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1,8:4,5-Bis(diseleno)naphthalene[1]

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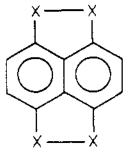
Sodium diselenide reacts with 1,4,5,8-tetrachloronaphthalene (**2**) in *N*,*N*-dimethylformamide to give 1,8:4,5-bis(diseleno)naphthalene (tetraselenonaphthalene, TSeN, **1**) and 1,8-diseleno-4,5-dichloronaphthalene (**3**) as minor and major products, respectively. Purification via gradient sublimation of crude TSeN leads to a black solid whose properties are not in accord with a previous report. Cyclic voltammetry of TSeN in benzonitrile solution reveals reversible one-electron transfers at +0.15 and +0.54 V vs. the Ag/Ag^+ reference. The electron spin resonance of $TSeN^+$, generated in dichloromethane solution with trifluoroacetic acid, exhibits a single line 10.4 G wide with $g = 2.0431$. Grown from chlorobenzene solution, TSeN is a monoclinic crystal of space group $P2_1/c$ with $a = 7.722$ (2) Å, $b = 4.226$ (1) Å, $c = 15.305$ (4) Å, $\beta = 102.15$ (3)°, $V = 488.3$ Å^3, and $Z = 2$. The structure, solved by Patterson and difference-Fourier syntheses, involves linear chains of TSeN molecules stacked along *b* with interstack Se···Se contacts at 3.626 and 3.534 Å.

Introduction

peri-Dichalcogenide substitution of polyacenes provides a viable mechanism for lowering the first ionization potential of a given hydrocarbon.[4-6] This results in materials whose cation–radical salts are not only isolable and stable at room temperature but also crystallize in linear chain arrays. The electronic structure of these ion radical solids permits high dark conductivity, and salts of tetrathiotetracene (TTT) and tetraselenotetracene (TSeT) are organic metals.[7] In addition, 1,4,5,8-tetrathionaphthalene (1,8:4,5-bis(dithio)naphthalene, TTN, **1a**) interacts with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give a highly conducting ion–radical solid with a uniform segregated stack crystal structure.[8]



1a, X = S
1b, X = Se

At the present time, stimulated by the observation[9] of ambient pressure superconductivity in the 2:1 perchlorate salt of tetramethyltetraselenafulvalene, i.e., $(TMTSF)_2ClO_4$, there is considerable interest in the synthesis of the heavier chalcogen analogues of donors which lead to metallic or other highly conducting ion radical solids. We have discussed the general physical and crystallographic bases for the interest in the heavier chalcogen materials,[1a,10] and we have argued, from structural packing considerations,[11] the importance of studying donors with nonbonded interactions which would differ from those of the $(TMTSF)_2X$ class of materials.

Experimentally, we made the first report of the synthesis of tetratellurotetracene (TTeT) as well as a high-precision structural determination.[12] Our synthetic activity was stimulated by the report[13] of a synthesis of TSeT from 5,6,11,12-tetrachlorotetracene (TClT) and a sodium diselenide reagent prepared directly from the elements in *N*,*N*-dimethylformamide (DMF). We extended this technique to sodium ditelluride,[12] and we have used these and the monochalcogenide reagents to synthesize a variety of molecular and polymeric materials, many of interest for their solid-state properties.[1,10,11,14,15] For the reasons discussed above, we were interested in using this metho-

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[1] Preliminary accounts of portions of this work were presented at (a) the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, Birmingham, U.K., July 25–29, 1983 and (b) the Symposium on Solid-State Chemistry, 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC, Nov 9–11, 1983.

[2] National Science Foundation Industrial Research Participation Program at GTE Laboratories, Summers, 1981–1983.

[3] The work at Brandeis University was supported in part by the Office of Naval Research.

[4] Sandman, D. J.; Ceasar, G. P.; Nielsen, P.; Epstein, A. J.; Holmes, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 202.

[5] (a) Riga, J.; Verbist, J. J.; Lamotte, C.; Andre, J.-M. *Bull. Soc. Chim. Belg.* **1978**, *87*, 163. (b) Riga, J.; Verbist, J. J.; Wudl, F.; Kruger, A. *J. Chem. Phys.* **1978**, *69*, 3221.

[6] Bock, H.; Brahler, G.; Dauplaise, D.; Meinwald, J. *Chem. Ber.* **1981**, *114*, 2662.

[7] Shchegolev, I. F.; Yagubskii, E. B. In "Extended Linear Chain Compounds"; Miller, J. S., Ed., Plenum Press: New York, 1982; Vol. 2, pp 385 ff.

[8] Wudl, F.; Schafer, D. E.; Miller, B. *J. Am. Chem. Soc.* **1976**, *98*, 252.

[9] Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440.

[10] Sandman, D. J.; Stark, J. C.; Rubner, M. F.; Hamill, G. P.; Acampora, L. A.; Samuelson, L. A.; McGrath, M. A.; Allen, G. W. "Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium".

[11] Sandman, D. J.; Stark, J. C.; Rubner, M. F.; Acampora, L. A.; Samuelson, L. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 293.

[12] Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739.

[13] Balodis, K. A.; Livdane, A. D.; Medne, R. S.; Neiland, O. Y. *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 343.

[14] Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549.

[15] Sandman, D. J.; Rubner, M. F.; Samuelson, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1133.

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dology for the synthesis of 1,4,5,8-tetraselenonaphthalene (TSeN, **1b**, 1,8:4,5-bis(diseleno)naphthalene; naphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2]diselenole).

Interest in the synthesis of TSeN has been previously mentioned.[8,16] Following the successful synthesis of the naphthalene 1,8-dichalcogenides via 1,8-dilithionaphthalene and related methods,[16,17] it was proposed[16] to extend these approaches to the 1,4,5,8-tetrachalcogenonaphthalenes. Experimentally, this approach was not successful for the case of TTN.[16]

This work reports the reaction of 1,4,5,8-tetrachloronaphthalene (**2**) with Na_2Se_2, the isolation of TSeN from this experiment, and its purification. The properties of the redox states of TSeN have been probed by cyclic voltammetry (CV) and electron spin resonance (ESR) techniques, and the crystal and molecular strcture of TSeN has been determined by single-crystal X-ray techniques. Subsequent to our initial description of these results,[1a] a report describing properties of TSeN at variance with those observed for our purified material appeared.[18] Also, in the Experimental Section, we give an improved procedure for the preparation and isolation of TClT, the key intermediate to TSeT and TTeT.

Experimental Section

General Procedures. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Electronic spectra were recorded on a Varian Cary 17 spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research Model 173 potentiostat, a Model 175 programmer, and a Hewlett-Packard 7046A recorder. ESR spectra were recorded on a Varian E-12 spectrometer as previously described.[19]

Reaction of Sodium Diselenide with 1,4,5,8-Tetrachloronaphthalene. To a sodium diselenide reagent, prepared under argon in *N,N*-dimethylformamide (DMF, 100 mL) from sodium (0.57 g, 0.024 mol) and selenium (1.92 g, 0.024 mol), was added 1,4,5,8-tetrachloronaphthalene[20] (0.99 g, 3.72 mmol) in DMF (20 mL). The mixture was heated at 100–110 °C for 17 h, cooled to room temperature, and poured into brine (800 mL). This mixture was filtered, washed with sodium sulfide solution, washed with water, and dried. The dried solid was Soxhlet extracted with hexane until the extracts were colorless. Purple crystals precipitated from the cooled hexane extract and were isolated by suction filtration, 0.72 g (55% yield), mp 202–204 °C. This solid was identified as 1,8-diseleno-4,5-dichloronaphthalene (**3**) by the isotopic cluster of the molecular ion in its mass spectrum. In chlorobenzene solution, this material exhibited an absorption maximum at 409 nm (log ϵ 3.9).

Anal. Calcd for $C_{10}H_4Cl_2Se_2$: C, 34.03; H, 1.14; Cl, 20.09; Se, 44.74. Found: C, 32.79; H, 1.34; Cl, 18.37; Se, 46.38.

The brown residue of the Soxhlet extraction was crude TSeN (10% yield), identified by the isotopic cluster of the molecular ion of its mass spectrum. Further purification of TSeN was achieved by gradient sublimation[21] on Kapton at 200–210 °C at 2–5 × 10^{-7} mm pressure to give a black solid, mp 355–358 °C dec. The intense absorption maxima of a 10^{-4} M bromobenzene solution of this solid are observed at 441 (log ϵ 4.34) and 417 nm (log ϵ 4.20).

Anal. Calcd for $C_{10}H_4Se_4$: C, 27.30; H, 0.92; Se, 71.79. Found: C, 26.93; H, 0.97; Se, 71.68.

Preparation and Purification of 5,6,11,12-Tetrachlorotetracene (TClT). 6,11-Dihydroxy-5,12-tetracenequinone[22] (18 g, 62 mmol) and PCl_5 (79 g, 0.38 mol) were mixed and ground in a mortar and pestle and subsequently transferred to a 500-mL flask. The mixture was heated at 185–195 °C for 80 min, and a liquid ($POCl_3$ and PCl_5) distilled as the reaction proceeded. A solution of stannous chloride (72 g, 0.38 mol), concentrated hydrochloric acid (88 mL), acetic anhydride (10 mL), and glacial acetic acid (6000 mL) was slowly added. The mixture was mechanically stirred at reflux for 1 h and subsequently cooled to room temperature. This mixture was filtered, and the solid was washed with water and vacuum dried to give crude TClT; yield greater than 90%, mp in the range 180–200 °C. Crude TClT (5.3 g) was slurried into chloroform (25 mL/g) with activated alumina (21.2 g). The resultant slurry was loaded into a large Soxhlet thimble and extracted with chloroform until the extracts were colorless (ca. 16 h). The red eluted solution was cooled to room temperature, and red needles were isolated by suction filtration and washed with cold hexane to give 4.9 g (92% recovery), mp 214–216 °C (lit.[13] mp 212–214 °C), homogeneous by thin-layer chromatography on silica gel, hexane elution. We have observed melting points of TClT as high as 224–225 °C.

Table I. Data for the X-ray Diffraction Study of $C_{10}H_4Se_4$

(A) Crystal Data at 21(1) °C

cryst system: monoclinic $V = 488.3$ Å
space group: $P2_1/c$ (C^5_{2h}; No. 14) $Z = 2$
$a = 7.722\ (2)$ Å cryst size: 0.04 × 0.12 × 0.50 mm
$b = 4.226\ (1)$ Å f_W: 440.0
$c = 15.305\ (4)$ Å ρ calcd = 2.99 g cm^{-3}
$\beta = 102.15\ (3)°$ $\mu = 161.0$ cm^{-1} (Mo K$\bar{\alpha}$)
cell constant determination: 12 pairs of $\pm(hkl)$ and refined $2\theta,\omega,\chi$ values in the range $22 < |2\theta| < 27°$ (λ (Mo K$\bar{\alpha}$) = 0.71073 Å).

(B) Measurement of Intensity Data

radiation: Mo K$\bar{\alpha}$, graphite monochromator
reflctns measd: $h,-k,\pm l$ (to $2\theta = 60°$)
scan type, speed: θ-2θ, 1.95-3.91°/min.
scan range: symmetrical, $\{1.6 + \Delta(\alpha_2 - \alpha_1)\}°$
no. of reflctns measd: 1514; 1421 in unique set; 999 data "observed" ($F \geq 3.92\sigma(F)$)
std reflctns: $0\bar{2}5$, $40\bar{6}$ measured after each 50 reflctns; variation less than $\pm 3\sigma(I)$ for each.
abs corr: empirical, normalized transmission factors 0.283-1.000
statistical information:[a] $R_s = 0.021$

(C) Solution and Refinement,[b] with 999 Data for Which $F > 3.92\sigma(F)$

weighting of reflectns: as before,[c] $p = 0.035$
solution: Patterson and difference-Fourier synthesis; routine refinement:
full-matrix least-squares
anisotropic temperature factors for Se, C atoms
isotropic temperature factors for H atoms
$R = 0.037$, $R_W = 0.048$; SDU = 1.06
structure factor calcn, all 1421 data: $R = 0.063$, $R_W = 0.053$
final difference-Fourier map: six peaks 0.50-0.80 e/Å^3 near Se atoms; other peaks random and <0.45 e/Å^3
weighting scheme analysis: no systematic dependence on magnitude of $|F_o|$, $(\sin\theta/\lambda)$ or indices

[a] $R_s = \Sigma\sigma(|F_o|)/|F_o|$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_W = \{\Sigma w\{|F_o| - |F_c|\}^2/\Sigma w|F_o|^2\}^{1/2}$; SDU = $\{\Sigma w\{|F_o| - |F_c|\}^2/(m - n)\}^{1/2}$ where m (=999) is the number of observations and n (=72) is the number of parameters. [c] Reference 23.

Collection and Reduction of Diffraction Data. Single crystals of TSeN suitable for structural determination were obtained by a slow cooling of a chlorobenzene solution. Laue

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(16) Dauplaise, D. L. Ph.D. Thesis, Cornell University, 1977.

(17) Meinwald, J.; Dauplaise, D.; Wudl, F.; Hauser, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 255.

(18) Yamahira, A.; Nogami, T.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1983**, 904.

(19) Jones, M. T.; Jansen, S.; Acampora, L. A.; Sandman, D. J. *J. Phys.* (*Orsay, Fr.*), *Colloq.* **1983**, *44*, C3-1159.

(20) Clar, E.; Marschalk, C., *Bull. Soc. Chim. Fr.* **1950**, 433.

(21) McGhie, A. R.; Garito, A. F.; Heeger, A. J. *J. Cryst. Growth* **1974**, *22*, 294.

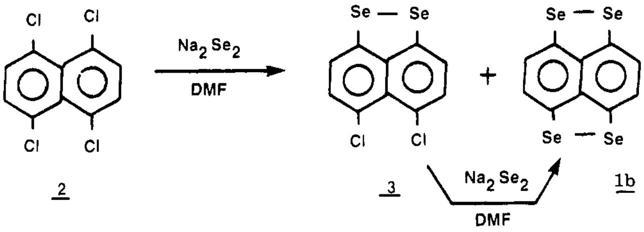
(22) Weizmann, C.; Haskelberg, L.; Berlin, T. *J. Chem. Soc.* **1939**, 398.

Table II. Atomic Coordinates for $C_{10}H_4Se_4$[a]

atom	x	y	z
Se(1)	0.39063 (7)	0.35782 (14)	0.15865 (4)
Se(2)	0.14771 (7)	0.13551 (14)	0.20860 (4)
C(1)	0.3032 (7)	0.7045 (14)	−0.0063 (4)
C(2)	0.2394 (7)	0.5256 (13)	0.0544 (3)
C(3)	0.0581 (7)	0.4479 (12)	0.0399 (3)
C(4)	−0.0125 (7)	0.2650 (13)	0.1014 (3)
C(5)	−0.1896 (7)	0.1866 (13)	0.0853 (4)
H(1)	0.412 (7)	0.759 (14)	0.005 (4)
H(5)	−0.229 (10)	0.07 (2)	0.135 (5)

[a] Standard deviations in the least significant digit appear in parentheses.

Scheme I. Synthesis of 1,8:4,5-Bis(diseleno)naphthalene



photographs of the crystal chosen for study indicated it to be of good quality; the crystal was transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[23] The analytical scattering factors of Cromer and Waber were used;[24a] real and imaginary components of anomalous scattering for Se atoms were included in the calculations.[24b] Details of the structure analysis and solution, in outline form, are presented in Table I. Table II lists the fractional coordinates for all atoms.

Results and Discussion

Synthesis and Purification of TSeN. Our synthetic studies are summarized in Scheme I and our procedure is given above in the Experimental Section. TSeN is the minor product of the reaction of Na_2Se_2 and 2. In our isolation procedure, crude TSeN, a brown powder, is further purified by gradient sublimation[21] to give a black solid which melts with decomposition above 350 °C. It is material of this quality that is used in the further characterization reported herein and in other experiments in progress.

The properties of purified TSeN described herein may be contrasted with those claimed for TSeN by Yamahira et al.,[18] who describe it as a brown powder, mp 180 °C dec. Such a melting point for TSeN is surprisingly low, since TTN was reported to have mp 282–286 °C dec,[8] and replacement of sulfur with selenium should enhance van der Waals forces, leading to a higher melting solid, as observed for our purified samples of TSeN.

In bromobenzene solution, TSeN exhibits its intense[25] absorption maxima at 441 (log ϵ 4.34) and 417 nm (log ϵ 4.20), a shift to lower energies compared to TTN, which has reported[8] maxima at 420 (log ϵ 4.26) and 397 (sh) rm (log ϵ 4.17). In the solid state, diffuse reflectance of TSeN reveals maxima at 440 and 255 nm.

The major product of the reaction of Na_2Se_2 with 2 is a violet solid identified as 1,8-diseleno-4,5-dichloronaphthalene (3) from its mass spectrum. The assorted samples of this material we have isolated typically melt in the range 200–210 °C, and while they are homogeneous by thin-layer chromatography on silica gel with benzene elution, it is not likely that it is a single compound on the basis of the elemental analysis (the observed analysis corresponds to a composition of $C_{10}H_{4.9}Cl_{1.90}Se_{2.15}$) and ESR spectrum. Additionally, we have detected 1,8-diseleno-4-chloronaphthalene, also observed by Yamahira et al.,[18] and naphthalene 1,8-diselenide in mass spectrometric analysis of solids isolated from these reactions. The detection of such compounds is not surprising, since we have detected analogous compounds in our syntheses of TTeT[12] and TSeT.[26] In chlorobenzene solution, 3 exhibits an intense absorption maximum at 409 nm (log ϵ 3.88), while naphthalene 1,8-diselenide in cyclohexane has its maximum at 380 nm (log ϵ 4.20).[17] TSeN is also isolated in ca. 15% crude yield by the reaction of 3 with Na_2Se_2 in DMF at 140 °C for 20 h.

Cyclic Voltammetry. The solution redox properties of TSeN, 2, and 3 were studied by CV techniques. Since TSeN is not sufficiently soluble in acetonitrile to obtain meaningful data, our experiments were performed in benzonitrile with 0.10 M tetraethylammonium perchlorate (TEAP) as support electrolyte and a Ag/Ag$^+$ couple [which is ca. +0.32 V vs. a saturated calomel electrode (SCE)] as reference electrode. TSeN (10^{-4} M) exhibits two reversible one-electron steps at +0.15 and +0.54 V vs. Ag/Ag$^+$. No

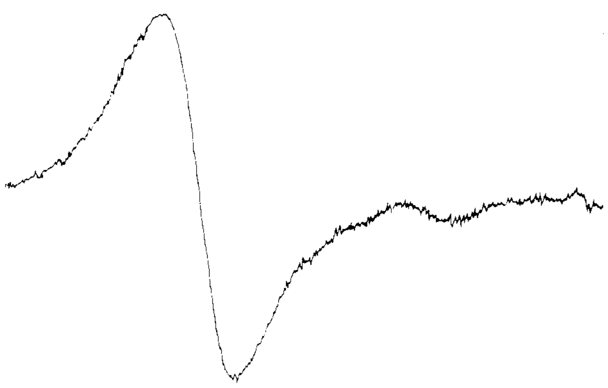


Figure 1. ESR spectrum of TSeN$^+$, produced by CF_3CO_2H oxidation in CH_2Cl_2 solution at room temperature. For parameters, see text.

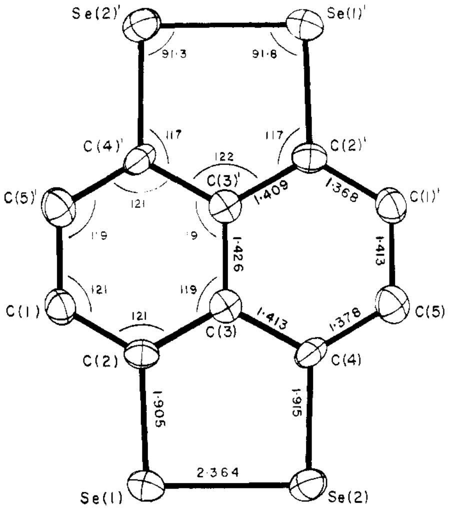


Figure 2. The molecular structure of $C_{10}H_4Se_4$, showing 50% probability ellipsoids for atoms with anisotropic thermal parameters.

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(23) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932. Foxman, B. M.; Mazurek, H. *Ibid.* **1979**, *18*, 113.

(24) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101, (b) pp 148–150.

(25) In addition to the intense absorption noted here, TSeN exhibits weaker absorption at lower energies, both in solution and solid-state spectra. This absorption, which could be analogous to that observed[4] in naphthalene 1,8-disulfide, will not be discussed here.

(26) Acampora, L. A., unpublished experiments.

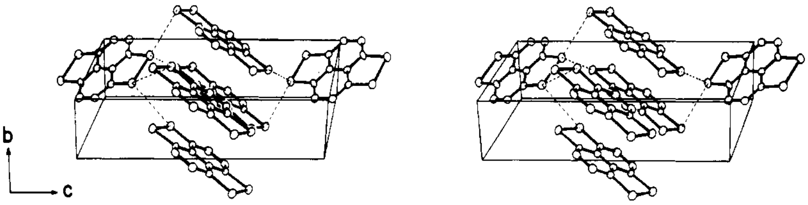

Figure 3. A stereoview of the packing of $C_{10}H_4Se_4$, showing (i) stacks of TSeN molecules along the *b* axis and (ii) short interstack Se–Se contacts (dashed lines).

Table III. Bond Lengths (Å) and Angles (deg) for $C_{10}H_4Se_4$[a]

Se(1)-Se(2)	2.364 (1)	C(3)-C(3)′	1.426 (14)
Se(1)-C(2)	1.905 (5)	C(3)-C(4)	1.413 (7)
Se(2)-C(4)	1.915 (5)	C(4)-C(5)	1.378 (8)
C(1)-C(2)	1.368 (8)	C(1)-H(1)	0.85 (6)
C(1)-C(5)	1.413 (8)	C(5)-H(5)	1.00 (8)
C(2)-C(3)	1.409 (7)		

C(2)-Se(1)-Se(2)	91.8 (2)	C(2)-C(3)-C(4)	122.5 (5)
Se(1)-Se(2)-C(4)	91.3 (2)	C(4)-C(3)-C(3)′	118.6 (8)
C(2)-C(1)-C(5)	120.9 (5)	C(3)-C(4)-Se(2)	117.2 (4)
C(1)-C(2)-Se(1)	122.0 (4)	C(5)-C(4)-Se(2)	121.5 (4)
C(3)-C(2)-Se(1)	117.3 (4)	C(3)-C(4)-C(5)	121.3 (5)
C(1)-C(2)-C(3)	120.7 (5)	C(4)-C(5)-C(1)	119.3 (5)
C(2)-C(3)-C(3)′	119.2 (8)		

[a] Primes indicates atoms related by a center of symmetry.

reduction of TSeN was observed to −0.90 V vs. Ag/Ag$^+$. The potential difference between the two potentials of TSeN (0.39 V) is comparable to that difference for TTN (0.38 V)[8] and that of the tetrachalcogenotetracenes (0.36–0.38 V).[19]

Our observation of reversible conversion of TSeN to TSeN^{+2} contrasts with the work of Yamahira et al.,[18] who report one redox process at +0.40 V vs. SCE in benzonitrile.

In acetonitrile solution with 0.10 M TEAP as support electrolyte, **3** (10^{-3} M) exhibits a reversible redox step at +0.53 V vs. Ag/Ag$^+$. This may be compared to naphthalene 1,8-diselenide which was observed[16] to have a half-wave potential at +0.76 V vs. SCE in acetonitrile.

At a sweep rate of 100 mV/s in acetonitrile 0.10 M in TEAP, **2** (10^{-3} M) reveals an irreversible reduction peak at −1.99 V vs. Ag/Ag$^+$.

Electron Spin Resonance. For ESR studies, the cation radicals of TSeN and **3** were prepared in dichloromethane solution by oxidation with trifluoroacetic acid at room temperature. We compared our results with those reported for TTN,[27] the naphthalene 1,8-dichalcogenides,[6] and the tetrachalcogenotetracenes.[19] Neither spectrum exhibits hyperfine coupling. The spectrum of TSeN,$^+$ displayed in Figure 1, is characterized by its line width, 10.4 G, and its isotropic *g* value, 2.0425. TTN$^+$ exhibits[27] a line width of 0.3 G and $g = 2.0094$. The increased line width and *g* value in TSeN$^+$ compared to that in TTN$^+$ follow from increased spin–orbit coupling in the selenium compound. Similar behavior is observed in the tetrachalcogenotetracenes[19] and the naphthalene 1,8-dichalcogenides.[6] Indeed, both series exhibit a linear relationship between the *g* value and the chalcogen spin–orbit interaction parameter.

The ESR spectrum of **3**$^+$ showed the superposition of two spectra with line widths of ca. 12 G and relative intensities of 3–4:1. The more intense spectrum exhibits a *g* of ca. 2.0431 and the other *g* is ca. 2.029. The cation–radical of naphthalene 1,8-diselenide has $g = 2.0397$.[6]

Crystal and Molecular Structure of TSeN. Figure 2 shows the molecular structure of TSeN. The observed C–C bond lengths (Table III) are in close agreement with those found in naphthalene.[28] The Se–Se and Se–C distances are near the values observed for "tetraselenaanthracene (TSA)" (Se–Se 2.342 (1), Se–C 1.916 (6) Å).[29] Bond lengths have not been reported to date for TSeT.[30,31]

The carbon atoms form a plane with no derivations >±0.007 (6) Å; however, the selenium atoms deviate markedly from this plane (Se(1), 0.101 (1); Se(2), −0.049 (1) Å). The C–Se–Se–C torsion angle is 4.4°. The packing of the molecules is shown in Figure 3. The plane-to-plane intrastack distance is 3.621 Å; further, there are short *interstack* Se(1)···Se(1) contacts of 3.626 Å and Se(2)···Se(2) contacts of 3.534 Å. Angles subtended at individual Se(1) and Se(2) atooms in these infinite chains are 71.3 and 73.4°, respectively. These distances are similar to those observed for TSA[29] (intrastack plane-to-plane distance, 3.59 Å; Se–Se contacts 3.467, 3.823 Å). For orthorhombic TSeT,[30] no Se–Se contacts shorter than 3.73 Å are reported.[32] The tilt angle to the *b* axis in TSeN is 31.0°, very similar to that observed for TTeT[12] (31.2°) and TSA (29.0°).

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Registry No. **1**, 52875-51-1; **1** radical cation, 83387-04-6; **2**, 3432-57-3; **3**, 89278-29-5; Na_2Se_2, 39775-49-0; TClT, 62409-66-9; 6,11-dihydroxy-5,12-tetracenequinone, 1785-52-0.

Supplementary Material Available: Tables of (i) anisotropic thermal parameters for Se and C atoms and isotropic thermal parameters for H atoms and (ii) observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(27) Bramwell, F. B.; Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 4612.

(28) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504. Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2855.

(29) Endres, H.; Keller, H. J.; Queckborner, J.; Schweitzer, D.; Veigel, J. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2855.

(30) Hilti, B.; Mayer, C. W.; Rihs, G. *Helv. Chim. Acta* **1978**, *61*, 1462.

(31) Sandman, D. J.; Stark, J. C.; Hamill, G. P.; Burke, W. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 79. Sandman, D. J.; Hamill, G. P.; Burke, W. A. *Ibid.* **1982**, *82*, 69.

(32) Using the established isomorphism of (TSeT)[31] and atomic coordinates of TTeT,[12] a plane-to-plane intrastack distance of 3.500 and Se–Se contacts of 3.554 Å are expected.