FIRST PREPARATION, STRUCTURAL DETERMINATION BY X-RAY CRYSTALLOGRAPHIC ANALYSIS AND MO-CALCULATIONS OF DIBENZO[*bc,fg*][1,4]DITHIAPENTALENE AND ITS SELENIUM ANALOGS

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Abstract-Dibenzo[*bc,fg*][1,4]dithiapentalene and its selenium analogs were prepared by thermolysis and photolysis of 1,9-disubstituted dibenzochalcogenophenes. The X-ray crystallographic analysis of dibenzochalcogenapentalenes revealed clearly that they have completely planar forms. PM3 molecular orbital (PM3 MO) calculation of pentalenes was carried out and their highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) were determined.

INTRODUCTION

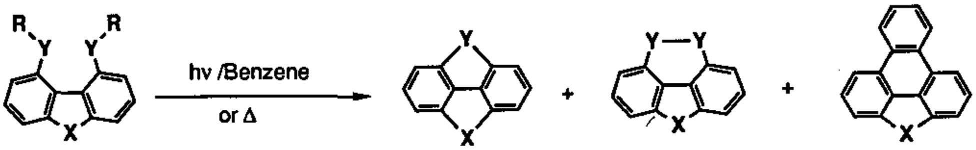
Thiophene derivatives have attracted much attention as important sources for new materials such as high electroconductive polythiophenes.[1] Thienothiophenes belong to one of the structurally interesting 10π-type bisthiophene derivatives, and there are four isomeric thienothiophenes among which thieno[3,4-*c*]thiophene is called nonclassical thiophene.[2] Since thieno[3,4-*c*]thiophene must use unusual bonding orbitals of the sulfur atoms to accommodate 10π electrons for resonance stabilization, the unsubstituted parent thieno[3,4-*c*]thiophene is rather unstable and has never been isolated in a stable structure.[3] Several stable thieno[3,4-*c*]thiophenes have been prepared and their structures were determined by X-ray crystallographic analysis, but they require four substituents for stabilization, such as phenyl or thienyl or alkylthio substituents at 2, 3, 5, and 7 positions.[4] On the other hand, their selenium analogs selenolo[3,4-*c*]selenophene and selenolo[3,4-*c*]thiophene are very unstable compounds, and hence they have never been isolated in stable forms.[5]

This paper is dedicated to Prof. Aran R. Katritzky for his 65th birthday.

Recently, we have succeeded in preparation of sterically congested 1,9-disubstituted dibenzothiophene derivatives.[6] In the course of studies of transannular interaction of these strained molecules, dibenzo[*bc,fg*]-[1,4]dithiapentalene (**5**), the dithia analog of dibenzo[*cd,gh*]pentalene which was prepared by Trost and his co-workers,[7] was obtained on pyrolysis or photolysis of 1,9-bis(methylthio)dibenzothiophene (**1**).[8] Furthermore, dibenzo[*bc,fg*][1,4]diselenapentalene (**6**) and dibenzo[*bc,fg*][1,4]selenathiapentalene (**7**) were also obtained similarly by thermolysis of 1,9-bis(phenylseleno)dibenzoselenophene (**2**) and 1,9-bis(phenylthio)dibenzoselenophene (**3**), respectively.[8,9] In this paper we report the first preparation of dithiapentalene (**5**) and its selenium analogs (**6**) and (**7**), determination of their structures by X-ray crystallographic analysis, molecular orbital (MO) calculation by PM3 method, and their electrochemical properties.

RESULTS AND DISCUSSION

In a typical procedure, compound (**1**) was placed in a long pyrex tube and heated gently with a burner flame (550-600 °C). The reaction mixture was separated and purified by column chromatography and preparative hplc to afford thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (**8**) in 61% yield, accompanied with dithiapentalene (**5**) in less than 1% yield. On the other hand, photolysis of compound (**1**) with a 400 W high pressure mercury lamp for 10 h gave the compounds (**5**) and (**8**) in 11% and 16% yields, respectively. Furthermore, diselenapentalene (**6**) and selenathiapentalene (**7**) were obtained by thermolysis of 1,9-disubstituted dibenzoselenophenes (**2**) and (**3**) in a pyrex tube as colorless needles together with selenolo[2,3,4,5-*lmn*][9,10]diselenaphenanthrene (**9**), selenolo[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (**10**), and triphenyleno[4,5-*bcd*]selenophene (**11**) (Scheme 1).[8,10]

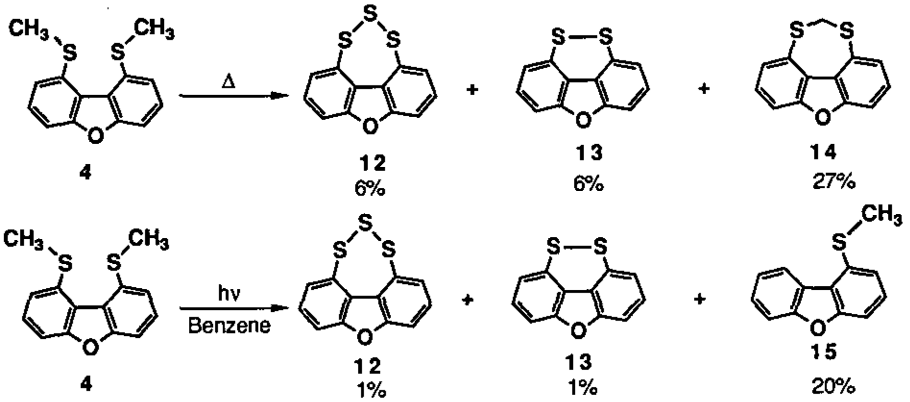


1 : X=Y=S, R=CH_3	Photolysis	: **5** 11%	**8** 16%	**11** 0%
	Thermolysis :	<1%	61%	0%
2 : X=Y=Se, R=Ph	Photolysis	: **6** 20%	**9** 0%	**11** 80%
	Thermolysis :	24%	28%	32%
3 : X=Se, Y=S, R=Ph	Thermolysis	: **7** 5%	**10** 12%	**11** 9%

Scheme 1

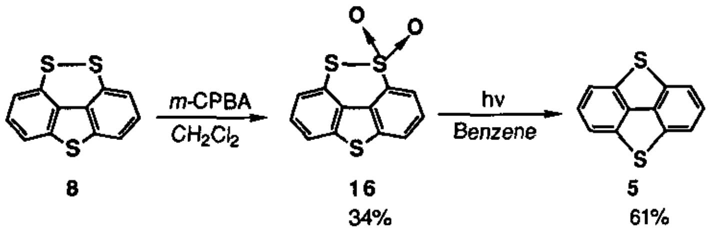
Although we carried out thermolysis and photolysis of 1,9-bis(methylthio)dibenzofuran (**4**) in order to prepare dibenzo[*bc,fg*][1,4]oxathiapentalene as an oxygen analog of dithiapentalene (**5**), the expected oxathiapentalene was not obtained at all, but several heterocyclic compounds such as dibenzo[*bc,hi*][1]oxa[4,5,6]trithiaazulene

(**12**), furo[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (**13**), dibenzo[*bc*,*hi*][1]oxa[4,6]dithiaazulene (**14**), and 1-(methylthio)dibenzofuran (**15**) were produced (Scheme 2).



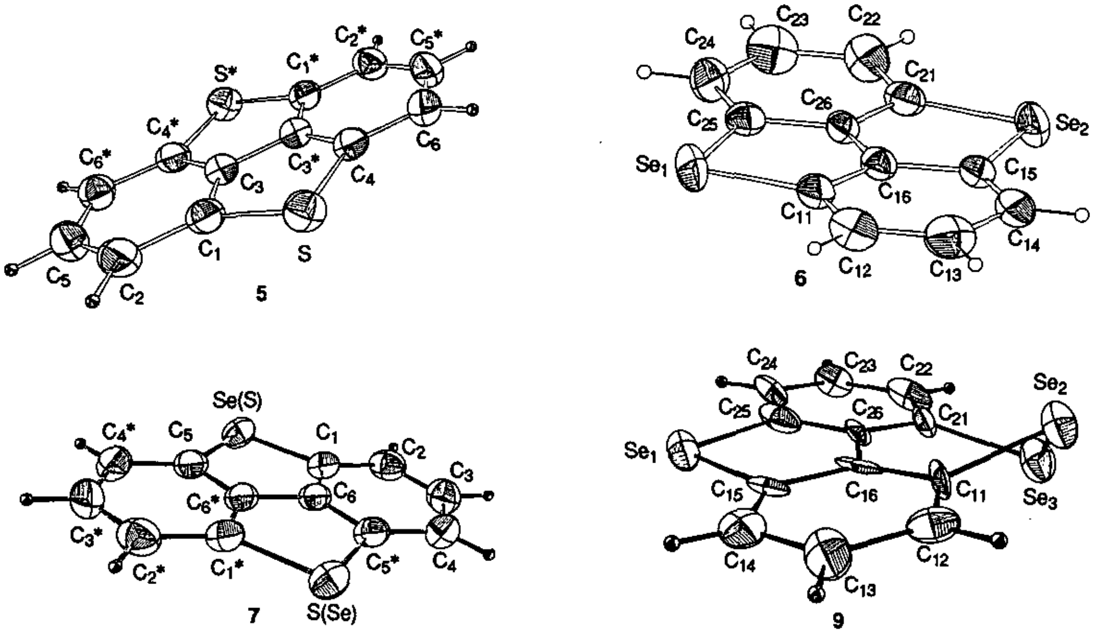
Scheme 2

Since thermolysis and photolysis of compound (**1**) seem not to be optimal procedure for preparation of pentalene (**5**), we intended to provide a more convenient procedure. It was expected that the ring contraction reaction of 1,8-dithionaphthalene-1,1-dioxide which was reported by Meinwald for preparation of naphtho[1,8-*bc*]thiete could be applied to the synthesis of dithiapentalene (**5**) from thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene-9,9-dioxide (**16**).[11] The photolysis of the thiosulfonate (**16**) which was readily available by the oxidation of disulfide (**8**) with *m*-chloroperbenzoic acid (*m*-CPBA) proceeded slowly under irradiation with a high pressure mercury lamp for 72 h in benzene to afford the compound (**5**) in 61% yield (Scheme 3).



Scheme 3

The structure determination of these pentalene derivatives was performed by X-ray crystallographic analysis (Figure 1). It is indicated clearly that dithiapentalene (**5**) is a completely planar molecule belonging to the point group D_{2h}. In the molecule, the C-S bonds of the thiophene rings are 1.791 and 1.790 Å, respectively, which are considerably longer than those of tetraphenylthieno[3,4-*c*]thiophene (1.705 and 1.707 Å)[4] and dibenzothiophene (1.740 Å).[12a] Furthermore, the benzene rings of dithiapentalene (**5**) are considerably distorted from those of a normal hexagonal structure by measuring the bond angles of C_1-C_3-C_4*, 128.5°; C_2-C_1-C_3, 116.1°; C_1-C_2-C_5, 116.8°; C_2-C_5-C_6*, 125.7°. The bond length of C_3-C_3* (1.386 Å) is shorter than that of tetraphenylthieno[3,4-*c*]thiophene (1.452 Å) suggesting that the two benzene rings would be stabilized by conjugation and the two sulfur atoms less participate to the essential π-conjugation than the usual thiophene ring. Similarly the structures of diselena- and selenathiapentalene derivatives (**6**), (**7**) and compound (**9**) were determined by X-ray crystallographic analysis (Figure 1).



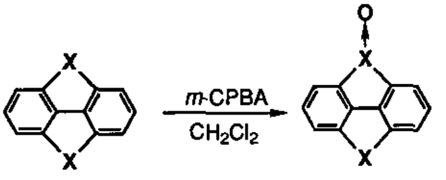
5 6 7 9

Figure 1. X-Ray Crystallographic Analysis of Compounds (**5**-**7**) and (**9**).

The bond lengths of the C-Se bonds of pentalene (**6**) (Se_1-C_{11}: 1.911 Å and Se_1-C_{25}: 1.930 Å) are slightly longer than those 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).[12b] The bond angles of the benzene ring of pentalene (**6**) 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}). On the other hand, the sulfur and selenium atoms of selenathiapentalene (**7**) could not be distinguished at all by X-ray crystallographic analysis, for their atoms are disordered in the crystal. Since the structure solution of compound (**7**) was carried out using a space group $P2_1/c$ (R=0.019, R_w=0.022), bond lengths and bond angles of selenathiapentalene (**7**) are obtained as mean values of those of dithiapentalene (**5**) and diselenapentalene (**6**). In the molecule, the bond distances of Se(S)-C_1 and C_6-C_6* are 1.857 and 1.388 Å, and the bond angles of the 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). Furthermore, in the structure of selenolo[2,3,4,5-*lmn*][9,10]diselenaphenanthrene (**9**), the torsional angle at C_{11}-C_{16}-C_{26}-C_{21} positions is 13.9° which means that the structure of compound (9) deviates from the plausible planar form. The bond distance between the two selenium atoms in compound (9) is 2.32 Å and the distance is nearly identical to the bond length of the normal diaryl diselenide (2.319 Å).[13]

The uv spectrum of dithiapentalene (5) lacks the visible band at around 530 nm observed in tetraphenylthieno[3,4-*c*]thiophene corresponding to the biradical structure,[4] suggesting that dithiapentalene (5) should have neither a biradical nor a charged structure and hence the bonding characters of dithiapentalene (5) should be different from that of tetraphenylthieno[3,4-*c*]thiophene. Similarly, in contrast to the λ_{max} values of uv spectra of 1,3-dicarbomethoxyselenolo[3,4-*c*]selenophene (563 nm) and 1,3-dicarbomethoxyselenolo[3,4-*c*]thiophene (536 nm) which have never been isolated in stable form,[5] the λ_{max} values of the spectra of diselenapentalene (6) and selenathiapentalene (7) were found at around 336 nm and 333 nm, respectively. These results also suggest that the unusual valence expansion of the sulfur and selenium atoms using *d*-orbitals is of no significance to the pentalene derivatives (5-7).

Furthermore, dithiapentalene (5) and diselenapentalene (6) were treated with *m*-CPBA in CH_2Cl_2 to produce the corresponding monosulfoxide (17) and monoselenoxide (18) as a stable colorless crystal, respectively (Scheme 4). The facile oxidation of compounds (5) and (6) is markedly contrasted to the oxidation of thieno[3,4-*c*]thiophene derivatives which are unstable for oxidation.[14]



5: X=S
6: X=Se

17: X=S : 47%
18: X=Se : 51%

Scheme 4

This spectroscopic evidence and facile oxidation of pentalene derivatives (5) and (6) demonstrate that the sulfur and selenium atoms do not participate in charge delocalization, which is different from the properties of thieno[3,4-c]thiophene derivatives. In order to ascertain this hypothesis, a molecular orbital (MO) calculation of pentalene derivatives (5) and (6) was carried out by the PM3 method using the results of X-ray crystallographic analysis to determine the HOMO and LUMO of compounds (5) and (6).[15] Since the selenium and sulfur atoms of selenathiapentalene (7) were disordered in the crystal by a resolution for a space group $P2_1/c$, the structure of pentalene (7) was resolved by another space group to discriminate between the sulfur and selenium atoms in the structure and to execute a similar MO calculation (Pc, R=0.064, Rw=0.084). The calculated levels of LUMO, HOMO, and next HOMO of pentalene derivatives (5-7) and (9) are shown in Table 1.

Table 1. Calculated HOMO and LUMO

Compound	5	6	7	9
LUMO (eV)	-0.95	-1.12	-1.02	-3.46
HOMO (eV)	-8.57	-8.84	-8.73	-8.72
next HOMO (eV)	-9.50	-9.69	-9.44	-9.07

Table 2. Oxidation Potentials (Ep)

Compd.	Ep (V)		Compd.	Ep (V)	
1	0.76	irrev	7	1.08	irrev
2	0.67	irrev	8	[a]0.91	rev
3	0.85	irrev	9	[a]0.63	rev
4	1.07	irrev	12	1.51	irrev
5	1.16	irrev	13	1.01	irrev
6	1.03	irrev	14	1.15	irrev

[a] The oxidation potential of compounds (8) and (9) represents the value of $E_{1/2}$ (V).
Dibenzothiophene: 1.31 V (irrev); Dibenzoselenophene: 1.02 V (irrev).
rev: reversible; irrev: irreversible.

Furthermore, the bond orders of C-S or C-Se bonds of pentalene derivatives (**5-7**) were also calculated and the results reveal that their C-S or C-Se bonds are nearly single bond characters unlike to those of thieno[3,4-c]thiophene derivatives.

The measurements of the electrochemical properties of pentalene derivatives (**5-7**) may provide possibilities for essential sources as electro-conducting materials. Hence, the oxidation potentials of compounds (**5-7**) were determined, together with other heteroaromatic compounds (**8**), (**9**), and (**12-14**), with cyclic voltammetry in acetonitrile at 20 °C, using a Pt electrode, Ag/0.01 M $AgNO_3$ as a reference electrode (scan rate: 200 mV/s), and are summarized in Table 2. On the other hand, since the cyclic voltammograms of dithia- and diselenaphenanthrene derivatives (**8**) and (**9**) were observed as reversible voltammograms (Table 2), the stable radical or radical cations of compounds (**8**) and (**9**) should be generated by oxidation. In fact in esr spectra of these compounds (**8**) and (**9**), one broad signals were observed in concd. sulfuric acid at 25 °C and their g values determined are **8**: g=2.0106, **9**: g=2.0104, respectively.

EXPERIMENTAL

Ir spectra were recorded on a JASCO FT/IR-5000 spectrometer. Nmr spectra were measured with $CDCl_3$ on a JEOL JNM-EX270 or a Bruker AM-500 spectrometer. Mass spectra were obtained with a JEOL JMX SX102 mass spectrometer. X-Ray data collection was performed on a Enraf-Nonius CAD4 computer controlled kappa axis diffractometer (23±1 °C), and all calculations for structure solution and refinement were performed on a

VAX computer using SDP/VAX. MO Calculation was carried out by Fujitu S-Family 4/5 GX using MOPAC Ver.6.1 PM3. For oxidation potential, a Hokuto Denko Co. Model HB-104 apparatus was used.

1,9-Bis(methylthio)dibenzothiophene (1). The compound (1) was prepared by ligand coupling reacion of 4,6-bis(methylthio)thianthrene-5-oxide.[7]

1,9-Bis(methylthio)phenoxathiin-10-oxide. Phenoxathiin-10-oxide (221 mg, 1.02 mmol) dissolved in THF (8 ml) was lithiated with 0.145 M LDA (15 ml, 2.18 mmol) at -78 °C for 2 h under N_2 atmospher.[16] Then dimethyl disulfide (0.4 ml, 4.44 mmol) was added. After stirring for 3 h at -78 °C and for 12 h at -20 °C, the solution was treated with H_2O (1.5 ml), and the solution was evaporated. The residue was extracted with CH_2Cl_2 (3x50 ml) and the organic layer was washed with $Na_2S_2O_3$ solution and then H_2O, and dried over $MgSO_4$. Evaporation of the solvent gave the residue, which was purified by column chromatography (silica gel; CH_2Cl_2) and preparative hplc to give 1,9-bis(methylthio)phenoxathiin-10-oxide (148 mg, 47%) and 1-(methylthio)phenoxathiin-10-oxide (42 mg 16%): 1,9-bis(methylthio)phenoxathiin-10-oxide: mp 180-181 °C (CH_2Cl_2-ethanol); ^{1}H-nmr δ 7.68-7.01 (m, 6H), 2.63 (s, 6H, CH_3); ir (KBr) 1029 cm^{-1} (SO); ms (m/z) 308 (M^+); Anal. Calcd for $C_{14}H_{12}O_2S_3$: C, 54.52; H, 3.92. Found: C, 54.58; H, 3.66; 1-(methylthio)phenoxathiin-10-oxide: mp 189-191 °C (CH_2Cl_2-ethanol); ^{1}H-nmr δ 8.00-7.18 (m, 7H), 2.64 (s, 3H, CH_3); ir (KBr) 1035 cm^{-1} (SO); ms (m/z) 262 (M^+); Anal. Calcd for $C_{13}H_{10}O_2S_2$: C, 59.52; H, 3.84. Found: C, 59.18; H, 3.66.

1,9-Bis(methylthio)dibenzofuran(4). To a THF (50 ml) solution of 1,9-bis(methylthio)phenoxathiine-10-oxide (309 mg, 1.00 mmol), 0.991 M EtMgBr/THF (10 ml, 9.91 mmol) was added dropwise and the solution was stirred for 3 h. Anhydrous $CuCl_2$ (2.018 mg, 15.01 mmol) was added and stirred for 6 h. After usual work-up, the crude product was purified by column chromatography (silica gel; CCl_4) to give **4** (108 mg, 41%): mp 105-106 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (500 MHz) δ 7.42 (t, J=7.9 Hz, 2H, 3,7-Ar-H), 7.38 (dd, J=7.9, 1.1 Hz, 2H, 4,6-Ar-H), 7.28 (dd, J=7.9, 1.1 Hz, 2H, 2,8-Ar-H), 2.58 (s, 6H, CH_3); ms (m/z) 260 (M^+); Anal. Calcd for $C_{14}H_{12}OS_2$: C, 64.58; H, 4.65. Found: C, 64.52; H, 4.59.

Selenanthrene. To the solution of diphenyl diselenide (12.48 g, 20.0 mmol) in 300 ml of acetic acid, a mixture of conc. sulfuric acid (30 ml) and acetic acid (40 ml) was added slowly at 80 °C and then the solution was stirred at refluxing temperature for 72 h. The solution was poured into ice water and neutralized with conc. NaOH solution. The solution was extracted with CH_2Cl_2 (3x500 ml) and the organic layer was dried over $MgSO_4$. After distillation, the crude product was purified by column chromatography (silica gel; benzen : hexan=1:6) to give a colorless crystal (2.7 g, 22%): mp 183-184 °C (lit.,[17] 183-184 °C); ^{1}H-nmr (500 MHz) δ 7.74-7.69 (m, 4H), 7.26-7.21 (m, 4H); ^{77}Se-nmr (51 MHz) δ 463.8; ms (m/z) 312 (M^+).

Selenanthrene-5-oxide. Selenanthrene (225 mg, 0.726 mg) in CH_2Cl_2 (100 ml) was oxidezed with *m*-CPBA (177 mg, 0.718 mmol, assay 70%) at -20 °C for 1 h. After treatment with NH_3 gas, a colorless precipitate was filtered off and the solution was evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and then ethyl acetate) to give a colorless crystal (228 mg, 96%): mp 203-204 °C (ethanol); ^{1}H-nmr (270 MHz) δ 7.99 (d, J=7.6 Hz, 2H), 7.80 (d, J=7.6 Hz, 2H), 7.58 (t, J=7.6 Hz, 2H), 7.42 (t, J=7.6 Hz, 2H); ^{77}Se-nmr (51 MHz) δ 850.6, 390.4; ir (KBr) 822 cm^{-1} (SeO); Anal. Calcd for $C_{12}H_8OSe_2$; C, 44.20; H, 2.47. Found C, 44.11; H, 2.46.

4,6-Bis(phenylthio)selenanthrene-5-oxide. Selenanthrene-5-oxide (3.91 g, 12.0 mmol) dissolved in THF (500 ml) was lithiated with 0.359 M LDA (100 ml, 35.9 mmol) at -78 °C for 3 h under N_2 atmosphere. Then diphenyl disulfide (7.85 g, 36.0 mmol) in 100 ml of THF was added and a mixture was stirred for 1 h at -78 °C. Then the solution was treated with O_2 gas until colorless precipitate was produced and the temperature was elevated gradually. After usual work-up, the product was purified by column chromatography (silica gel; CH_2Cl_2, ethyl acetate and then CH_2Cl_2 : ethanol=5:1) to give 4,6-bis(phenylthio)selenanthrene-5-oxide (3.39 g, 52%): ^{1}H-Nmr (270 MHz) δ 7.80 (m, 2H), 7.38-7.25 (m, 14H); ^{77}Se-nmr (51 MHz) δ 834.1, 437.1; ir (KBr) 822 cm^{-1} (SeO); ms (m/z) 544 (M$^+$).

4,6-Bis(phenylseleno)selenanthrene-5-oxide. Selenanthrene-5-oxide (3.91 g, 12.0 mmol) dissolved in THF (500 ml) was lithiated with 0.359 M LDA (100 ml, 35.9 mmol) at -78 °C for 3 h under N_2 atmosphere. Then a solution of diphenyl diselenide (12.0 g, 38.2 mmol) in THF (100 ml) was added and a mixture was stirred for 1 h at -78 °C. After work-up as described above, 4,6-bis(phenylseleno)selenanthrene-5-oxide was obtained (5.90 g, 77%): ^{1}H-Nmr (270 MHz) δ 8.32-8.27 (m, 2H), 7.60-7.25 (m, 14H); ir (KBr) 820 cm^{-1} (SeO); ms (m/z) 640 (M$^+$).

1,9-Bis(phenylthio)dibenzoselenophene (3). 4,6-Bis(phenylthio)selenanthrene-5-oxide (123 mg, 0.23 mmol) dissolved in THF (25 ml) was treated with 1.02 N PhLi (0.25 ml, 0.26 mmol) for 3 h at -78 °C. After usual work-up and purification by column chromatography (silica gel; CCl_4), **3** was obtained (30 mg, 30%): mp 176-177 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (270 MHz) δ 7.83 (dd, J=7.8, 1.1 Hz, 2H, 4,6-ArH), 7.58 (dd, J=7.8, 1.1 Hz, 2H, 2,8-ArH), 7.33 (t, J=7.8 Hz, 2H, 3,7-ArH), 7.15-7.04 (m, 6H, Ph-H), 6.93-6.87 (m, 4H, Ph-H); ^{77}Se-nmr (51 MHz) δ 470.6; ms (m/z) 448 (M$^+$); Anal. Calcd for $C_{24}H_{16}S_2Se$; C, 64.42, H, 3.60. Found C, 64.23; H, 3.43.

1,9-Bis(phenylseleno)dibenzoselenophene (2). A THF (35 ml) solution of 4,6-bis(phenylseleno)-selenanthrene-5-oxide (200 mg, 0.314 mmol) was treated with 1.02 N PhLi (0.30 ml, 0.31 mmol) for 3 h at -78 °C to give **2** (25 mg, 15%): mp 190 °C (decomp.) (CH_2Cl_2-ethanol); ^{1}H-nmr (500 MHz) δ 7.84 (dd, J=7.8, 1.0

Hz, 2H, 2,8-Ar-H), 7.75 (dd, J=7.8, 1.0 Hz, 2H, 4,6-Ar-H), 7.27 (t, J=7.8 Hz, 2H, 3,7-Ar-H), 7.10-7.04 (m, 6H, 3,4-Ph-H), 6.99-6.94 (m, 4H, 2-Ph-H); ^{13}C-nmr (67 Hz) δ 141.1, 140.0, 137.1, 134.8, 131.0, 129.5, 128.9, 127.7, 126.6, 125.3; ^{77}Se-nmr (51 MHz) δ 468.7, 427.0; ms (m/z) 542 (M^+); Anal. Calcd for $C_{24}H_{16}Se_3$; C, 53.26; H, 2.98. Found; C, 53.39; H, 2.87.

Thermolysis of 1,9-bis(methylthio)dibenzothiophene (1). The compound (**1**) (11 mg, 0.04 mmol) was placed in a pyrex tube and heated gradually with a Bunsen burner for a few min. The reaction mixture was extracted with CH_2Cl_2. After purification with column chromatography *(silica gel;* CH_2Cl_2*) and preparative* hplc, **5** and **8** were obtained in <1% (trace) and 61% (6 mg) yields: **5**: mp 165 °C (sublimed) (CH_2Cl_2-ethanol); ^{1}H-nmr (500 MHz) δ 7.76 (d, J=7.7 Hz, 4H), 7.60 (t, J=7.7 Hz, 2H); ^{13}C-nmr (125 MHz) δ 141.6, 135.7, 128.3, 116.2; ms (m/z) 214 (M^+); uv λ_{max} (ε) 243 (32000), 270 (4300), 329 (1900); Anal. Calcd for $C_{12}H_6S_2$: C, 67.25; H, 2.83. Found: C, 67.34; H, 2.90; the crystal data for **5**: $C_{12}H_6S_2$, monoclinic, $P2_1/c$, a=7.641(1) Å, b=4.000(0) Å, c=14.909(2) Å, β=95.23(6)°, V=453.8 Å^3, z=2, D_x=1.57 g/cm^3, μ(Mo-Kα)=5.1 cm^{-1}, R=0.029 (R_w=0.033); **8**: mp 132.5-133°C (lit.,[10] 126); ^{1}H-nmr (270 MHz) δ 7.71 (d, J=7.9 Hz, 2H), 7.40 (t, J=7.9 Hz, 2H) 7.25 (d, J=7.9 Hz, 2H); ms (m/z) 246 (M^+); uv λ_{max} (ε) 224(9200), 250(9800), 357(1400).

Photolysis of 1,9-bis(methylthio)dibenzothiophene (1). The compound (**1**) (100 mg, 0.36 mmol) in 5 ml of benzene was irradiated with a 400 W high pressure mercury lamp for 10 h at 20 °C. After distillation of the solvent, the residue was purified by column chromatography (silica gel; CH_2Cl_2) and preparative hplc, and **5** and **8** were obtained in *11% (8.5 mg) and 16% (14.6 mg) yields.*

Thermolysis of 1,9-bis(methylthio)dibenzofuran (4). The compound (**4**) was treated with the similar manner as described above and after purification with preparative tlc (silica gel; *n*-hexane), **12**, **13** and **14** were obtained in 6%, 6% and 27% yields; **12**: mp 97-98 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (500 MHz) δ 7.59 (dd, J=7.6, 1.7 Hz, 2H), 7.43 (t, J=7.6 Hz, 2H) 7.41 (dd, J=7.6, 1.7 Hz, 2H); ms (m/z) 262 (M^+); Anal. Calcd for $C_{12}H_6OS_3$: C, 54.93; H, 2.31. Found: C, 55.11, H, 2.07; **13**: mp 100-102 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (500 MHz) δ 7.37 (t, J=7.8 Hz, 2H), 7.33 (d, J=7.8 Hz, 2H), 7.08 (d, J=7.8 Hz, 2H); ms (m/z) 230 (M^+); Anal. Calcd for $C_{12}H_6OS_2$: C, 62.58; H, 2.63. Found: C, 62.48; H, 2.56; **14**: mp 189-190 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (270 MHz) δ 7.41 (dd, J=8.1, 1.1 Hz, 2H), 7.34 (t, J=8.1 Hz, 2H), 7.25 (dd, J=8.1, 1.1 Hz, 2H), 4.48 (s, 2H, CH_2); ms (m/z) 244 (M^+); Anal. Calcd for $C_{13}H_8OS_2$: C, 63.91; H, 3.30. Found: C, 63.57; H, 3.15.

Photolysis of 1,9-bis(methylthio)dibenzofuran (4). The compound (**4**) was photolyzed for 60 h at 20 °C as described above to give **12** *(1%),* **13** *(1%) and* **15** *(20%);* **15**: *mp 85 °C* (CH_2Cl_2-*ethanol*); ^{1}H-nmr (500 MHz) δ 8.33 (d, J=7.8 Hz, 1H), 7.57 (d, J=7.8 Hz, 1H), 7.47 (t, J=7.8 Hz, 1H), 7.42 (t, J=7.8 Hz, 1H), 7.38

(t, J=7.8 Hz, 1H), 7.38 (d, J=7.8 Hz, 1H), 7.17 (d, J=7.8 Hz, 1H), 2.66 (s, 3H, CH_3); ms (m/z) 214 (M^+); Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70. Found: C, 72.84, H, 4.66.

Thermolysis of 1,9-bis(phenylseleno)dibenzoselenophene (2). Thermolysis of **2** was carried out similarly as described above, and after purification by preparative tlc (silica gel; *n*-hexane), **6** (24%), **9** (28%) and **11** (32%) were obtained: **6**: mp 213 °C (cyclohexane); ^{1}H-nmr (270 MHz) δ 7.77 (d, J=7.8 Hz, 4H), 7.43 (t, J=7.8 Hz, 2H); ^{13}C-nmr (67 MHz) δ 145.9, 134.5, 127.3, 121.5; ^{77}Se-nmr (51 MHz) δ 600.5; Anal. Calcd for $C_{12}H_6Se_2$: C, 46.78; H, 1.96. Found: C, 46.60; H, 1.72; the crystal data for **6**: $C_{12}H_6Se_2$, 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, D_x=2.11 g/cm^3, μ(Mo-Kα)=74.9 cm^{-1}, R=0.047 (R_w=0.056); **9**: mp 186-187 °C (cyclohexane); ^{1}H-nmr (270 MHz) δ 7.77 (dd, J=7.6, 1.1 Hz, 2H), 7.46 (dd, J=7.6, 1.1 Hz, 2H), 7.31 (t, J=7.6 Hz, 2H); ^{13}C-nmr (67 MHz) δ 141.6, 136.7, 128.0, 125.6, 125.4, 122.9; ^{77}Se-nmr (51 MHz) δ 455.6, 245.1; ms (m/z) 388 (M^+); Anal. Calcd for $C_{12}H_6Se_3$: C, 37.24; H, 1.56. Found; C, 37.57; H, 1.40; the crystal data for **9**: $C_{12}H_6Se_3$, monoclinic, $P2_1/a$, a=11.958(2), b=11.168(1), c=16.760(4) Å, β=108.68(2)°, V=2120.3 Å^3, z=8, D_x=2.42 g/cm^3, μ(Mo-Kα)=102.6 cm^{-1}, R=0.054 (R_w=0.066); H, 1.40; **11**: mp 184-185 °C (cyclohexane); ^{1}H-nmr (270 MHz) δ 8.77-8.70 (m, 2H), 8.53 (d, J=7.8 Hz, 2H), 8.11 (d, J=7.8 Hz, 2H), 7.81 (t, J=7.8 Hz, 2H), 7.79-7.71 (m, 2H); ^{13}C-nmr (67 MHz) δ 138.8, 133.4, 130.5, 130.2, 127.7, 126.9, 124.0, 123.6, 117.9; ^{77}Se-nmr (51 MHz) δ 458.1; ms (m/z) 306 (M^+); Anal. Calcd for $C_{18}H_{10}Se$: C, 70.83; H, 3.30. Found; C, 70.71; H, 3.23.

Photolysis of 1,9-bis(phenylseleno)dibenzoselenophene (2). The compound (**2**) was treated similarly as described above and compounds (**6**) and (**11**) were obtained in 20% and 80% yields.

Thermolysis of 1,9-bis(phenylthio)dibenzoselenophene (3). The compound (**3**) was treated similarly as described above. After purification by column chromatography (silica gel; CH_2Cl_2) and preparative hplc, **7** (5%), **10** (12%) and **11** (9%) were obtained: **7**: mp 163 °C (sublimed) (cyclohexane); ^{1}H-nmr (270 MHz) δ 7.75 (dd, J=7.6, 1.1 Hz, 4H), 7.51 (t, J=7.9 Hz, 2H); ^{13}C-nmr (67 MHz) δ 143.7, 135.6, 134.2, 127.7, 121.2, 118.5; ^{77}Se-nmr (51 MHz) δ 622.6; ms (m/z) 262 (M^+); Anal. Calcd for $C_{12}H_6SSe$: C, 55.18; H, 2.32. Found: C, 54.89; H, 2.37; the crystal data for **7**: $C_{12}H_6SeS$: 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, D_x=1.86 g/cm^3, μ(Mo-Kα)=41.5 cm^{-1}, R=0.019 (R_w=0.022); **10**: ^{1}H-nmr (270 MHz) δ 7.76 (dd, J=7.6, 1.4 Hz, 2H), 7.34 (t, J=7.6 Hz, 2H), 7.28 (dd, J=7.6, 1.4 Hz, 2H); ^{13}C-nmr (67 MHz) δ 140.0, 134.6, 130.1, 128.1, 125.0,122.9; ^{77}Se-nmr (51 MHz) δ 468.6; ms (m/z) 294 (M^+); hr-ms Calcd for $C_{12}H_6S_2Se$: 293.9075. Found: 293.9031 (M^+).

Photolysis of 1,9-bis(phenylthio)dibenzoselenophene. The compound (**3**) was irradiated as described above for 8 h at 20 °C to give **11** in 77% yield.

Oxidation of thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (8). To a solution of **8** (132 mg, 0.54 mmol) in 30 ml of CH_2Cl_2, *m*-CPBA (370 mg, 1.5 mmol) in 30 ml of CH_2Cl_2 was added at 20 °C. The solution was stirred for 12 h, and treated with NH_3 gas. After usual work-up, the residue was purified by column chromatography (silica gel; CH_2Cl_2-ethyl acetate) to give **16** (51 mg, 34%): **16**: mp 220-221 °C (CH_2Cl_2-ethanol); ^{1}H-nmr (270 MHz) δ 8.17 (dd, J=8.1, 0.5 Hz, 1H), 8.03 (dd, J=7.6, 0.5 Hz, 1H), 7.94 (dd, J=8.1, 0.5 Hz, 1H), 7.78 (t, J=8.1 Hz, 1H), 7.62 (t, J=7.6 Hz, 1H), 7.49 (dd, J=7.6, 0.5 Hz, 1H); ^{13}C-nmr (67 MHz) δ 141.3, 140.9, 137.2, 130.9, 128.4, 127.9, 127.7, 127.0, 126.8, 123.7, 122.3, 115.5; ir (KBr) 1317, 1149 cm^{-1} (SO_2); ms (m/z) 278 (M^+); Anal. Calcd for $C_{12}H_6O_2S_3$: C, 51.78; H, 2.17. Found C, 51.68; H, 2.22.

Photolysis of thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene-9,9-dioxide (16). The compound (**16**) (15 mg, 0.05 mmol in 3 ml of benzene) was irradiated for 72 h to give **5** in 61% (7 mg) yield.

Oxidation of dibenzo[*bc,fg*][1,4]dithiapentalene (5). The compound (**5**) (20 mg, 0.1 mmol) was treated with *m*-CPBA (25 mg, 0.1 mmol) in 40 ml of CH_2Cl_2 for 36 h at -20 °C. After work-up as described above and purification with column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2 : ethyl acetate=1:1), **17** was obtained as a colorless crystal (10 mg, 47%); **17**: mp 224-227 °C (decomp.) (CH_2Cl_2-ethanol); ^{1}H-nmr (270 MHz) δ 7.87 (d, J=8.1 Hz, 2H), 7.81 (d, J=8.1 Hz, 2H), 7.58 (t, J=8.1 Hz, 2H); ^{13}C-nmr (67 MHz) δ 143.1, 140.6, 136.6, 130.1, 126.1, 122.0; ir (KBr) 1044 cm^{-1} (SO); ms (m/z) 230 (M^+); Anal. Calcd for $C_{12}H_6OS_2$: C, 62.58; H, 2.63. Found: C, 62.28; H, 2.76.

Oxidation of dibenzo[*bc,fg*][1,4]diselenapentalene (6). The compound (**6**) (34 mg, 0.11 mmol) was treated with *m*-CPBA (27 mg, 0.11 mmol) in 50 ml of CH_2Cl_2 for 24 h at -20 °C. After work-up as described above and purification with column chromatography (silica gel; CH_2Cl_2, ethyl acetate and then CH_2Cl_2 : methanol=5:1), a colorless crystal (18 mg, 51%) was obtained; **18**: mp 212 °C (decomp.) (CH_2Cl_2-ethanol); ^{1}H-nmr (270 MHz) 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. Calcd for $C_{12}H_6OSe_2$: C, 44.47; H, 1.87. Found: C, 44.50; H, 2.01.

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