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Cyclic polysulfides fused to polyaromatics

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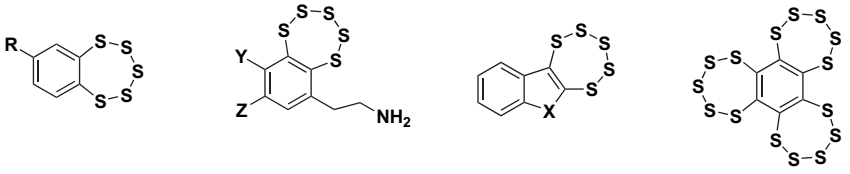
Abstract—Pentathiepins fused to naphthalene and phenanthrene have been synthesized by a simple method. Ring size depends on the stability of generated products related to steric and electronic factors. Sometimes, delocalized π-electron of polyaromatics shows synergistic effect on the stabilization of polysulfur rings. The structures of two polysulfides were also studied by X-ray crystallography and phenanthrene bearing C_2S_5 ring showed different solid-state properties than corresponding phenanthrene bearing C_2S_3 ring.

1. Introduction

Organic polysulfides have generated significant interest among organic chemists, initially for their interesting physical properties and potential for synthetic utilities.[1] Remarkable stability of seven-membered rings, the high-energy barrier for the inversion of the chair like pentathiepins and their potent biological activities is also significant.[2a] Simple benzo-fused pentathiepin (**B**) was also recently shown to display DNA-cleaving properties.[2b] Considerable efforts have also been devoted to develop the syntheses[3] of the cytotoxic alkaloid varacins (**C** and **D**) as these are highly toxic toward human colon cancer. Pentathiepins have been constructed on various heterocycles including benzo[*b*]indole,[4] benzo[*b*]thiophene and benzo[*b*]furan (**E**).[5] Recently, pentathiepins (**F**) are also expanding on various dimensions to fulfill the growing demand of material sciences.[6] Surprisingly, all of these are restricted to benzene and other simple heterocyclic systems and thus we turned our attention in appending the pentathiepin ring to polyaromatics (Fig. 1).

Various researches are performed by our group on seven-membered sulfur rich heterocycles in terms of synthesis and chemistry of benzopentathiepins. Previously, we synthesized five-membered polysulfur rings on naphthalenes[7] but those compounds gradually changed to oligomeric forms under air after several hours. Therefore, it was encouraging to synthesize stable polysulfur on polyaromatic systems. Despite all previous contributions in this field, many aspects of pentathiepin chemistry still remain to be explored, and there is also need for developing new types of pentathiepins in order to provide molecules for biological studies.[5] Naphthalene is the simple polycyclic aromatic hydrocarbon that has some structural advantage to bear polysulfur rings.



A (R = H) **B (R = Me)** **C (Y = X = OMe)** **D (X = OH, Y = OMe)** **E (X = N,O,S)** **F**

Figure 1.

Keywords: Cyclic polysulfides; Pentathiepin; Trithiole; Naphthalene; Phenanthrene; X-ray structures.
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C_1–C_2, C_2–C_3, and C_1–C_8 positions of naphthalene were tried to be utilized as hetero-binding sites to bear polysulfur rings. Pentathiepins have been synthesized by several strategies.[8] Easier approach involves the formation of pentathiepin rings by addition of sulfur monochloride (S_2Cl_2) to an appropriate dithiol or dithiolate precursor.[8a,9] For S_2Cl_2, trithiole is generated along with corresponding pentathiepin, which is difficult to separate by usual chromatography as well as it lowers the yield of pentathiepin. Therefore, we selected our reported method[10] as it is mild, clean to generate intermediate dithiols and relatively the process delivers selective seven-membered ring in high yields.

2. Results and discussion

2.1. Synthesis

2-Naphthalenethiol was treated with 4 equiv of *n*-BuLi and brown suspension of lithium salt[11] i.e. lithiation intermediate (**1**) was generated extensively (Scheme 1).

In an initial attempt at the thiation[3c] of **1**, using S_8, we are gratified to find that naphthalene[2,3-*f*]pentathiepin (**3**) had been formed in only 18% yield, accompanied, however by some oligomeric products. A more reliable route to **3** was afforded by prior conversion of the dilithiated intermediate **1** to stable stannole **2** by successive thiation, reduction, acidification and protection with dimethyltin(IV) dichloride.

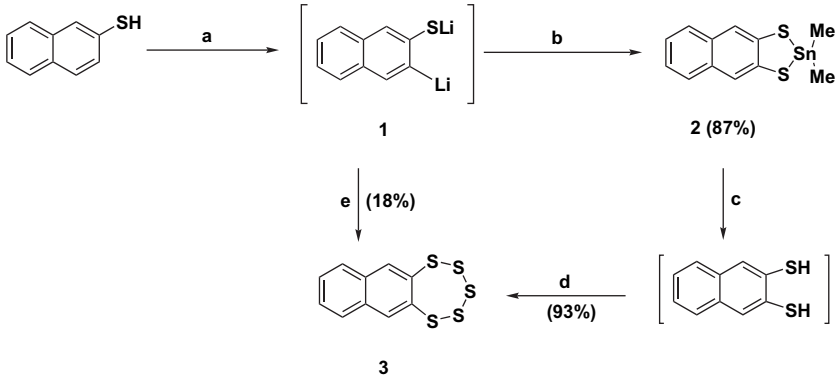
Naphthalene[2,3-*f*]dithiastannole (**2**) was treated with excess concd HCl in CH_2Cl_2 to generate respective dithiol precursor. Subsequent thiation of dithiol intermediate with S_8/NH_3 in CH_2Cl_2 yielded pentathiepin **3** in 93% yield, after chromatography. The interaction between naphthalenedithiolate anion and elemental sulfur in the presence of catalyst NH_3 generates naphthopentathiepin, which is the most stable compound among possible cyclic polysulfides.

To get polysulfur compounds at C_1–C_2 position, 1-naphthalenethiol was also lithiated with *n*-BuLi according to Scheme 2. Stannole **6** was obtained from intermediate **5** in 16% yield by successive sulfurization with S_8, reduction with $LiAlH_4$ and protection of dithiol with Me_2SnCl_2.

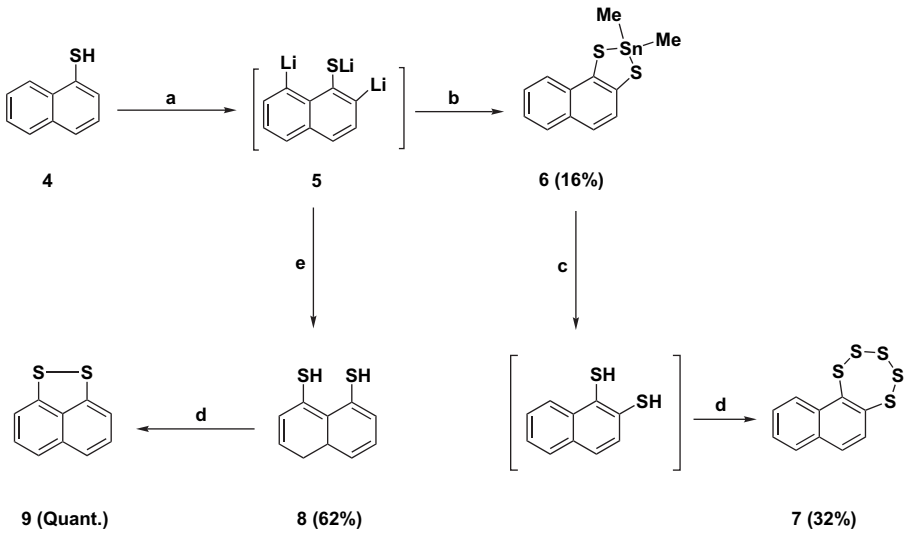
We also obtained 1,8-naphthalenedithiol[12] from the reaction mixture as stable product in 62% yield without using any protector. Lithiation occurred both in 8- and 2-positions. Dithiastannole at bay region is unstable due to steric strain of *peri–peri* substituents although lithium preferentially attacks at *peri* position. 1,8-Naphthalenedithiol was also treated with S_8/NH_3 in CH_2Cl_2 at identical condition to get polysulfur compounds around *peri*-positions. But it afforded naphthalene-1,8-naphthalenedisulfide[13] (**9**) quantitatively. At bay region[14] substituents are strained thus disulfide is the most stable molecule. C_1–C_2 bond of naphthalene is more double bond character than corresponding C_2–C_3 bond, as bond lengths are 1.36 and 1.42 Å, respectively. Therefore, among three isomeric positions of naphthalene, C_2–C_3 site is the best hetero-binding base to hold C_2S_5 ring.

It is clear that synthesis of pentathiepin at C_2–C_3 position is easier than C_1–C_2 or C_1–C_8 position as shown in Schemes 1 and 2. Next, we attempted to make seven-membered rings on phenanthrene as it allow symmetrical C_9–C_{10} binding site to bear cyclic polysulfide. 9-Bromophenanthrene was converted to corresponding 9-phenanthrenethiol[15] (**10**) by conventional Grignard reaction in 86% yield. Phenanthro[9,10-*d*]dithiastannole was obtained only in 8% yield (Scheme 3). Interestingly, thiation of 9,10-phenanthrenedithiol with S_8/NH_3 in CH_2Cl_2 yielded two products **13** and **14** simultaneously in 55 and 18% yield, respectively. Five-membered cyclic polysulfide rings on naphthalene are labile[7] where as both five and seven-membered polysulfur rings are stable on phenanthrene.

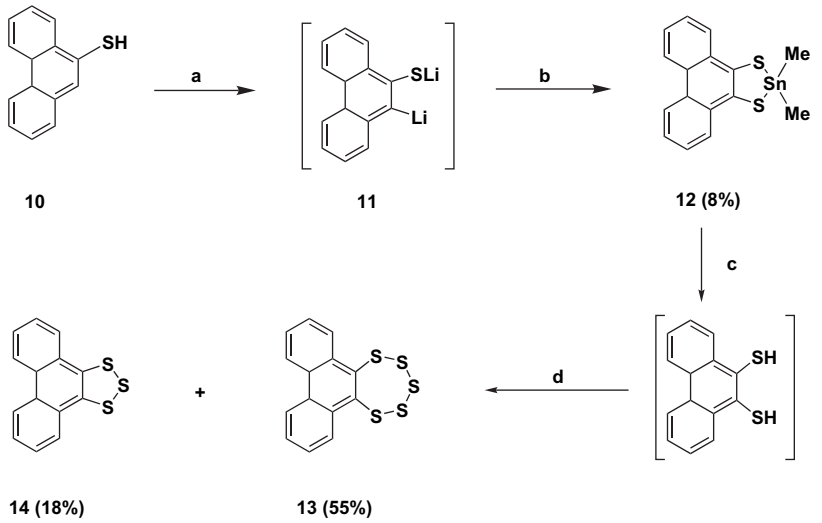
There are some problems inherent in the identification of cyclic polysulfides as trithioles are often formed along with pentathiepins or equilibrate the mixtures on standing. Mass spectroscopy may also be a misleading method for analysis as dimers and pentathiepins decomposition products such as trithioles are often thermolyzed on probe to give false monomeric parent peaks. Therefore, to verify the structure, two pentathiepins[22,23] were subjected to an X-ray analysis.



Scheme 1. Reagents and conditions: (a) TMEDA, *n*-Hex., *n*-BuLi, 24 h, rt; (b) 1. S_8, 12 h, H^+; 2. THF, Reflux, 6 h, H^+, Me_2SnCl_2; (c) Concd HCl, CH_2Cl_2, 7 h; (d) S_8/NH_3, CH_2Cl_2, 48–72 h; and (e) S_8, 24 h.



Scheme 2. Reagents and conditions: (a) TMEDA, *n*-Hex., *n*-BuLi, 24 h, rt; (b) 1. S_8, 12 h, H^+; 2. THF, Reflux, 6 h, H^+, Me_2SnCl_2; (c) Concd HCl, CH_2Cl_2, 7 h; (d) S_8/NH_3, CH_2Cl_2, 48–72 h; and (e) 1. S_8, 12 h; 2. THF, Reflux, 6 h; 3. H^+/H_2O.



Scheme 3. Reagents and conditions: (a) TMEDA, *n*-Hex., *n*-BuLi, 24 h, rt; (b) 1. S_8, 12 h, H^+; 2. THF, Reflux, 6 h, H^+, Me_2SnCl_2; (c) Concd HCl, CH_2Cl_2, 7 h; and (d) S_8/NH_3, CH_2Cl_2, 48–72 h.

2.2. Solid-state properties in terms of X-ray crystallography

We tried to investigate the solid-state properties of polysulfides as all of the pentathiepins are bound to large π-systems. The crystallographic information is described in Table 1 along with the results of benzopentathiepin's X-ray data[16] as a reference. The similarity of S–S bond lengths within the group of C_2S_5 pentathiepin is quite remarkable while some reported pentathiepins showed in wide variation in S–S distances. Seven-membered ring with the sulfur substituted to carbon to form CS_6 and S_7 rings, and six-membered pentasulfide ring containing a carbon atom (CS_5) or a metal atom (MS_5) as a sixth member. Alternating long–short bonds, usually ranging from 2.02 to 2.08 Å, have been reported in hexathiepane (CH_2S_6), pentathiane (CH_2S_5), and dibenzylpentathiane [$(PhCH_2)_2CS_5$].[17]

Of all the polysulfides, S_7 shows the most variation in S–S bond lengths: 1.995–2.182 Å.[18] Among the organometallic complexes with MS_5 rings, the amount of variation highly depends on the nature of the metal atom.[19] The consistency of the S–S bond lengths in compounds **3** and **13** is closely parallel to the structural results for S_6[20] and S_8. The average bond length is 2.049 Å for three pentathiepin (Table 1), 2.057 Å for S_6, and 2.051 Å for S_8.

The S–S–S bond angles of the three pentathiepins are between the average of S_6 and S_8. The S–S–S–S torsional angles of compounds **3** and **13** are closely similar to S_6, which means that the synthesized pentathiepins fused to polyaromatics show comparable stability with respect to both S_6 and S_8. On the other hand, all bond lengths and angles of compound **13** are almost similar to compound **14** but C–S–S–S torsional angle for C_2S_5 ring (93°) is greater than corresponding C_2S_3 ring (40°) (Figs. 2 and 3).

Table 1. Pentathiepins geometry

	3	13	A
Bond lengths, Å			
C(1)–C(2)	1.423(3)	1.372(2)	1.382(8)
C(1)–S(1)	1.776(2)	1.778(2)	1.774(5)
C(2)–S(5)	1.777(19)	1.787(2)	1.774(5)
S(1)–S(2)	2.056(6)	2.040(7)	2.041(2)
S(4)–S(5)	2.057(7)	2.052(8)	2.048(2)
S(2)–S(3)	2.049(7)	2.058(7)	2.045(2)
S(3)–S(4)	2.057(8)	2.055(7)	2.039(2)
S(1)–S(5)	3.410(4)	3.361(3)	3.366(3)
S(2)–S(5)	3.231(3)	3.182(4)	3.192(3)
Bond angles, deg			
C(2)–C(1)–S(1)	122.5(14)	121.0(16)	123.7(4)
C(1)–C(2)–S(5)	123.4(14)	121.3(15)	124.4(4)
C(1)–S(1)–S(2)	104.1(7)	103.15(7)	104.5(2)
C(2)–S(5)–S(4)	103.9(6)	103.53(7)	104.6(2)
S(1)–S(2)–S(3)	104.8(3)	102.59(3)	104.6(1)
S(3)–S(4)–S(5)	104.8(2)	104.57(3)	105.1(1)
S(2)–S(3)–S(4)	103.9(2)	103.65(3)	102.8(1)
Torsional angles, deg			
S(1)–C(1)–C(2)–S(5)	−1.5(2)	−4.5(2)	0.4
C(1)–S(1)–S(2)–S(3)	91.9(8)	93.39(7)	88.6
C(2)–S(5)–S(4)–S(3)	−91.3(7)	−94.27(7)	−89.5
S(1)–S(2)–S(3)–S(4)	−73.7(3)	−72.43(3)	−74.8
S(5)–S(4)–S(3)–S(2)	72.9(3)	71.24(3)	74.7

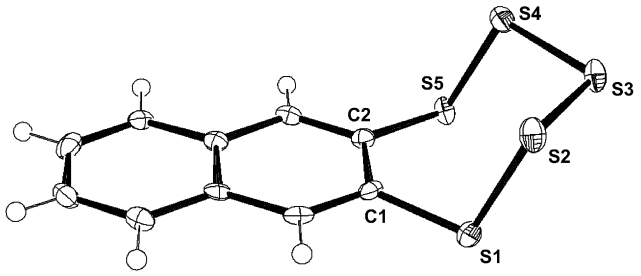


Figure 2. Typical boat conformation of compound **3**. Thermal ellipsoids are drawn at 50% probability.

For phenanthropentathiepin,[23] it was observed that crystal packing of seven-membered ring is different than corresponding five-membered system. Two sulfur atoms bound to carbon are almost co-planar with the phenanthrene ring, while the remaining three sulfur atoms lie out of plane to form conventional chair and boat conformations. In solid-state naphthalene, anthracene and phenanthrene have herringbone packing[21] but in phenathrene trithiole, molecules are stacked by their naphthalene units and polysulfur rings are arranged on same side due to helical arrangement of six molecules.[7]

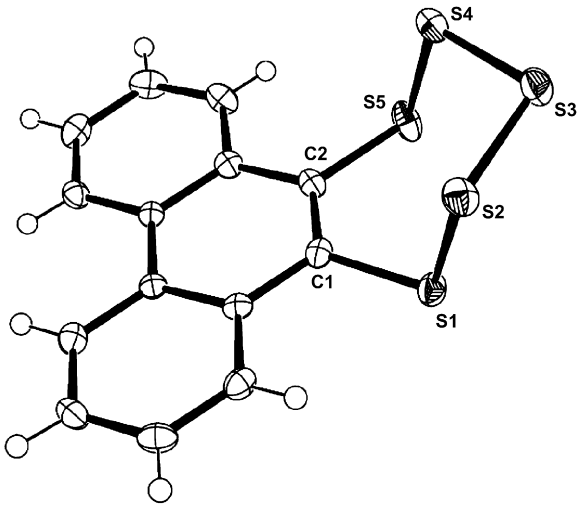


Figure 3. Typical boat conformation of C_2S_5 ring of compound **13**. Thermal ellipsoids are drawn at 50% probability.

In phenanthropentathiepin, molecules are also stacked to one another by their naphthalene units but pentathiepin rings are arranged alternatively on the opposite side and form a kinetically favorable dimeric butterfly chain in place of helical stacking (see Fig. 4). Large ring size of pentathiepin, their conformational variation, and intermolecular polysulfur repulsion prohibit them to aggregate into helical arrangements. In the unit cell, the two molecules stack each other with their distorted pentathiepin rings sticking out from phenanthrene column.

Generation of cyclic polysulfides on organic substrate is a matter of thermodynamic stability. For phenanthrotrithiole (**14**), density gradient of virtual HOMOs is dispersed on both the aromatic and the trithiole rings resulting in extra stabilization of five-membered ring.[7] Large π-conjugated system of phenanthrene gives remarkable thermodynamic stability to cyclic polysulfides.

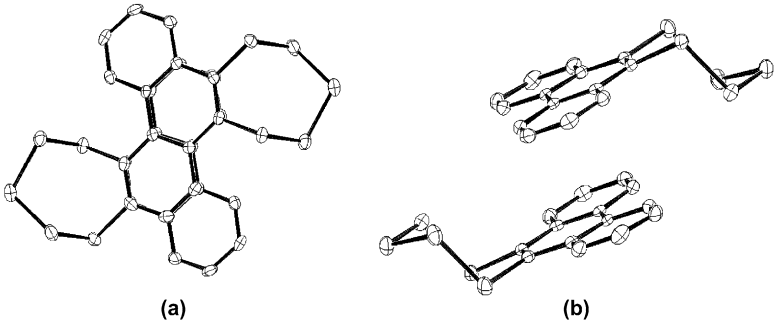


Figure 4. Packing view: (a) Butterfly arrangements of dimeric rings (top view), which is different from corresponding trithioles stacking and (b) π–π Stacking in a dimer (side view).

3. Conclusion

Some novel pentathiepins fused to naphthalene systems have been synthesized and characterized, and their solid-state properties were studied. Naphthalene pentathiepin and benzopentathiepin are almost same in crystal parameters, which have been observed by an X-ray crystallographic analysis. Surprisingly, phenanthropentathiepin showed different packing pattern than naphthopentathiepin or phenanthrotrithiole. We plan to extend this approach to the syntheses of both sulfur and selenium bearing seven-membered rings and related heterocycles on polyaromatic systems.

4. Experimental

4.1. General

Melting points were measured with a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra are recorded on a Bruker AC-400P instrument with $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are given in relative parts per million from the internal TMS. ^{13}C NMR chemical shifts are given in relative parts per million from the internal $CDCl_3$. Mass spectra are recorded with a Hitachi M-2000 or JEOL JMS SX 102 spectrometer under electron ionization (70 eV). IR spectra were recorded on KBr disk with a JASCO FT/IR-7300 spectrometer. *n*-Hexane, CH_2Cl_2, and THF were freshly distilled according to standard laboratory procedure prior to use. Commercial grade TMEDA was purified by atmospheric distillation before use. Wakogel C-200 was used for silica gel column chromatography. Elemental analyses were recorded using Yanaco MT-5 apparatus at the elemental analysis division of Iwate University.

4.1.1. 2,2-Dimethylnaphtho[2,3-*b*][1,3,2]dithiastannole (2). 2-Naphthalenethiol (20 mmol, 3.2 g) was taken in the two-neck flask under nitrogen. TMEDA (20 ml) and *n*-hexane (25 ml) were added into the reactor to dissolve the substrate and the reaction mixture was placed in an ice bath. *n*-BuLi (4 equiv, 2.55 mol/l) was added slowly into the reaction mixture under constant stirring. The reaction mixture was stirred for 24 h at room temperature and it was changed into brown suspension due to extensive generation of lithium salts.[11] The reaction mixture was quenched with water, acidified with concd HCl, and extracted with CH_2Cl_2. After being dried over $MgSO_4$, the solvent was evaporated in vacuo. The reaction mixture was successively redissoved in THF, reduced with $LiAlH_4$, quenched with ice water, acidified with HCl and at neutral pH the generated 2,3-dithiol was protected with dimethyltin(IV) dichloride. Recrystallization from *n*-hexane/CH_2Cl_2 (1:1), afforded compound **2** in 55% yield.

Colorless needles, mp 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 6H, –CH_3), 7.32 (dd, J=6.2, 3.2 Hz, 2H, ArH), 7.59 (dd, J=6.2, 3.2 Hz, 2H, ArH), 7.96 (s, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 2.16, 125.5, 126.1, 127.6, 131.1, 137.2; IR (KBr) 1566, 1482, 1426, 1097, 878, 767, 745 cm^{-1}; EIMS (70 eV) *m*/*z* 340 (M^+); Anal. Calcd for $C_{12}H_{12}S_2Sn$: C, 42.51; H, 3.57. Found: C, 42.40; H, 3.54.

4.1.2. Naphtho[2,3-*f*]pentathiepin (3). This compound was synthesized by following two distinct routes. (a) 2-Naphthalenethiol (20 mmol, 3.2 g) was lithiated with *n*-BuLi (4 equiv, 2.55 mol/l) to generate the respective lithium intermediate (**1**). This brown suspension of lithium intermediate was treated with elemental sulfur and the reaction mixture immediately turned into yellow suspension. After overnight stirring, the mixture was quenched with ice water acidified with HCl and extracted with dichloromethane. The crude mixture was separated by chromatography with *n*-hexane as an eluent and the product **3** (0.859 g) was isolated only in 18% yield. (b) Dithiastannole **2** (1.00 mmol, 0.339 g) was treated with 30 ml concd HCl in 25 ml CH_2Cl_2 for 7 h at room temperature. After being acidified over HCl, the solution was dried over $MgSO_4$. The solution was diluted up to 200 ml by addition of fresh CH_2Cl_2 in a conical flask. Elemental sulfur was added to it, and under constant stirring 5 ml of gaseous NH_3 was flushed into the solution by using a titanium autoclave and a glass needle. The reaction mixture was stirred over for a long period (40–60 h) in a draft chamber at room temperature for complete evaporation of residual NH_3. At neutral pH, the solution was washed with water, dried over $MgSO_4$, and residual solvent was evaporated by vacuo. Compound **3** (266 mg, 93%) was isolated by using a silica gel column with *n*-hexane as an eluent.

Pale yellow crystals, mp 135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J=6.5, 3.3 Hz, 2H, ArH), 7.61 (dd, J=6.5, 3.3 Hz, 2H, ArH), 8.34 (s, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.6, 132.9, 128.9, 128.0; IR (KBr) 1483, 1301, 902, 888, 750, 471 cm^{-1}; EIMS (70 eV) *m*/*z* 286 (M^+); Anal. Calcd for $C_{10}H_6S_5$: C, 41.93; H, 2.11. Found: C, 42.07; H, 2.25.

4.1.3. 2,2-Dimethylnaphtho[1,2-*b*][1,3,2]dithiastannole (6). The synthetic procedure of compound **6** was as same as that of compound **2**. 1-Naphthalenethiol was used as substrate in that case. This compound was isolated in low yield due to extensive lithiation of respective *peri* position. During synthesis of compound **6**, compound **9** was also separated as side product.

Colorless crystals, mp 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 6H, –CH_3), 7.37 (td, J=7.6, 1.2 Hz, 1H, ArH), 7.44 (d, J=8.6 Hz, 1H, ArH), 7.51 (td, J=7.6, 1.2 Hz, 1H, ArH), 7.55 (d, J=7.7 Hz, 1H, ArH), 7.73 (d, J=7.7 Hz, 1H, ArH), 8.32 (d, J=8.6 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 2.69, 124.5, 124.7, 126.6, 126.7, 127.7, 128.1, 131.2, 133.8, 134.0, 135.7; IR (KBr) 1543, 1497, 1333, 1112, 805, 769, 747 cm^{-1}; EIMS (70 eV) *m*/*z* 340 (M^+); Anal. Calcd for $C_{12}H_{12}S_2Sn$: C, 42.51; H, 3.57. Found: C, 42.59; H, 3.54.

4.1.4. Naphtho[1,2-*f*]pentathiepin (7). The synthetic procedure of compound **7** was as same as that of compound **3**. Here, gaseous NH_3 process (route b) was used in the presence of elemental sulfur in dilute condition. The compound was found as white crystal (92 mg, 32%).

Mp 120.0–121.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J=8.2 Hz, 1H, ArH), 7.88 (d, J=8.2 Hz, 1H, ArH), 7.87 (d, J=8.5 Hz, 1H, ArH), 7.81 (d, J=8.5 Hz, 1H, ArH), 7.67 (td, J=7.6, 1.2 Hz, 1H, ArH), 7.59 (td, J=7.6, 1.2 Hz,

1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.5, 135.5, 134.0, 131.4, 130.8, 128.5, 128.4, 128.2, 127.8; IR (KBr) 1574, 1491, 1301, 1247, 815, 740 cm^{-1}; EIMS (70 eV) *m/z* 286 (M^+); Anal. Calcd for $C_{10}H_6S_5$: C, 41.93; H, 2.11. Found: C, 42.18; H, 2.07.

4.1.5. 1,8-Naphthalenedithiol (8). For isolation of 1,8-naphthalenedithiol, the generated lithium intermediates were thiated with elemental sulfur, reduced with $LiAlH_4$, and refluxed in THF for 6 h. The reduced mixture was quenched, acidified, and extracted with CH_2Cl_2. Recrystallization of crude product from the same solvent, gave product **8** in 62% yield as bright yellow crystal.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 2H, ArH), 7.23 (t, 2H, ArH), 7.87 (d, *J*=7.3 Hz, 2H, ArH), 7.81 (d, *J*=7.3 Hz, 2H, ArH).

4.1.6. 1,8-Naphthalenedisulfide (9). Compound **8** was treated with S_8/NH_3 in dilute solution of CH_2Cl_2 and product **9** was isolated quatitatively.[13]

4.1.7. 2,2-Dimethylphenanthro[9,10-*d*][1,3,2]dithiastannole (12). The synthetic procedure was as same as that of compound **2** or **6**. The compound was isolated only in 4% yield because of the extensive lithiation of the *peri* position as same as 1-napthalenethiol.

Colorless crystal, mp 202.0–209.5 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J*=8.0, 1.4 Hz, 2H, ArH), 8.54 (dd, *J*=8.0, 1.2 Hz, 2H, ArH), 7.63 (td, *J*=8.0, 1.4 Hz, 2H, ArH), 7.54 (td, *J*=8.0 Hz, 2H, ArH), 1.08 (s, 6H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 132.5, 129.0, 128.0, 127.0, 125.7, 122.7, 2.4; IR (KBr) 3066, 1554, 1511, 1480, 1274, 1197, 882, 749, 714 cm^{-1}; EIMS (70 eV) *m/z* 390 (M^+); Anal. Calcd for $C_{10}H_{14}S_2Sn$: C, 49.39; H, 3.63. Found: C, 49.19; H, 3.60.

4.1.8. Phenanthro[9,10-*f*]pentathiepin (13). The synthetic procedure was as same as that of product **3** or **7**. Two products were isolated in 55 and 18% yield, respectively. After complete identification, it was found that the two products are phenanthrene having C_2S_7 and C_2S_3 rings, respectively. Products were isolated by usual column chromatography with *n*-hexane as an eluent. Compound **13** was found as yellow crystal.

Mp 148.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.79 (m, 4H, ArH), 8.75 (dd, *J*=6.4, 2.2 Hz, 2H, ArH), 7.81 (dd, *J*=6.7, 2.3 Hz, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.9, 127.9, 128.7, 129.6, 131.5, 132.3, 142.6; IR (KBr) 1478, 1443, 1146, 757, 719 cm^{-1}; EIMS (70 eV) *m/z* 272 (M^+-2S); Anal. Calcd for $C_{14}H_8S_5$: C, 49.96; H, 2.40. Found: C, 49.60; H, 2.56.

4.2. Crystallographic information

X-ray crystal data for compounds **3** and **13** have been deposited in Cambridge Crystallographic Data Center as supplementary publication number CCDC 626593 and CCDC 626594, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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22. Crystal data for compound **3**: M=286.46, $C_{10}H_6S_5$, monoclinic, space group $P2_1/n$ (#14), a=7.0641(16) Å, b=24.249(4) Å, c=7.0603 (14) Å, β=113.922(9)°, V=1105.5(4) Å^3, Z=4, D_{calcd}=1.721 g cm^{-3}, T=123 K, radiation Mo Kα (λ=0.7107 Å). A yellow platelet crystal of approximate dimensions of 0.60×0.20×0.10 mm was used for the measurement. The structure was solved by the direct methods (SIR 97) and expanded using Fourier technique (DIRDIF-99). All the calculations were performed using crystal structure 3.5.1 crystal structure analysis package of Rigaku and Rigaku/MSC. The final cycle of full matrix least squares refinement was based on 2526 observed reflections (I>2.00$\sigma(I)$) and 161 variables parameters with R_1=0.0350 and wR_2=0.0266 (all data).
23. Crystal data for compound **13**: M=336.52, $C_{14}H_8S_5$, monoclinic, space group $P2_1/n$ (#14), a=10.790(4) Å, b=7.472(3) Å, c=16.779(5) Å, β=98.33(3)°, V=1338.5(8) Å^3, Z=4, D_{calcd}=1.670 g cm^{-3}. An orange block crystal of approximate dimensions of 0.50×0.30×0.25 mm was used for the measurement at 123 K on Rigaku RAXIS-RAPID diffractometer employing Mo Kα (λ=0.7107 Å) radiation. The structure was solved by the direct methods (SIR 97) and expanded using Fourier technique (DIRDIF-99). All the calculations were performed by using crystal structure 3.5.1 crystal structure analysis package of Rigaku and Rigaku/MSC. The final cycle of full matrix least squares refinement was based on 3037 observed reflections (I>2.00$\sigma(I)$) and 204 variables parameters with R_1=0.0298 and wR_2=0.0559 (all data).