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N,*N*-Dimethylformamide-Mediated Sodium Reduction of *trans*-3,3′-Benzo[*c*]thienylidene-1,1′-dithione and *trans*-3,3′-Benzo[*c*]selenonylidene-1,1′-dithione

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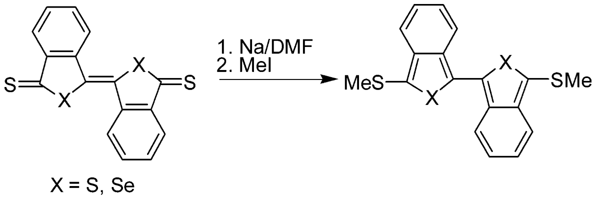
ABSTRACT



The synthesis of stable methylthio-capped biisothianaphthene and biisoselenophene derivatives has been achieved using DMF-mediated sodium reduction of cyclic thiocarbonyl compounds.

Very little is known concerning the sulfur and selenium analogues of cyclic anhydrides. Our laboratory is involved in the synthesis and studies of this class of heterocycles.[1−5] We reported the synthesis of the stable thionothiophthalic anhydride **1** in 1988.[2] In contrast, all of our attempts to bring about the synthesis of trithiophthalic anhyhdride **2** by thionation of the carbonyl group in **1**, using classical thionation reagents, gave rise to a black polymeric material from which *trans*-3,3′-benzo[*c*]thienylidene-1,1′-dithione (**3**) was isolated in very low yield.[3] Compound **3** was obtained in good yield by the reaction of *trans*-3,3′-bithiophthalide (**4**) with Lawsson's reagent.[6,7] Recently, we resumed our interest in this class of compounds and reported the synthesis of the stable selenium analogues **5** and **6**.[5] Thionation of the known selenophthalic anhydride (**7**)[8] gave rise to insoluble, dark polymeric materials. Apparently, seleno dithiophthalic anhydride (**8**) should have formed and, in analogy to the trithiophthalic anhydride (**2**), must have polymerized.[5]

However, the above cyclic thiocarbonyl compounds are useful precursors for many interesting transformations. Our present investigation was concerned with examining the reduction of the stable dithione derivatives **3** and **6**. Electrochemical reduction of thiocarbonyl compounds have received only very little attention,[9] probably due to the limited solubility as well as their stability of in organic solvents. In general, stable thiones are reduced more easily

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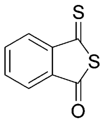

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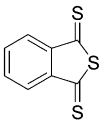

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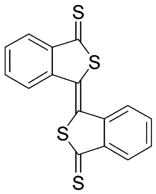

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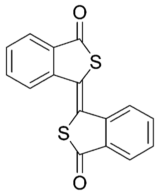

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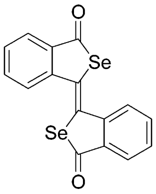

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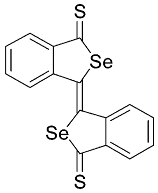

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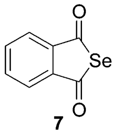

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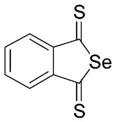

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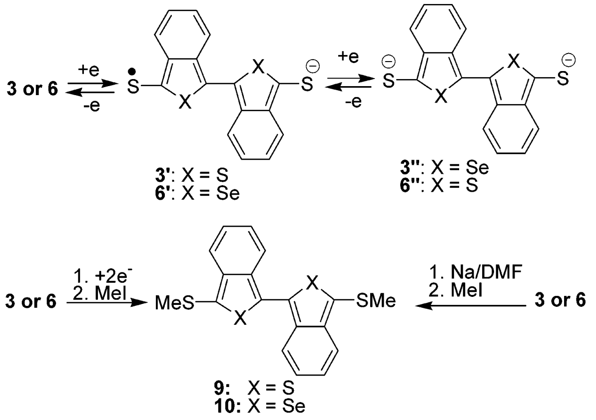
than the corresponding carbonyl structures, and stable aromatic thioketones, such as thiobenzophenone, upon one-electron reduction, produce a highly stable anion radical, which has been demonstrated to play the role of a nucleophile toward a variety of alkylating agents.[9]

The electron-accepting properties of the stable thiocarbonyl derivatives **3** and **6** were studied by cyclic voltammetry (CV). The voltammograms of DMF solutions of **3** and **6** exhibit two reversible one-electron reduction waves corresponding to the generation of the anion radical and the dianion, respectively (Scheme 1). A representative voltammogram is shown in Figure 1. Judging from the first reduction potential (E_{pc1}, Table 1), the all sulfur derivative **3** exhibits slightly stronger accepting ability than the selenium analogue **6**. The reversibility of the two reduction processes was observed at different scanning rates and was established by the separation of 50−60 mV between cathodic (E_{pc}) and anodic (E_{pa}) peak potentials. This observation indicates the stability of the generated anion radical and dianion under the CV experimental conditions. Formally, both the anion radical and the dianion derived from compounds **3** or **6** can be presented in more than one mesomeric structure. However, mesomeric forms **3′**, **6′**, **3″**, and **6″**, incorporating heteroaromatic *o*-quinonoid structures, describe better the nature of bonding of the partially and fully reduced species. In separate CV experiments, an excess of the strongly alkylating methyl iodide was added to the electrochemical cell. In this case, the reversibility of the two reduction processes vanished and a new oxidation wave was observed. Apparently, the generated dianion (**3″** or **6″**) was trapped (alkylated) with methyl iodide and the observed new oxidation wave corresponds to the S-methylated products **9** or **10** (Scheme 1).

Scheme 1



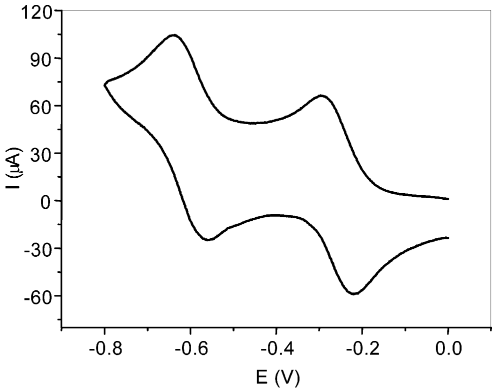


Figure 1. CV of compound **3** in DMF, Bu_4NBF_6 (0.1 M), Pt working electrode, SCE reference electrode, 100 mV/s scan rate.

Table 1. Electrochemical Behavior[a] of Dithioketone Derivatives **3** and **6**

compd	E_{pc1} (V)	E_{pc2} (V)	E_{pa1} (V)	E_{pa2} (V)	ΔE_1 (mV)	ΔE_2 (mV)
3	−0.22	−0.55	−0.28	−0.61	55	60
6	−0.29	−0.60	−0.34	−0.66	50	59

[a] CVs experimental conditions: in DMF, Bu_4NBF_6 (0.1 M), Pt working electrode, SCE reference electrode, 100 mV/s scan rate.

The solution electrochemical properties of **3** and **6** directed our attention to the possibility of bringing about the same reduction chemically. In particular, the metal reduction of compounds **3** and **6** was especially attractive. For this purpose, we noted that the well-known reduction of carbon disulfide was best achieved in DMF mediated by sodium.[10] Not surprisingly, the same reduction medium proved to work very well for our present purpose. In a typical experiment,

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2 equiv of finely divided sodium was added to a thoroughly dried DMF solution of **3** under inert atmosphere. A deep blue color developed within a few minutes, and the sodium was consumed completely within 2 h. At that point, methyl iodide was added, and the mixture was stirred under nitrogen atmosphere for an additional 15 min. Working up the reaction mixture gave the expected 3,3′-bis(methylthio)-1,1′-biisothianaphthene **9** in 56% yield.[11] Compound **6** reacted under the same reduction conditions in similar manner, and the corresponding biisoselenophene **10** was formed in 43% yield.[11] Compounds **9** and **10** were found to be very stable under normal laboratory conditions. Derivatives of biisothianaphthene have received considerable theoretical attention since they present model systems for understanding the structural and physical properties of higher oligoisothianaphthenes.[12,13] In this regard, it is notable that the number of chemical approaches and types of biisothianaphtene derivatives are rather limited.[14] Interestingly enough, bismethylthio derivative **10**, represents the first example of a dimeric benzo[*c*]selenophene.

The redox properties of the new dimers **9** and **10** were examined by cyclic voltammetry. On anodic scanning, compound **9** exhibits an one-electron irreversible oxidation wave at 0.38 V (SCE reference electrode) (Figure 2). Similar CV features were observed for the selenium analogue **10**. Compound **10**, however, oxidized at 0.30 V under the same experimental conditions, indicating the enhanced donating ability of selenium. A similar one-electron irreversible oxidation process was observed for the known diformyl-capped biisothianaphthene.[14b] The optical absorption spectra of **9** contains three main peaks in the range 200−500 nm, which is in accordance with the calculated and experimental UV−vis spectra of biisothianaphthene model compound.[13] The longest absorption maxima (λ_{max}) of the derivative **9** is located at 436 nm and for derivative **10** is located at 445 nm. Theoretical calculations have shown that the lowest energy transition of model biisothianaphthene originated from π to π^* transition, which primarily involved the excitation of an electron from the HOMO to the LUMO.[13] Judging from the different lowest energy absorptions and the difference in the first oxidation potentials, it appears that the replacement of the sulfur atom on dimeric *o*-quinonoid heterocycle **9** by the more polarizable selenium atom fine tunes the electronic properties of the system.

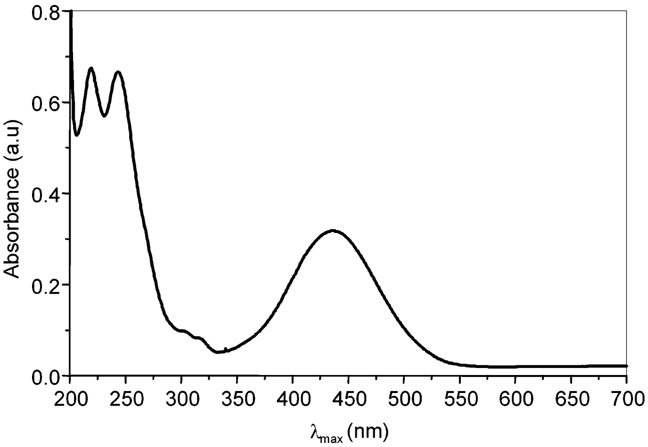

Figure 2. UV−vis spectrum of 9 in CH_2Cl_2.

In conclusion, the synthesis of stable methylthio-capped biisothianaphthene (**9**) and biisoselenophene (**10**) derivatives has been achieved using DMF-mediated sodium reduction of cyclic thiocarbonyl compounds. Sulfur and selenium dimeric *o*-quinonoid heterocycles appear to possess slightly different electronic properties. In view of the great interest in conducting polymers derived from isothianaphthene, studies aimed at the synthesis and properties of polyisoselenophene are highly desirable.[15]

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Supporting Information Available: Experimental details and selected NMR and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Selected spectroscopic data. Compound **8**: ^{1}H NMR (360 MHz, $CDCl_3$, relative to TMS) δ 2.55 (s, 6H), 7.11−7.22 (m, 4H), 7.78−7.82 (m, 4H); ^{13}C NMR (360 MHz, $CDCl_3$, relative to TMS) δ 128.1, 144.0, 137.0 132.6, 124.2, 123.1, 123.8, 122; MS *m*/*e* 358 (M^+, 55), 344 (23), 342 (100), 326 (21), 264 (38). Anal. Calcd for $C_{18}H_{14}S_4$: C, 60.29; H, 3.94; S, 35.77. Found: C, 60.21; H, 3.84; S, 35.69. Compound **9**: ^{1}H NMR (360 MHz, $CDCl_3$, relative to TMS) δ 2.48 (s, 6H), 7.11−7.20 (m, 4H), 7.78−7.82 (m, 4H); ^{13}C NMR (360 MHz, $CDCl_3$, relative to TMS) δ 128.1, 144.0, 137.0 132.6, 124.2, 123.1, 123.8, 122. Anal. Calcd for $C_{18}H_{14}S_2Se_2$: C, 47.79; H, 3.12; S, 14.18. Found: C, 47.71; H, 3.14; S, 14.29.

(12) Quattrocchi, C.; Lazzaroni, R.; Bredas, J. L.; Kiebooms, R.; Vanderzande, D.; Gelan, J.; Van. Meervelt, L. *J. Phys. Chem.* **1995**, *99*, 3932.

(13) Kwon, O.; McKee, M. L. *J. Phys. Chem*, **2000**, *104*, 7106.

(14) To the best of our knowledge, the only known derivatives of biisothianaphthenes are *tert*-butyldimethylsilyl-capped biisothianaphthene, which was reported by us: (a) Okuda, Y.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1991**, *56*, 6024. The formyl-capped biisothianaphthene, which was reported recently: (b) Shimizu, Y.; Shen, Z.; Ito, S.; Uno, H.; Daub, J.; Ono, N. *Tetrahedron Lett.* **2002**, *43*, 8485.

(15) Interestingly enough, the only patent describing the preparation of conductive poly-benzo[c]selenophene was reported in 1991 but was not further examined: Kubota, F. JP application no. 1989-86323; *Chem. Abstr.* **1991**, *115*, 2029.