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2,2'-Bitellurophene and 2,2':5',2"-Tertellurophene as Novel High Homologues of Tellurophene

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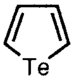
Abstract: The title heterocycles were prepared from tellurophene, and their spectroscopic and electrochemical properties were systematically compared together with those of other chalcogenophene congeners. Their electropolymerizations gave poly(bitellurophene) and poly(tertellurophene) as black films, which both had higher electrical conductivities than poly(tellurophene) similarly obtained.

Tellurium-containing compounds are of current interest as components of organic metals, because tellurium might contribute to effective intermolecular electronic interactions.[1] Tellurophene (**1**), the heaviest member of the series of chalcogenophenes, is one of such potential compounds, but studies of its chemistry are hampered by poor availability and lability of material.[2] Polythiophene and its derivatives are attracting growing attention among conducting polymers because of their excellent electrical properties, processibility, and environmental stability,[3] and various oligothiophenes have been developed as their model compounds.[4] In contrast, almost nothing has been studied about tellurophene system. Only a report[5] and a few Japanese patents[6] on polytellurophene already appearred, but its possibility as a conductive polymer still remains obscure. In this regard, we have been interested in the conjugated homologues of tellurophene. Here we like to report on the first syntheses and spectroscopic and electrochemical properties of 2,2'-bitellurophene (**2**) and 2,2':5',2"-tertellurophene (**3**).



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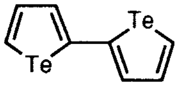

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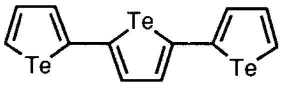

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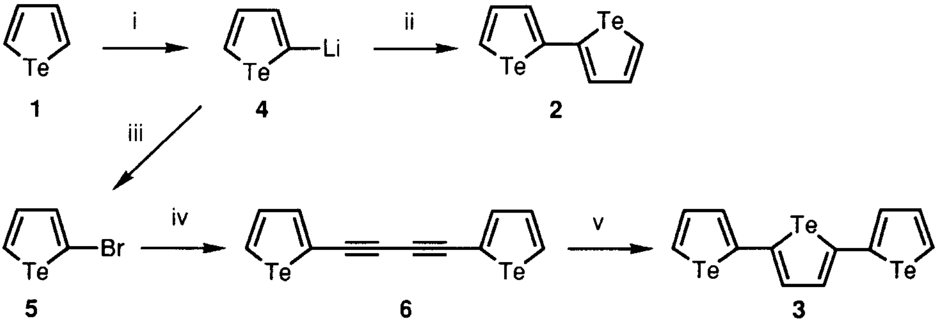
Compounds **2** and **3** were derived from tellurophene (**1**),[7] as shown in Scheme 1. Thus, **1** was reacted with butyllithium in dry ether producing 2-lithiotellurophene (**4**),[8] which was then treated in situ with copper(II) chloride to give **2** in 39% yield.[9] An alternative treatment of **4** with 1,2-dibromotetrachloroethane gave 2-bromotellurophene (**5**)[10] in 64% yield, and a subsequent coupling reaction with 1,4-bis(trimethylsilyl)butadiyne in the presence of catalytic tetrakis(triphenylphosphine)palladium, copper iodide, benzyltrimethylammonium chloride, and sodium hydroxide at 40 °C[11] gave 1,4-(tellurophen-2-



Scheme 1. Reagents and Conditions: i) BuLi, ether, -20°C then RT, 45 min; ii) $CuCl_2$, -70°C then RT, 1d; iii) $BrCl_2CCBrCl_2$, -60°C, 3h; iv) $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, $Pd(PPh_3)_4$, CuI, $PhCH_2NEt_3Cl$, NaOH, C_6H_6, 40°C, 1d; v) Na_2Te, EtOH-DMF, reflux, 1d.

yl)butadiyne (**6**) in 52% yield. A ring closure of **6** with sodium telluride, generated from sodium hydroxide and Rongalite in ethanol-dimethylformamide led to the formation of **3** in 35% yield.

In contrast to a colorless oil of **1**, compounds **2** and **3** are rather stable solids, which are yellow- or orange-colored. Figure 1 shows the electronic spectra of tellurophenes **1**-**3**, which demonstrates large bathochromic shifts with an increase in the number of the linked rings. In addition, Table 1 shows a comparison of their absorption bands with those of the other chalcogenophene series; all tellurophene congeners absorb at markedly longer wavelengths than do the corresponding thiophenes and selenophenes. Although the electronic spectrum of tellurophene has not been theoretically interpreted yet, this result indicates that tellurophene has the smallest HOMO-LUMO energy gap among chalcogenophenes, which also holds for the conjugated series.

The structure of **2** were elucidated by an X-ray crystal analysis.[12] As shown in Fig. 2, the molecular structure is planar with a two-fold axis at the center and the geometry of the two tellurophene rings around the central single bond is arranged in a transoid form. The length of the central single bond is 1.46 Å, reflecting a reasonable conjugation between both rings. The bond lengths and angles of the tellurophene ring are nearly similar to those of tellurophene (**1**) which was determined on the basis of its microwave spectrum.[13] The crystal structure is characterized by relatively loose packing and no shortened intermolecular contacts are obtained.

Table 1 also shows the oxidation potentials of tellurophenes, which were measured by cyclic voltammetry. Tellurophene (**1**) shows an irreversible oxidation wave with a peak at 1.54 V, which is markedly lower than those (>1.8 V) of thiophene and selenophene. This is consistent with the low ionization potential of tellurophene, which is considered to arise from the less electronegativity of tellurium atom than sulfur or selenium atom.[14] Furthermore, an increase in the linked rings serves to steadily lower the oxidation potential as expected, and the oxidation peaks of **2** and **3** appearred at 1.19 and 0.94 V, respectively. This is expected to permit a ready electrochemical polymerization for the high homologues. In fact, a galvanostatic polymerization of **1** in benzonitrile including tetrabutylammonium perchlorate as a supporting electrolyte required a high electrical current of 1 mA, giving a black powder of poly(tellurophene) which had a conductivities of 1.3×10^{-7} Scm^{-1}. The low conductivity is supposed to be due to partial decomposition or branching of the polymer chain formed under the severe electrolytic conditions. In contrast, similar

Table 1. Electronic spectra and oxidation potentials of a series of chalcogenophenes

Chalcogenophene	λ_{max} (log ε)/nm[a]	E_{ox}/V[b]
Tellurophene (**1**)	245(3.32), 281(3.91)	1.54
2,2'-Bitellurophene (**2**)	216(4.00), 230(3.95), 304(4.03), 317(4.04), 362(3.98), 385sh(3.77)	1.19
2,2':5',2"-Tertellurophene (**3**)	209(4.31), 254(3.89), 343(3.98), 423(4.36), 452sh(4.18)	0.94
Selenophene	250(3.87)	>1.8
2,2'-Biselenophene	273(3.94), 328(4.06)	1.34
2,2':5',2"-Terselenophene	220(4.01), 274(3.98), 386(4.39)	1.04
Thiophene	230(3.90)	>1.8
2,2'-Bithiophene	248(3.76), 304(4.09)	1.46
2,2':5',2"-Terthiophene	216(3.95), 253(3.95), 353(4.37)	1.13

a) Measured in THF.

b) Measured at 100 mV/sec in benzonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte. The working and counter electrodes were a platinum wire and the reference electrode an Ag/AgCl standard electrode.

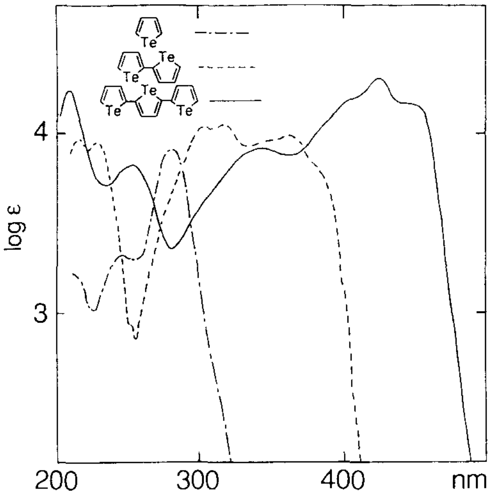


Fig.1. Electronic spectra of a series of tellurophenes **1**-**3** in THF

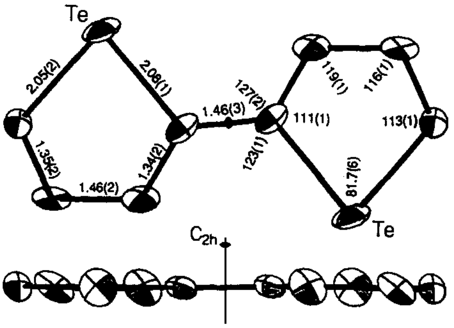


Fig.2. Molecular structure of 2,2'-bitellurophene

polymerizations of **2** and **3** readily occurred under 50 μA, giving black films. The resulting poly(bitellurophene) and poly(tertellurophene) displayed improved conductivities of 7.6 × 10^{-6} and 1.3 × 10^{-5} Scm^{-1} in order.

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