CHEMISTRY LETTERS, pp. 1129-1132, 1987.

Preparation, Properties, and Crystal Structure of [1,2,5]Selenadiazolotetracyanonaphthoquinodimethan

Takanori SUZUKI, Chizuko KABUTO,+ Yoshiro YAMASHITA, and Toshio MUKAI*

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980
+Instrumental Analysis for Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

The title compound was prepared which forms a two-dimensional "ribbon dimer" network by strong Se--Se and Se--N interactions in the crystal.

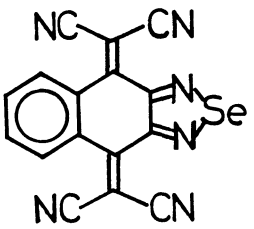
BTDA-TCNQ (bis[1,2,5]thiadiazolotetracyanoquinodimethan) (**2**)[1] is a new type of electron acceptor which gives highly conductive CT complexes[2] and anion-radical salts with a two-dimensional "sheet" or "ribbon" network by strong S--N≡C interactions.[3] Since selenium atom enhances the interheteroatom interactions more effectively than sulfur atom,[4] we have attempted to substitute the selenium atoms for the sulfur atoms of BTDA-TCNQ. We report here the preparation and properties of [1,2,5]selenadiazolotetracyanonaphthoquinodimethan (SDA-TCNNQ) (**1**) along with the crystal structure, from which the effects on the substitution of a thiadiazole ring by a selenadiazole ring are discussed.

1 was prepared by a $TiCl_4$-catalyzed condensation reaction of the corresponding diketone, naphtho[2,3-c][1,2,5]selenadiazole-4,9-dione,[5] with malononitrile in 66% yield.[6] The half-wave reduction potentials were measured by cyclic voltammetry, and the semiquinone formation constant K_{sem} was calculated as log $K_{sem} = (E_1-E_2)/0.058$ (Table 1). The K_{sem} value of **1** is smaller than that of TCNQ or **2**, and nearly the same with that of TDA-TCNNQ (**3**). The small K_{sem} value shows that the anion-radical of **1** is thermodynamically unstable, and this is due to the nonplanar structure of **1** caused by the steric hindrance between the dicyanomethylene groups and hydrogen atoms at the peri-positions. However, the fact that this value is larger than that of the heavily butterfly-shaped TCNAQ (**4**)[7] shows that the molecular planarity is improved in **1** compared with **4**. Although the electron withdrawing property of a selenadiazole ring is stronger than that of a thiadiazole ring,[8] **1** has lower first (E_1) and second (E_2) reduction potentials than **3**. This may be explained by considering that the aromatic energy which stabilizes the anion-radical and dianion species as shown in **7** is larger in naphtho[2,3-c][1,2,5]thiadiazole (**5**) than in naphtho[2,3-c][1,2,5]selenadiazole (**6**) since the contribution of d-orbital of sulfur to the π-electron system is larger

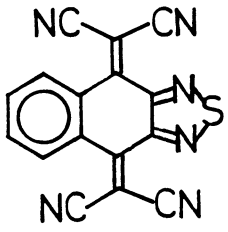
Table 1. Reduction potentials[a] and semiquinone formation constants of acceptors

Acceptor	E_1	E_2	log K_{sem}	E_3	E_4
SDA-TCNNQ (1)	-0.32	-0.43	1.90	-1.37	-1.96[c]
BTDA-TCNQ (2)[b]	-0.02	-0.49	8.10	-1.21	-1.76
TDA-TCNNQ (3)[b]	-0.21	-0.38	2.93	-1.50	-
TCNAQ (4)[b]	-0.37[d]	-	-0.03	-	-
TCNQ	+0.18	-0.36	9.31	-	-

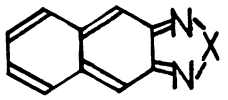
a) All values here were measured under the same conditions: V vs. SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}. b) Ref.1.
c) Irreversible. Calculated as E_{pc} (cathodic peak potential) + 0.03 V.
d) Two-electron reduction.



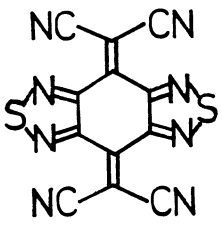
SDA-TCNNQ 1



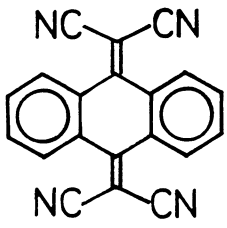
TDA-TCNNQ 3



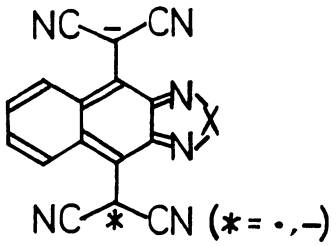
5 ; X = S
6 ; X = Se



BTDA-TCNQ 2



TCNAQ 4



7

than that of selenium. On the other hand, the third reduction potential (E_3) of **1** is higher than that of **3**, indicating that the E_3 corresponds to the one-electron reduction of the aromatic ring. To investigate the possible interheteroatom interactions as well as to confirm the improvement of the molecular planarity, X-ray structural analysis of SDA-TCNNQ (**1**) was carried out.[9] Unexpectedly, as shown in Fig. 1, **1** is a heavily deformed molecule with the dihedral angle of 144.5° between two fused rings. The central ring takes a boat form with the dihedral angles of 27.2° (plane C(1), C(3), C(5)) and 29.7° (plane C(2), C(4), C(6)) for the plane defined by C(1), C(2), C(5), and C(6) atoms. These values indicate that the degree of the deformation is the same as the case of TCNAQ (**4**),[7] while the twisting of exomethylene double bonds also occurs so as to minimize the steric interactions with the peri-hydrogens in this case. The structure of **1** does not possess a mirror plane expected from the structural formula. Especially, one exomethylene double bond [C(4)=C(12) 1.387 Å] is significantly longer than the other [C(3)=C(11) 1.336 Å], and the twisting angles are different (16.8° vs. 12.1°). The unsymmetrical structure of **1** as well as the large molecular deformation is

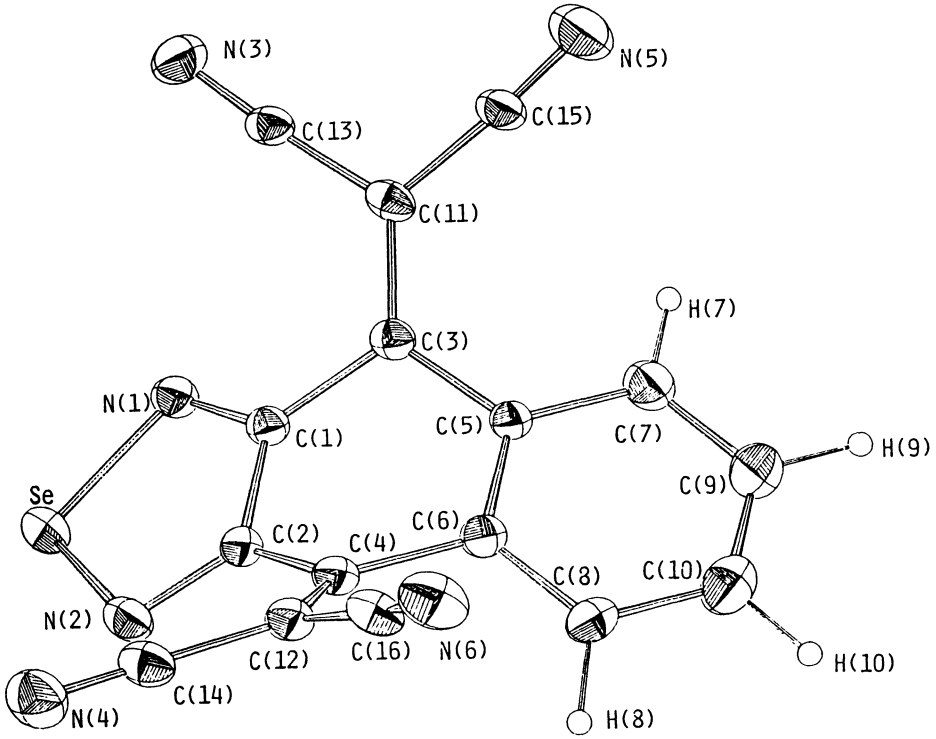


Fig. 1. ORTEP drawing of **1**. Selected bond lengths: Se-N(1) 1.790, Se-N(2) 1.814, N(1)-C(1) 1.322, N(2)-C(2) 1.318, N(3)-C(13) 1.135, N(4)-C(14) 1.136, N(5)-C(15) 1.129, N(6)-C(16) 1.149, C(1)-C(2) 1.440, C(1)-C(3) 1.484, C(2)-C(4) 1.480, C(3)-C(5) 1.471, C(3)-C(11) 1.336, C(4)-C(6) 1.475, C(4)-C(12) 1.387, C(5)-C(6) 1.414, C(5)-C(7) 1.408, C(6)-C(8) 1.403, C(7)-C(9) 1.386, C(8)-C(10) 1.408, C(9)-C(10) 1.367, C(11)-C(13) 1.436, C(11)-C(15) 1.451, C(12)-C(14) 1.449, C(12)-C(16) 1.456 Å.

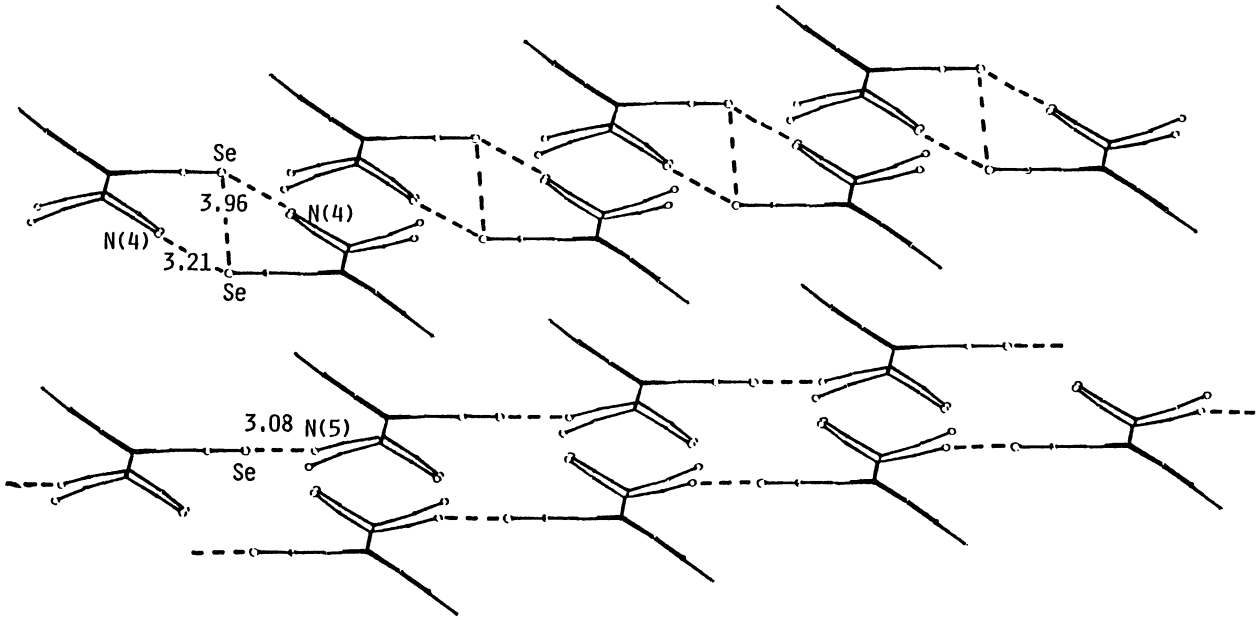


Fig. 2. "Ribbon dimer" network of **1** (side view). Se--Se and Se--N(4)≡C(14) interactions in the "dimer" (upper), and Se--N(5)≡C(15) interactions in the "ribbon" (lower) are indicated by broken line.

attributable to the "dimer" formation in the crystalline state.[10] As shown in Fig. 2, the dimer is formed by strong Se--Se (3.96 Å) and Se--N(4)≡C(14) (3.21 Å) interactions which cause the elongation of C(4)=C(12) bond. In the crystal, the dimer is not isolated but connected by strong Se--N(5)≡C(15) interactions (3.08 Å) to form a two-dimensional "ribbon dimer" network along the b axis. It is noteworthy that the distance is significantly shorter than the sum of Van der Waals radii (Se--N, 3.55 Å).[11] Although the CT complex of **1** with dimethyldihydrophenazine (1:1, decomp. 180-190 °C, ν_{CN} 2212 cm^{-1}) showed very low electrical conductivity ($\rho_{RT} > 10^{12}$ Ω cm) for the low first reduction potential of **1** resulting in the small degree of charge transfer, it is shown here that the substitution of a selenadiazole ring for a thiadiazole ring enhances the interheteroatom interactions.

References

1) Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, J. Chem. Soc., Chem. Commun., 1985, 1044; Y. Yamashita, T. Suzuki, and T. Mukai, Nippon Kagaku Kaishi, 1986, 268.

2) Y. Yamashita, T. Suzuki, G. Saito, and T. Mukai, Chem. Lett., 1985, 1759.

3) C. Kabuto, T. Suzuki, Y. Yamashita, and T. Mukai, Chem. Lett., 1986, 1433; C. Kabuto, T. Suzuki, Y. Yamashita, T. Mukai, and G. Saito, submitted for publication

4) J. M. Williams, M. A. Beno, H. H. Wang, P. C. Leung, T. J. Emge, U. Geiser, and K. D. Carlson, Acc. Chem. Res., 18, 261 (1985).

5) R. Neidlein, D. Tran-Viet, A. Gieren, M. Kokkinidis, R. Wilckens, H. Geserich, and W. Rűppel, Chem. Ber., 115, 2898 (1982).

6) **1** : Yellow crystals, decomp. 330-350 °C; satisfactory C, H, N, elemental analyses; MS (m/e) 360 (100%,M^+), 358 (59%,M^+); NMR (δ ppm,CD_2Cl_2) 7.7-7.9 (2H,m), 8.3-8.5 (2H,m); IR (KBr) 2220 cm^{-1} (CN); UV (MeCN) max 351 (log ε 4.43), 317 (4.37) nm.

7) U. Schubert, S. Hűnig, and A. Auműller, Leibigs Ann. Chem., 1985, 1216; C. Kabuto, Y. Fukazawa, T. Suzuki, Y. Yamashita, T. Miyashi, and T. Mukai, Tetrahedron Lett., 27, 925 (1986).

8) The first reduction potentials of naphthothiadiazole (**5**) and napthoselenadiazole (**6**) measured under the same conditions described in Table 1 are -1.17 and -1.05 V, respectively.

9) Crystal data for **1** : MF $C_{12}H_4N_6Se$, MW 359.2, triclinic, space group $P\bar{1}$, a=10.382(2), b=10.247(2), c=7.019(1) Å, α=75.63(1), β=97.40(1), γ=107.59(1)°, V=688.3(4) $Å^3$, Z=2, D_{calcd}=1.73 g cm^{-3}. A total of 4167 reflections was collected by Rigaku automated four-circle diffractometer (AFC-6A) using graphite monochromated CuK_α radiation, and dissolved by the direct method. Refinement was carried out by the block-diagonal least-squares method to R=0.061 for 2616 reflections within $|Fo| > 3\sigma |Fo|$.

10) This type of "dimer" formation and molecular deformation is reported for some calcogen based electron donor. K. Lerstrup, D. O. Cowan, T. J. Kistenmacher, J. Am. Chem. Soc., 106, 8303 (1984).

11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Conell University Press, Ithaca, N.Y. (1960), p. 260, Tables 7-20.

(Received March 13, 1987)