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The First Preparation and Structures of Dibenzo[*bc,fg*][1,4]-diselenapentalene and -selenathiapentalene

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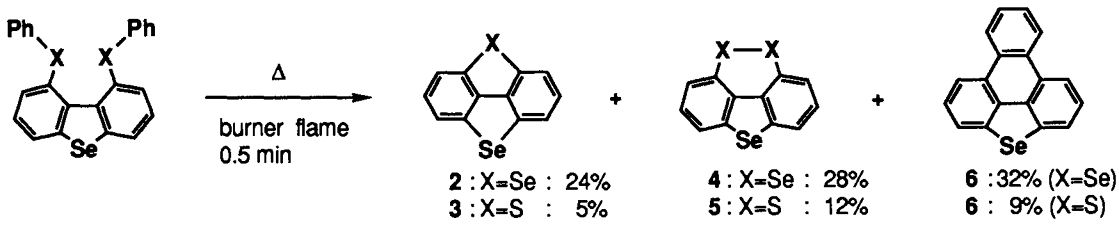
Dibenzodiselenapentalene and dibenzoselenathiapentalene were prepared by thermolysis of 1,9-disubstituted dibenzoselenophenes and their structures were determined by X-ray crystallographic analysis.

Recently, we have reported that dibenzo[*bc,fg*][1,4]dithiapentalene (**1**) and polyaromatic thiophene derivatives were obtained by photolysis of 1,9-disubstituted dibenzothiophenes and their chemical behavior on the electrode surface was similar to that of polythiophenes.$^{1)}$ In order to investigate the diselena and selenathia analogs of dithiapentalene (**1**), dibenzo[*bc,fg*][1,4]diselenapentalene (**2**) and dibenzo[*bc,fg*][1,4]selenathiapentalene (**3**) were prepared by thermolysis of 1,9-bis(phenylseleno)- and 1,9-bis(phenylthio)dibenzoselenophenes. This communication reports the first preparation, structures and electrochemical properties of **2** and **3**.



Scheme 1.

The pentalene **2** and **3** were obtained by thermolysis of 1,9-disubstituted dibenzoselenophenes in a pylex tube as colorless needles together with seleno[2,3,4,5-*lmn*][9,10]diselenaphenanthrene (**4**), selenodithiaphenanthrene (**5**) and triphenyleno[4,5-*bcd*]selenophene (**6**)$^{1)}$ (Scheme 1). The structures of **2** and **3** were determined by X-ray crystallographic analysis (Fig. 1).$^{2)}$ The bond lengths of the C-Se bonds of **2** (Se_1-C_{11}: 1.911 Å and Se_1-C_{25}: 1.930 Å) are slightly longer than that of the C-Se bond of dibenzoselenophene (1.899 Å), while the C_{16}-C_{26} bond (1.38 Å) is shorter than the corresponding C-C bond of dibenzoselenophene (1.453 Å).$^{3)}$ The bond angles of the benzene ring of **2** are 124.0° (C_{11}-C_{16}-C_{15}), 117.2° (C_{12}-C_{11}-C_{16}), 117.8° (C_{11}-C_{12}-C_{13}), and 125.3° (C_{12}-C_{13}-C_{14}) indicating that the benzene ring is distorted from a normal hexagonal structure. However, the sulfur and selenium atoms of **3** could not be distinguished at all by X-ray crystallographic analysis, since their atoms are disordered in the crystal. Hence bond lengths and bond angles of **3** are obtained as mean values of those of **1** and **2**.$^{1)}$ In the molecule, the distances of Se(S)-C_1 and C_6-C_6* are 1.857 and 1.388 Å, and the bond angles of benzene ring are 126.4° (C_1-C_6-C_5*), 117.1° (C_2-C_1-C_6), 117.2° (C_1-C_2-C_3), and 125.0° (C_2-C_3-C_4). In contrast to the UV spectra of 1,3-dicarbomethoxyseleno[3,4-*c*]selenophene (563 nm) and 1,3-dicarbomethoxyseleno[3,4-*c*]thiophene (536 nm) which have never been isolated in the stable forms,$^{4)}$ the λ_{max} values of **2** and **3** were found at around 336 nm and 333 nm suggesting that the unusual valence expansion of the sulfur and selenium atoms using *d*-orbitals is of no significance to **2** and **3**. Furthermore, since **2** was treated with *m*-chloroperbenzoic acid to produce monoselenoxide **7**,5) **2** should have properties different from those for selenoselenophenes. Oxidation potentials of **2** and **3** were 1.03 V (irreversible) and 1.08 V (irreversible), respectively (Ep vs. Ag/0.01 M $AgNO_3$ in CH_3CN at 20 °C).

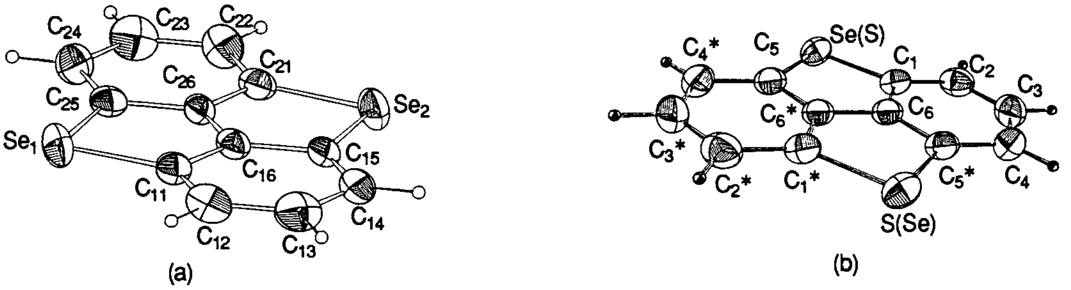


Fig. 1. ORTEP Drawings of Dibenzodiselenapentalene (**2**) (a) and Dibenzoselenathiapentalene (**3**) (b).

It has been known that electron donating compounds such as tetrathiafulvalene derivatives are converted to the charge transfer complexes by treatment with acceptor molecules.6) Then **2** was mixed with tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) and their UV spectra were measured in CH_2Cl_2 at 25 °C. In the spectra, one broad absorption was found at around 600 nm; λ_{max} (ε) in CH_2Cl_2: **2**-TCNE, 652 nm (15); **2**-TCNQ, 672 nm (31). The composition of the crystal of **2**-TCNQ was determined to be a 1 : 1 complex by elemental analysis. Further investigation is in progress in this laboratory.

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2) **2**: Mp 213 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.77 (d, J=7.8 Hz, 4H), 7.43 (t, J=7.8 Hz, 2H); ^{77}Se NMR (51 MHz, $CDCl_3$) δ 600.5; Anal. Found: C, 46.60; H, 1.72%. Calcd for $C_{12}H_6Se_2$: C, 46.78; H, 1.96%; the crystal data for **2**: monoclinic, $P2_1/c$, a=7.922(2), b=8.606(1), c=14.286(3) Å, β=94.52(0)°, V=970.9 $Å^3$, z=4, ρ=2.11 g/cm^3, μ(Mo-Kα)=74.9 cm^{-1}, R=0.047 (R_w=0.056), 1520 with $Fo^2>3.0\sigma(Fo^2)$; **3**: Mp 167 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.75 (dd, J_1=7.9 Hz, J_2=1.1 Hz, 4H), 7.51 (t, J=7.9 Hz, 2H); ^{77}Se NMR (51 MHz, $CDCl_3$) δ 622.6; Anal. Found: C, 54.89; H, 2.37%. Calcd for $C_{12}H_6SSe$: C, 55.18; H, 2.32%; the crystal data for **3**: monoclinic, $P2_1/c$, a=7.717(1), b=4.070(0), c=14.904(2) Å, β=94.90(1)°, V=466.4 $Å^3$, z=2, ρ=1.86 g/cm^3, μ(Mo-Kα)=41.5 cm^{-1}, R=0.019 (R_w=0.022), 721 with $Fo^2>3.0\sigma(Fo^2)$.

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5) **7**: Mp 212 °C (decomp); ^1H NMR (270 MHz, $CDCl_3$) δ 7.93 (d, J=7.8 Hz, 2H), 7.80 (d, J=7.8 Hz, 2H), 7.48 (t, J=7.8 Hz, 2H); IR (KBr) 801 cm^{-1} (SeO); Anal. Found: C, 44.50; H, 2.01%. Calcd for $C_{12}H_6OSe_2$: C, 44.47; H, 1.87%.

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