Naphthaceno[1,12-*cd*: 4,5-*c′d′*]bis[1,2]diselenole as a New Electron Donor

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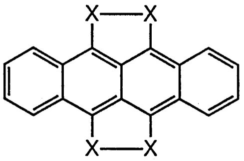
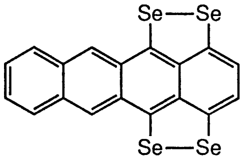
Synopsis. The title compound, an isomeric TSeT, was prepared as the first example of unsymmetrical peri-dichalcogenide derivatives of naphthacene. Like symmetrical TSeT, it is a good electron donor and forms electrically high-conductive complexes with various electron acceptors.



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



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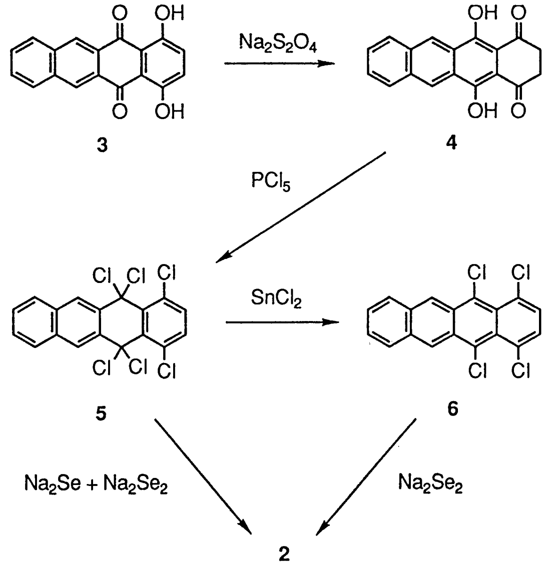
Naphthaceno[5,6-*cd*: 11,12-*c′d′*]bis[1,2]dithiole (**1a**), often called tetrathiotetracene or TTT, is a representative electron donor like tetrathiafulvalene (TTF) and can form highly conductive complexes.[1] Though the study has been extended to its derivatives including the selenium (**1b**, TSeT)[1] and tellurium (**1c**, TTeT)[2] analogs, the compounds prepared were limited to only the symmetrical form bridged at 5,6- and 11,12-peri positions. In the search for new synthetic metals, the development of unsymmetrical electron donors is of current interest.[3] As a part of these efforts, we have studied an unsymmetrical isomer bridged at 1,12- and 4,5-peri positions of naphthacene. We now like to report the synthesis and properties of naphthaceno[1,12-*cd*: 4,5-*c′d′*]bis[1,2]diselenole (**2**) as the first example of such structural type.

The synthesis of **2** was carried out as follows. Reduction of 1,4-dihydroxy-5,12-naphthacenequinone (**3**)[4] with sodium dithionite in acetone-water (1 : 1) under reflux for 1 h gave 2,3-dihydro-5,12-dihydroxy-1,4-naphthacenequinone (**4**) in 80% yield. The subsequent treatment of **4** with phosphorus pentachloride in *o*-dichlorobenzene at 140 °C for 24 h led to 1,4,5,5,12,12-hexachloro-5,12-dihydronaphthacene (**5**) in 49% yield. It was then dechlorinated with tin(II) chloride in refluxed acetic acid for 2 h to give 1,4,5,12-tetrachloronaphthacene (**6**) in 39% yield. Reaction of **6** with sodium diselenide, in situ prepared by preheating an equimolar mixture of sodium and selenium, in dry dimethylformamide at 80 °C for 20 h gave the desired compound (**2**) in 30% yield. A similar treatment of **5** with a mixed reagent of sodium selenide and diselenide (1 : 2), in situ prepared from a mixture of 3 equiv sodium and 2 equiv selenium, directly afforded the same product (**2**) in 20% yield.

Compound (**2**) is a deep green material and absorbs light at long-wavelengths in carbon disulfide solution as shown in Fig. 1; λ_{max} 396 nm ($\log \varepsilon$ 3.82), 460 (3.58), 653 (3.74), and 707 (3.88). Although the absorption peaks reveals a small blue-shift, the electronic spectrum of **2** closely resembles that of **1b**, indicating a similarity in electronic structures of both chromophores. The cyclic voltammogram of **2** exhibits two reversible redox waves, whose half-wave oxidation potentials are +0.27 and +0.60 V vs. an Ag/AgCl reference electrode in benzonitrile. These values are a little higher than the corresponding ones ($E_{1/2}$ +0.21 and +0.56 V) of **1b**, but still lower than TTF ($E_{1/2}$ +0.31 and +0.71 V). It, therefore, has a potential as a good electron donor. In addition, the better solubil-



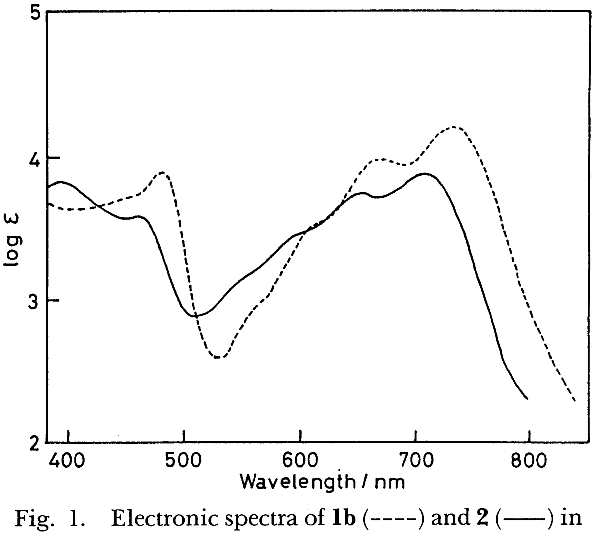


Fig. 1. Electronic spectra of **1b** (----) and **2** (——) in carbon disulfide.

Table 1. Complexation of **2** with Various Electron Acceptors[a)]

Complex	D:A	Appearance	Found (Calcd)[b)]/%			Dp/°C	ν_{CN}/cm^{-1}	Conductivity[c)] /S cm^{-1}
			C	H	N			
2·TCNQ	1:1	Black powder	48.40; (48.41;	1.74; 1.63;	6.31 7.53)	263	2173	4.2
2·TCNQF$_4$	1:1	Deep blue powder	44.32; (44.14;	1.19; 0.99;	5.68 6.86)	257	2188	1.5×10^{-1}
2·DMTCNQ	2:1	Black powder	47.62; (45.76;	2.59; 1.84;	5.08 4.27)	>300	2173	2.2
2·TNAP	1:1	Blackish green crystals	50.43; (51.41;	2.05; 1.78;	5.74 7.05)	>300	2174	34
2·TCNE	2:1	Black crystals	40.00; (41.75;	1.92; 1.33;	5.29 4.63)	256	2191	1.4×10^{-2}
2·DDQ	1:1	Black powder	40.32; (40.71;	1.13; 1.05;	3.63 3.65)	>300	2208	5.4×10^{-2}
2·I$_3$[d)]	2:1	Black powder	30.34; (29.59;	1.44 1.10)		>300	—	1.2

a) Obtained from 1,1,2-trichloroethane. b) Calculated as stoichiometry indicated. Some discrepancy between the found and calculated values suggests contamination with complexes of different stoichiometry. c) Measured on compressed pellets with a four-probe method. d) Prepared by treating **2** with tetrabutylammonium triiodide.

ity of unsymmetrical **2** relative to symmetrical **1b** can facilitate its complexation. In fact, it formed charge-transfer complexes with various electron acceptors. Table 1 summarizes the properties of its complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro derivative (TCNQF$_4$), 2,5-dimethyl derivative (DMTCNQ), 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP), tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and iodine. All the complexes are electrically high-conductive. The conductivities are roughly equal to those of the corresponding complexes of **1b**; TCNQ 1.1 S cm^{-1}, TCNQF$_4$ 9.5×10^{-3} cm^{-1}, DMTCNQ 37 S cm^{-1}, and TNAP 37 S cm^{-1}. Thus **2** is qualified as a novel component for organic metals.

Experimental

General. Melting points are uncorrected. All solvents are of reagent grade. NMR spectra were recorded on a JEOL spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. IR spectra were taken on a Hitachi 260-30 or on a Perkin-Elmer 1600 FTIR spectrophotometer with a KBr disk method. MS spectra were measured on a Shimadzu QP-1000A mass spectrometer at 70 eV using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

2,3-Dihydro-5,12-dihydroxy-1,4-naphthacenequinone (4). A mixture of 1,4-dihydroxy-5,12-naphthacenequinone (**3**) (21 g, 0.072 mol), anhydrous sodium carbonate (17.5 g, 0.165 mol), acetone (350 cm^3), and water (350 cm^3) was stirred for one hour, and sodium dithionite (35 g, 0.200 mol) was added into the solution, which was then stirred at room temperature for 1 h and further refluxed for 1 h. Water (500 cm^3) was added, and the resulting precipitate was collected and dried. It was dissolved in chloroform (600 cm^3) and filtered through a short column of silica gel. The filtrate was concentrated to ca. 100 cm^3 volume and diluted with hexane (200 cm^3), precipitating yellow needles of **4** (16.99 g, 80%): mp 230—232 °C; IR ν 1620 cm^{-1} (C=O); ^{1}H NMR δ=3.062 (4H, s, CH$_2$), 7.60—7.70 (2H, m, ArH), 8.04—8.15 (2H, m, ArH), 8.965 (2H, s, ArH), and 14.122 (2H, s, OH). Found: C, 73.89; H, 4.00%. Calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.14%.

1,4,5,5,12,12-Hexachloro-5,12-dihydronaphthacene (5). A mixture of **4** (10 g, 0.0342 mol), phosphorus pentachloride (42.7 g, 0.205 mol), and *o*-dichlorobenzene (16 cm^3) was heated at 140 °C for 24 h. The resulting precipitate was collected by filtration and washed with pet. ether to give white prisms of **5** (7.37 g, 49%): decomp 163 °C; IR ν 1560 and 1590 cm^{-1}; ^{1}H NMR δ=6.750 (2H, s, ArH), 7.40—7.70 (4H, m, ArH), and 7.623 (2H, s, ArH); MS *m/z* 436 (M$^+$), 401, and 366. Found: C, 49.44; H, 1.77%. Calcd for $C_{18}H_8Cl_6$: C, 49.48; H, 1.85%.

1,4,5,12-Tetrachloronaphthacene (6). A mixture of **5** (7.37 g, 0.0169 mol), tin(II) chloride hydrate (26.6 g, 0.118 mol), hydrochloric acid (32.7 cm^3), and acetic acid (43.6 cm^3) was refluxed for 2 h. Water (200 cm^3) was added, and the resulting precipitate was collected. It was then purified by column chromatography on alumina with chloroform and recrystallization from chlorobenzene to give red needles of **6** (4.895 g, 79%): mp 257—259 °C; IR ν 1595, 1290, and 880 cm^{-1}; ^{1}H NMR δ=7.408 (2H, s, ArH), 7.50—7.61 (2H, ArH), 8.07—8.18 (2H, m, ArH), and 9.307 (2H, s, ArH). Found: C, 59.06; H, 2.26%. Calcd for $C_{18}H_8Cl_4$: C, 59.06; H, 2.20%.

Naphthaceno[1,12-*cd*: 4,5-*c′d′*]bis[1,2]diselenole (2). A) From 1,4,5,12-Tetrachloronaphthalene (6). A suspension of sodium (0.202 g, 8.8 mmol) and selenium (0.695 g, 8.8 mmol) in anhydrous DMF (50 cm^3) was heated with magnetically stirring at 130 °C for 2 h in an argon atmosphere. After the temperature was lowered to 80 °C, **6** (0.732 g, 2.0 mmol) was added, and the reaction was continued at the temperature for 20 h. After cooling to room temperature, the resulting precipitate was collected, washed successively with water and acetone, and dried at 100 °C under 0.1 mmHg. It was then extracted with carbon disulfide by using a Soxhlet extractor, and the extract was collected and recrystallized from the same solvent, giving a deep green fine crystals of **2** (0.329 g, 30%): mp>300 °C; MS *m/z* 542 (M$^+$) involving an isotopic pattern expected for tetraselenium species. Found: C, 40.02; H, 1.44%. Calcd for $C_{18}H_8Se_4$: C, 40.03; H, 1.49%.

B) From 1,4,5,5,12,12-Hexachloronaphthacene (5). In the same way as described for Method A, sodium (0.375 g, 16.5 mmol) was first treated with selenium (0.896 g, 11 mmol) at 130 °C in anhydrous DMF (75 cm^3), and the resulting mixed reagent of sodium selenide and diselenide (1 : 2) was then allowed to react with **5** (1.09 g, 2.5 mmol) at 80 °C for 20 h. The same work-up gave a green material of **2** (0.275 g, 20%).

Preparation of Molecular Complexes. All complexes described in Table 1 were each prepared by direct reactions of donor and acceptor in hot 1,1,2-trichloroethane solutions. They precipitated out immediately or on cooling appropriately, and were collected by filtration and dried in vacuo.

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