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Preparation and Crystal Structures of Tetracyanoquinodimethans Fused with [1,2,5]Selenadiazole Units

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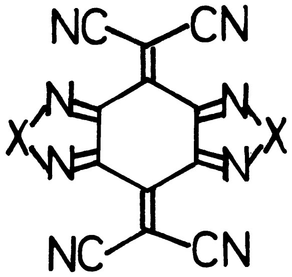
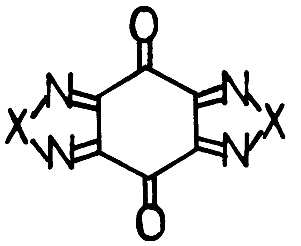
The title electron acceptors, TSDA (**2**) and BSDA (**3**), were prepared which crystallize isomorphously with the sulfur analogue, BTDA (**1**). The molecular interactions are enhanced in **2** and **3** compared with **1**, which connect the molecules to form two-dimensionally expanded "sheet-like" networks and their infinite layers.

Recent advances in the study on the conducting organic solid reveal the importance of two-dimensional structures formed by the interheteroatom interactions which stabilize the metallic state against the metal-insulator transition.[1)] We have recently found that BTDA **1** containing thiadiazole rings forms two-dimensional networks by S--N≡C interactions[2)] which induce the electrical conductivity along the side-by-side directions in some anion radical salts.[3)] In this connection, it is very intriguing to substitute selenium atoms for sulfur atoms in BTDA **1** which enhances the interheteroatom interactions.[4)] We report here the preparation and properties of [1,2,5]thiadiazolo[1,2,5]selenadiazolotetetracyanoquinodimethan (TSDA)(**2**) and bis[1,2,5]selenadiazolotetracyanoquinodimethan (BSDA) (**3**) along with their crystal structures.

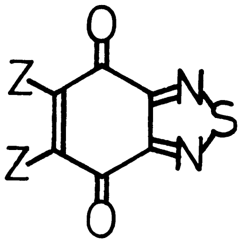
The preparation of **2** was started from 4,7-dihydroxybenzo[2,3-c][1,2,5]thiadiazole **7**[5)] which can be obtained in 45% yield from p-dimethoxybenzene by five steps. **7** was treated with three equivalents of bromine to give **8** (mp 224-226 °C), which was subjected to Gabriel Synthesis to give diamine **10** (decomp. > 350 °C) via **9** (sublim. > 345 °C). Treating **10** with selenium oxychloride in the presence of triethylamine resulted in the cyclization to give the dione **5** (mp > 400 °C) in 57% yield starting from **7**. Condensation reaction of **5** with malononitrile in the presence of $TiCl_4$ and dry pyridine gave TSDA **2** in 72% yield as stable yellow crystals which was purified by sublimation (330 °C, 4×10^{-2} Torr) [mp > 400 °C; IR (KBr) 2224 cm^{-1}; UV (MeCN) λ_{max} 367 (log ε 4.47), 327 (4.52), 248 (3.97 sh), 239



BTDA 1 :X=S,S
TSDA 2 :X=S,Se
BSDA 3 :X=Se,Se



BTDA-BQ 4 :X=S,S
TSDA-BQ 5 :X=S,Se
BSDA-BQ 6 :X=Se,Se



8 :Z=Br
9 :Z=phthalimino
10 :Z=NH_2

(4.06) nm]. Although this preparation method consists of many steps, it should be noted that the procedures are easy without using chromatography to purify, and no symmetrical analogues such as **1** and **3** are formed. BSDA **3** was analogously prepared by the condensation reaction of **6**$^{6)}$ and malononitrile under nitrogen in 71% yield and purified by sublimation (390 °C, 4 x 10^{-2} Torr) [mp > 400 °C; IR (KBr) 2223 cm^{-1}; UV (MeCN) λ_{max} 380 (log ε 4.46 sh), 351 (4.62), 242 (4.02) nm].

The half-wave reduction potentials of **2** and **3** were measured by cyclic voltammetry. TSDA **2** undergoes four reversible one-electron reductions like **1** while third and fourth reduction steps of BSDA **3** are quasi-reversible. The semiquinone formation constants were calculated as $\log K_{sem} = (E_1-E_2)/0.058$. These results are summarized in Table 1. The lower values of E_1 of **2** and **3** compared with that of **1** are attributed to the smaller aromatic stabilization of the fused selenadiazole ring compared with that of the fused thiadiazole ring in the reduction forms.$^{4)}$ The more important finding is that the K_{sem} values of **2** and **3** are smaller compared with that of **1** or TCNQ. These contractions of the K_{sem} values are not resulted from the molecular deformation since the K_{sem} value of dione **5** is also smaller than that of **4**. Therefore, the smaller K_{sem} values of **2** and **3** can be attributed to the decrease in intramolecular Coulomb repulsion caused by the incorporation of selenium atoms with large polarizability.

In order to invesigate the effects of substitution of selenium atoms for the sulfur atoms on the interheteroatom interactions and molecular geometry, X-ray structural analyses for **2** and **3** were carried out.$^{7)}$ Crystal data for **2** and **3** are summarized in Table 2 along with those for **1** which clearly indicate that **2** and **3**

Table 1. Reduction potentials$^{a)}$ and semiquinone formation constants of acceptors

Acceptor	E_1	E_2	$\log K_{sem}$	E_3	E_4
BTDA **1**	-0.02	-0.49	8.10	-1.21	-1.76
TSDA **2**	-0.12	-0.55	7.41	-1.10	-1.63
BSDA **3**	-0.23	-0.55	5.52	-1.1$^{b)}$	-1.5$^{b)}$
TCNQ	+0.18	-0.36	9.31		
BTDA-BQ **4**	-0.58	-1.21	10.86		
TSDA-BQ **5**	-0.64	-1.09	7.76		
BQ	-0.53	-1.23	12.07		

a) V vs. SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}. The very low solubility of BSDA-BQ **6** in MeCN prevented the CV study.
b) Quasi-reversible.

Table 2. Crystal data for BTDA **1**, TSDA **2**, and BSDA **3**

	1	2	3
MF (MW)	$C_{12}N_8S_2$ (320.32)	$C_{12}N_8SSe$(367.21)	$C_{12}N_8Se_2$(414.11)
space group	monoclinic, C2	monoclinic, C2/m	monoclinic, C2/m
a(Å)	8.990(1)	9.089(1)	9.203(1)
b(Å)	13.042(1)	13.226(1)	13.388(1)
c(Å)	5.538(1)	5.418(1)	5.314(1)
β(°)	99.01(1)	98.89(1)	98.53(1)
V(Å^3)	641.30(2)	643.49(2)	647.51(2)
D_{calcd}(g cm^{-3})	1.66	1.90	2.12
Z	2	2	2

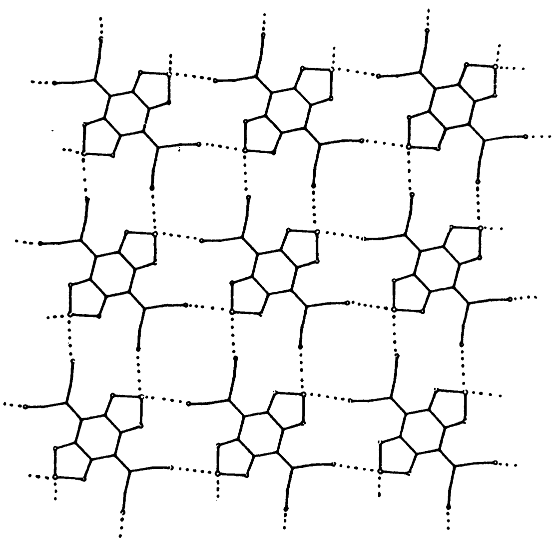


Fig. 1. "Sheet-like" network in 3.

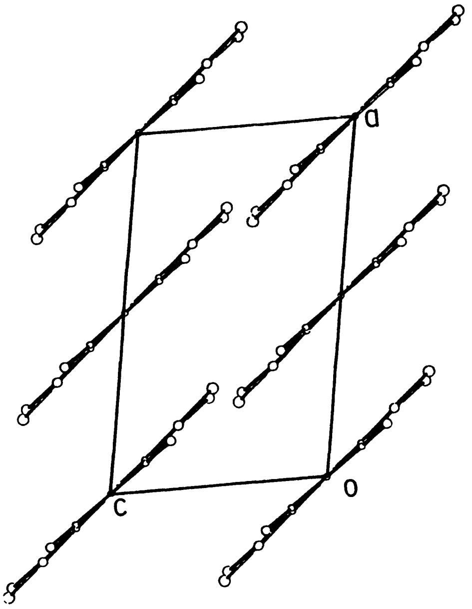


Fig. 2. "Sheet" forms infinite layer in 2.

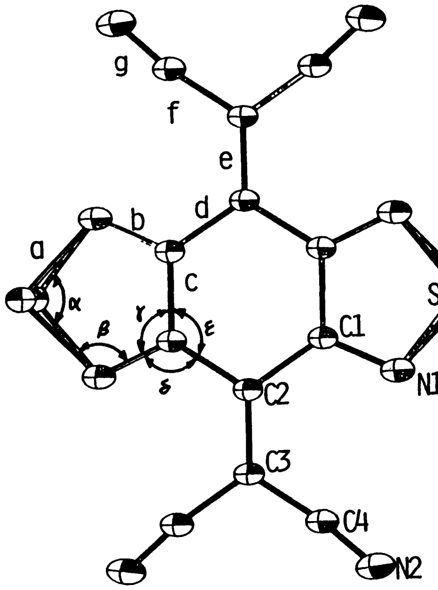


Fig. 3. Thermal ellipsoid of 2.

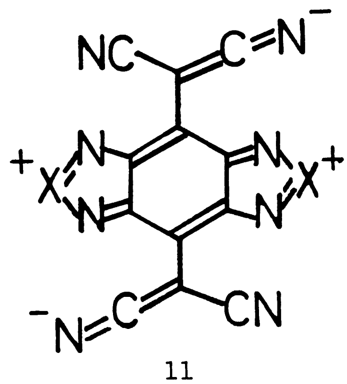
Table 3. Comparison of bond length (Å)

Bond	1	2	3
a(X=Se)	-	1.780(9)	1.790(3)
a(X=S)	1.616(6)	1.627(11)	-
b	1.330(4)	1.319(12)	1.309(5)
c	1.422(6)	1.432(13)	1.453(6)
d	1.457(6)	1.469(13)	1.459(6)
e	1.356(7)	1.359(14)	1.367(6)
f	1.438(6)	1.431(14)	1.438(6)
g	1.143(5)	1.128(14)	1.132(6)

Table 4. Comparison of bond angle (°)

Angle	1	2	3
α(X=Se)	-	91.0(6)	92.7(2)
α(X=S)	99.6(3)	102.5(6)	-
β(X=Se)	-	109.6(6)	107.9(2)
β(X=S)	107.0(2)	103.7(6)	-
γ	113.2(2)	114.8(8)	115.7(3)
δ	123.4(3)	122.0(8)	122.0(3)
ε	123.4(3)	123.1(8)	122.2(3)

crystallize isomorphously with **1**, and the sulfur and selenium atoms in **2** are completely disordered in the crystal. **2** and **3** are almost planar molecules possessing a high symmetry of mmm. The structure of **1** which consists of a coplanar sheet-like network and its infinite layer is maintained in both **2** and **3** (Figs. 1 and 2). The intermolecular distances of S--N≡C are 3.03 and 3.04 Å in **1** and 3.06 Å for **2**, while those of Se--N≡C are 2.92 Å for **2** and 2.94 Å in **3** [sum of Van der Waals radii: 3.40 Å for S--N; 3.55 Å for Se--N]. This fact shows that the molecular interactions are enhanced by replacing the sulfur atoms with the selenium atoms. Tables 3 and 4 show the bond lengths and angles of **2** and **3** along with those of **1**. The notable differences in the molecular geometry have appeared in the fused heterocycles (Fig. 3). The C=N bonds (bond b) are shortened in the order of **1**, **2**, and **3** while C-C bonds (bond c) are elongated in the same order. This can be attributed to the small aromaticity of the selenadiazole ring compared with that of the thiadiazole ring. Furthermore, the exomethylene bonds (bond e) are elongated in the order of **1**, **2**, and **3**. The stronger molecular interactions in **2** and **3** are rationalized by the much contribution of the polarized form[8] such as **11** which is favoured for **2** and **3** fused with the selenadiazole rings with small aromaticity.



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7) A total of 2313 reflections within $2\theta = 65°$ for **2** and that of 1886 reflections within $2\theta = 60°$ for **3** were collected on a Rigaku automated four-circle diffractometer (AFC-5R) using graphite monochromated MoK_α radiation. The structures were solved by the direct method and refined by the block-diagonal least-squares method with anisotropic temperature factors. The final R value of **2** is 9.84% for 1016 unique reflections with $|Fo| > 3\sigma|Fo|$, which is relatively large since the calcogen atoms are disordered in **2**. Because of the large linear absorption coefficient for **3** ($\mu = 56.589\ cm^{-1}$), absorption correction was applied to give the final R value of 4.43% for 1649 reflections with $|Fo| > 3\sigma|Fo|$.

8) The S--N interaction between thiadiazole rings is caused by the polarized sulfur nitrogen bond. A. Gieren, V. Lamm, R. C. Haddon, M. L. Kaplan, J. Am. Chem. Soc., 101, 7277 (1979); 102, 5070 (1980).

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