours. After 1,4,5,8-tetrachloro-2-methylnaphthalene (**2**) (100 mg, 0.36 mmol) had been added, the mixture was heated for an additional 17 hours at 120°C, exposed to air overnight at RT, and then poured into brine (40 mL). The resulting solid was collected by filtration, dried, and purified by column chromatography on silica gel using carbon disulfide as eluant, followed by sublimation at a temperature over 200°C under a high vacuum $<10^{-1}$ torr. Recrystallization of the sublimate from 1:1 benzene-methanol gave a yellowish brown powder of MTTN (10 mg, 10%): m.p. 146–147°C; MS m/z 266 (M^+); $^1\text{H NMR}$ ($\text{CDCl}_3\text{-CS}_2$) δ 2.15 (s, 3H, CH_3), 6.69 (s, 1H, ArH), 6.76 (d, $J = 7.8$ Hz, ArH), 6.78 (d, $J = 7.8$ Hz, ArH); Anal. Calcd for $\text{C}_{11}\text{H}_6\text{S}_4$: C, 49.59; H, 2.27%. Found: C, 49.58; H, 2.24%.

DMTTN was similarly obtained in 23% yield from 1,4,5,8-tetrachloro-2,6-dimethylnaphthalene (**5**): reddish brown needles from 1:1 benzene-methanol; m.p. 136–137°C; MS m/z 280 (M^+); $^1\text{H NMR}$ ($\text{CDCl}_3\text{-CS}_2$) δ 2.15 (s, 6H, CH_3), 6.70 (s, 2H, ArH); Anal. Calcd for $\text{C}_{12}\text{H}_8\text{S}_4$: C, 51.40; H, 2.88%. Found: C, 51.36; H, 2.83%.

3-Methylnaphtho[1,8-c,d:4,5-c'd']bis[1,2]diselenole (MTSN) and 3,7-Dimethylnaphtho[1,8-c,d:4,5-c'd']bis[1,2]diselenole (DMTSN)

A mixture of red selenium powder (203 mg, 2.57 mmol) and sodium (59.2 mg, 2.57 mmol) in DMF (8 mL) was heated at 120°C for 5 hours to generate the

Na_2Se_2 reagent. After 1,4,5,8-tetrachloro-2-methylnaphthalene (**2**) (100 mg, 0.36 mmol) had been added, the mixture was refluxed for 22 hours, exposed to air overnight at RT, and then poured into brine (70 mL). The resulting solid was collected by filtration, dried, and washed with methanol and then with a small amount of carbon disulfide. After sublimation at a temperature over 200°C under a high vacuum $<10^{-1}$ torr, recrystallization of the sublimate from 2:1 benzene-carbon disulfide gave a black powder of MTSN (85 mg, 52%): m.p. 228–229°C; MS m/z 458 (M^+ based on ^{80}Se) with the isotopic pattern of four Se atoms; $^1\text{H NMR}$ ($\text{CDCl}_3\text{-CS}_2$) δ 2.18 (s, 3H, CH_3), 6.93 (s, 1H, ArH), 6.98 (d, $J = 7.7$ Hz, 1H, ArH), 7.01 (d, $J = 7.7$ Hz, 1H, ArH); Anal. Calcd for $\text{C}_{11}\text{H}_6\text{Se}_4$: C, 29.10; H, 1.33%. Found: C, 29.18; H, 1.30%.

DMTSN was similarly obtained in 41% yield from 1,4,5,8-tetrachloro-2,6-dimethylnaphthalene (**5**): black needles from 2:1 benzene-carbon disulfide; m.p. 296–297°C; MS m/z 472 (M^+ based on ^{80}Se) with the isotopic pattern of four Se atoms; $^1\text{H NMR}$ ($\text{CDCl}_3\text{-CS}_2$) δ 2.18 (s, 6H, CH_3), 6.91 (s, 2H, ArH); Anal. Calcd for $\text{C}_{12}\text{H}_8\text{Se}_4$: C, 30.78; H, 1.72%. Found: C, 30.80; H, 1.65%.

Preparation of Charge-Transfer Complexes

The hot saturated solution of the donor component in chloroform was mixed with that of an equimolar amount of TCNQ in chloroform, and, after cooling, the resulting solid of charge-transfer complex was collected by filtration and thoroughly washed with cold dichloromethane.

Anal. of MTTN·TCNQ complex, Found: C, 58.58; H, 2.17; N, 10.64% (Calcd. for 1.2:1 stoichiometry: C, 55.75; H, 2.26; N, 11.21%). DMTTN·TCNQ, Found: C, 59.32; H, 2.61; N, 11.51% (Calcd. for 1:1 stoichiometry: C, 59.48; H, 2.50; N, 11.56%). MTSN·TCNQ, Found: C, 42.54; H, 1.51; N, 8.99% (Calcd. for 1:1 stoichiometry: C, 42.83; H, 1.54; N, 9.08%). DMTSN·TCNQ, Found: C, 42.88; H, 1.86; N, 8.35% (Calcd. for 1:1 stoichiometry: C, 42.88; H, 1.80; N, 8.33%).

X-Ray Crystallographic Analyses of DMTSN

The X-ray diffraction experiment was performed at RT on a Rigaku AFC6S diffractometer with graphite-monochromated Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The intensity data were measured using the ω -2 θ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares

techniques with anisotropic temperature factors for the nonhydrogen atoms. The authors deposited atomic coordinates with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. Crystal data: formula $C_{12}H_8Se_4$; formula wt. 468.04; crystal dimensions $0.80 \times 0.05 \times 0.04$ mm; crystal system monoclinic; space group $P2_1/n$; a 14.967(2) Å; b 4.737(3) Å; c 18.083(2) Å; β 109.098(7)°; V 1211.6(8) Å³; Z 4; D_C 2.566 gcm⁻³; NDTA [$|Fo| \geq 3.0\sigma (|Fo|)$] 1299 ($I > 3\sigma(I)$); R 0.052; R_w 0.064.

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