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Extensively Conjugated Homologues of Selenophene-TCNQ as New Electron Acceptors

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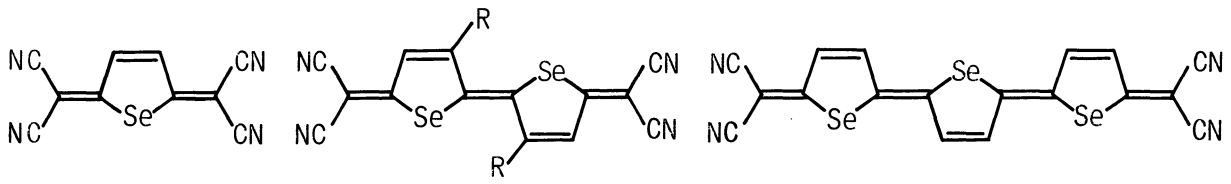
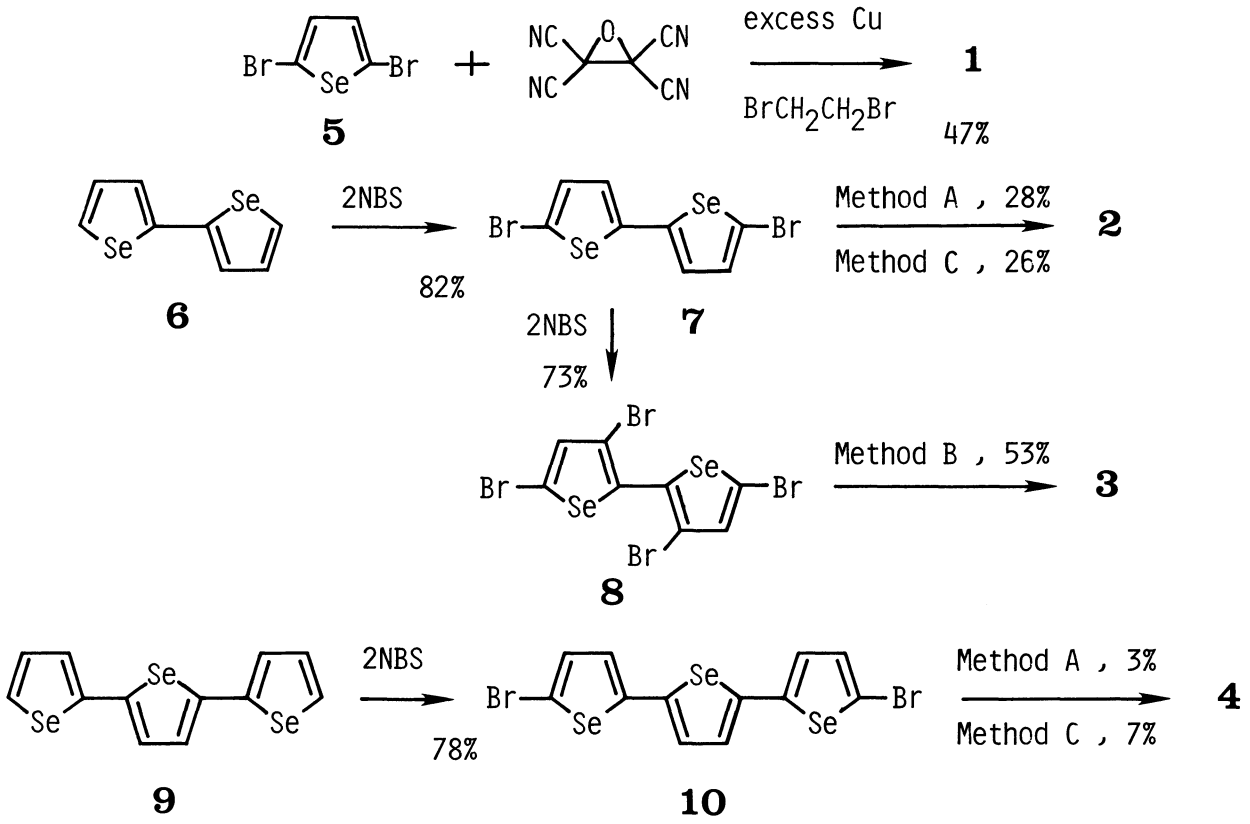
5,5'-Bis(dicyanomethylene)-5,5'-dihydro-2,2'-biselenophene, its 3,3'-dibromo derivative, and 5,5"-bis(dicyanomethylene)-5,5"-dihydro-2,2':5',2"-terselenophene have been synthesized as extensively conjugated homologues of selenophene-TCNQ. The 3,3'-dibromo compound posseses a considerably better accepting character than selenophene-TCNQ or the other extended homologues and can form highly conductive molecular complexes.

Although 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene, so-called thiophene-TCNQ, is a poor electron acceptor,[1] our recent research has revealed that extension of the central conjugated moiety to bi- or terthiophene and condensed thiophene systems effectively improves the accepting character with very small on-site Coulomb repulsion, being capable of forming highly conductive molecular complexes.[2] In addition, the mutual contacts of the sulfur atoms were demonstrated to play an important role on intermolecular interactions in the complex state.[3] These features have stimulated us to examine the selenium analogues of the above compounds because more polarizable seleniums might interact more strongly on each other. Gronowitz and Uppström previously reported 2,5-bis(dicyanomethylene)-2,5-dihydroselenophene (selenophene-TCNQ) (**1**), which has, however, received no attention as an electron acceptor.[4] We now wish to report the syntheses and properties of its extensively conjugated homologues, 5,5'-bis(dicyanomethylene)-5,5'-dihydro-2,2'-biselenophene (**2**), 3,3'-dibromo derivative (**3**), and 5,5"-bis(dicyanomethylene)-5,5"-dihydro-2,2':5',2"-terselenophene (**4**) as new electron acceptors.



1 **2**: R=H **4**

3: R=Br



Method A: TCNEO(4 equiv.), Cu(10 equiv.) in 1,2-dibromoethane, reflux, 2 h.
Method B: TCNEO(10 equiv.) in 1,3-dibromopropane, reflux, 2 h.
Method C: 1) $CH_2(CN)_2$ (4 equiv.), NaH (8 equiv.), cat. $(Ph_3P)_4Pd$, in 1,2-dimethoxyethane, reflux, 60-80 min; 2) Bromine water.

Gronowitz and Uppström reported that selenophene-TCNQ (**1**) was formed in 26% yield by the action of 2.4-fold amount of 2,5-dibromoselenophene (**5**) on tetracyanoethylene oxide (TCNEO) in 1,2-dibromoethane under reflux.[4] The excess of **5** is necessary to scavage bromine which is stoichiometrically generated in the reaction. We found that the addition of a large amount of copper powder is effective to quench the bromine, having the advantage of not only reducing the amount of less available **5** but also raising the yield of **1**. Thus an equimolar treatment of **5** and TCNEO in the presence of excess copper powder gave **1** in 47% yield. The conjugated homologues **2**-**4** were similarly synthesized as follows. 2,2'-Biselenophene (**6**)[5] was treated with 2 molar N-bromosuccinimide (NBS) in chloroform-acetic acid (1:1 v/v) at r.t. for 5 h to give 5,5'-dibromo-2,2'-biselenophene (**7**) as pale yellow leaflets with mp 174.5-175.5 °C in 82% yield. Its treatment with TCNEO and excess copper powder in refluxing 1,2-dibromoethane for 2 h afforded **2** as black fine crystals with mp>300 °C in 28% yield.[6] Further treatment of **7** with 2 molar NBS in a mixed solution of carbon disulfide-chloroform-acetic acid (12:15:8 v/v) under reflux gave 3,3',5,5'-tetrabromo-2,2'-biselenophene (**8**) as colorless needles with mp 180.5-182 °C in 73 % yield. The pyrolytic reaction of **8** and TCNEO smoothly proceeded without copper in refluxing 1,3-dibromopropane, affording **3** as deep green fine crystals with mp>300 °C in 53%

Table 1. Complexation of acceptors **1**-**3** with typical donors.

Complex[a,b]	Appearance	D.p./°C	$\nu_{C\equiv N}/cm^{-1}$	Conductivity[c]/S cm^{-1}
1•TTF	gold yellow needles	178	2230	1.3×10^{-9}
1•HMTTeF	black fine crystals	229	2223	3.9×10^{-9}
2•TTT	green fine needles	>300	2222	1.1×10^{-4}
2•HMTTeF	black fine crystals	230	2221	6.2×10^{-8}
3•TTT	dark green fine needles	>300	2200	11
3•HMTTeF	reddish black powder	258	2190	86

a) TTF: tetrathiafulvalene; HMTTeF: Hexamethylenetetratellurafulvalene; TTT: tetrathiotetracene. b) The composition of all the complexes is 1:1 of acceptor and donor except 1:2 of **2**•HMTTeF. c) Conductivities were measured on a compressed pellet at r.t. with a four- or two-probe method .

yield. 2,2':5',2"-Terselenophene (**9**)[7] was brominated with 2 molar NBS in a mixed solution of carbon disulfide-chloroform-acetic acid (1:2:1 v/v) to 5,5"-dibromo-2,2':5',2'-terselenophene (**10**) as golden orange leaflets with mp 175.5-177.5 °C in 78% yield, and the subsequent reaction gave **4** as deep green powder with mp>300 °C in only 3% yield. As an alternative method, nucleophilic substitution of the dibromide **7** or **9** with sodium dicyanomethanide in refluxing 1,2-dimethoxyethane for 60-80 min in the presence of a catalytic amount of tetrakis(triphenylphosphine) palladium(0),[8] followed by oxidation with bromine water afforded **2** in 26% yield or **4** in 7% yield.

The electrochemical properties of **1**-**4** were examined by cyclic voltammetry.[9] The compounds **1**-**3** showed two reversible redox waves, whereas **4** showed one coalescent wave: **1**, $E_{1/2}$ +0.03 and -0.54 V; **2**, $E_{1/2}$ -0.05 and -0.25 V; **3**, $E_{1/2}$ +0.15 and -0.08 V; **4**, $E_{1/2}$ -0.07 V vs. Ag/AgCl. Selenophene-TCNQ (**1**) is a slightly weak electron acceptor than thiophene-TCNQ ($E_{1/2}$ +0.07 and -0.54 V). This probably arises from smaller electronegativity of selenium than sulfur. The first half-wave reduction potentials of the conjugated compounds **2** and **4** are rather lower than that of the weak electron acceptor **1**, so that the extended conjugation does not help to improve the accepting strength. However, the introduction of bromo functions at 3,3'-positions in **2** fairly improves the accepting strength, and, as a result, **3** is qualified as a strong acceptor. The difference between the first and the second reduction potentials decreases with extended conjugation, indicating the diminution of on-site Coulomb repulsion in the dianion state. A similar trend was observed in the previous thiophene-TCNQ series,[2] but it is more appreciable in the present selenium series.

The electrical conductivities and other properties of molecular complexes consisting of acceptors **1**-**3** and typical donors are shown in Table 1. Selenophene-TCNQ **1** with TTF and with HMTTeF formed 1:1 crystalline complexes whose conductivities were quite low. The extended acceptor **2** formed semi-conductive complexes with TTT and with HMTTeF. The further extended acceptor **4** was expected to form more conductive complexes due to much smaller on-site Coulomb repulsion, but its complexation was quite difficult due to its low solubility. On the other hand, both TTT and HMTTeF complexes of **3** exhibited extremely high conductivities

which attained to metallic regions. Thus **3** is unambiguously a superior electron acceptor whose complexation is considered to be facilitated by a combination of the extended conjugation system, the enhanced electron affinity, and the mutual interaction of the selenium atoms. Further investigation on its complexation is in progress.

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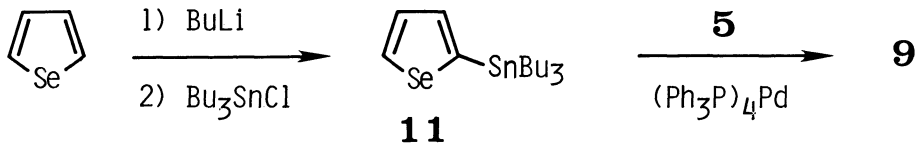
6) All new compounds were characterized by elemental and spectroscopic analyses. Compounds **2-4** have a possibility of taking both trans and cis configurations, but the molecular models favor the trans configuration.

7) 2,2':5,2"-Terselenophene (**9**) was prepared as follows. Selenophene was treated with butyllithium in THF at 0°C followed by chlorotributyltin to give tributyl-(2-selenenyl)tin (**11**) in 22% yield. The subsequent coupling of 2,5-dibromoselenophene (**5**) and 2 molar **11** in the presence of a catalytic amount of tetrakis(triphenylphosphine) palladium(0) in refluxing toluene gave **9** as yellow leaflets with mp 175.5-177.5 °C in 60% yield.



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9) Cyclic voltammetry was carried out in dichloromethane containing 0.1 M Bu_4NClO_4 as supporting electrolyte, with a platinum working electrode and a Ag/AgCl reference electrode at a scan rate of 100 mV/s.

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