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Electronic control of product formation in the rearrangement of 1,3-dithian-2-yl-arylmethanols

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Abstract—1,3-Dithian-2-yl-phenylmethanols undergo efficient rearrangement to afford 2-phenyl-6,7-dihydro-5*H*-1,4-dithiepines. The reactions were found to show remarkable variation in products formation that is dictated by the substituents on the aryl ring.

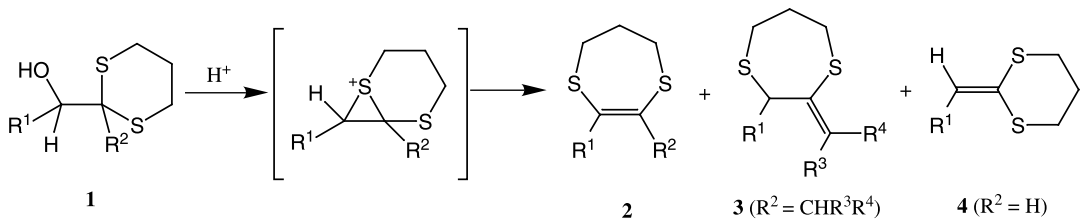
1. Introduction

Ring expansion of α-hydroxydithiane derivatives **1** into 5,6-dihydro-7*H*-1,4-dithiepines **2** has been widely described in the literature.[1–5] In general, dithiane derivatives with a good leaving group at the α-position such as an acetate,[6] a chloride,[7] a mesylate,[5] an amide,[8] or an epoxide[9] have all been reported to undergo rearrangement to the 5,6-dihydro-7*H*-1,4-dithiepines. Furthermore, it has been shown that the presence of an α-hydrogen atom in the R^2 substituent of **1** (R^2=CHR^3R^4) can lead to the formation of both the *endo*- and *exo*-dithiepanes **2** and **3**.[3] Recently, it has also been shown that the *endo*-double bond of dithiepines **2** can undergo photo-induced 1,3-hydrogen migration to give the *exo*-dithiepanes **3**,[10] a property which may be useful for the design of a photo-switch. Additionally, dithianylidenes **4**[11] are formed when the R^2 group of **1** is a hydrogen atom. Scheme 1 summarizes the products that have been obtained from the reaction of α-hydroxydithiane derivatives **1**.

In the present work, we report the first complete overview of the electronic control of the aromatic ring on the product formation for acid catalyzed reactions of α-hydroxydithiane derivatives.

2. Results and discussion

The 1,3-dithian-2yl-arylmethanols **5a**–**d** for this study were prepared by the reaction of 2-lithio-1,3-dithiane with the corresponding arylaldehyde in good yields according to reported procedures.[3,10,12] The reaction of 1,3-dithian-2-yl-phenylmethanol **5a** with a catalytic amount of concentrated sulfuric acid in refluxing toluene led to the formation of the 2-phenyl-6,7-dihydro-5*H*-1,4-dithiepine (**6a**) in 25% yield together with non-polar hydrocarbon derivative 2-phenyl-naphthalene (**7**) in 10% yield. Compound (**7**) was identified by its ^{1}H NMR spectrum, mass and melting point.[13,14] The reaction was monitored by t.l.c until the complete disappearance of starting material, approximately 24 h. A substantial amount of polymeric material was also observed. This reaction sequence was not confined to **5a**. Interestingly, 1,3-dithian-2-yl-2-naphthylmethanol (**5b**), under similar conditions, also gave the corresponding ring expansion product, 2-(2-naphthalenyl)-6,7-dihydro-5*H*-1,4-dithiepine (**6b**) in 20% yield together with 3-naphthalen-2-yl-phenanthrene (**8**) in 10% yield. The ^{1}H NMR spectrum of **8** showed the presence of protons at δ 9.03 (singlet) and δ 8.84 (doublet) typical of the 4- and 5-positions in 3-substituted phenanthrenes. This ruled out the formation of the other



1 **2** **3** (R^2 = CHR^3R^4) **4** (R^2 = H)

Scheme 1. Possible products from the reaction of α-hydroxydithiane **1** with acid.

Keywords: 1,3-dithian-2-yl-arylmethanol; rearrangement; dimerization; cyclodimerization; electronic factors.
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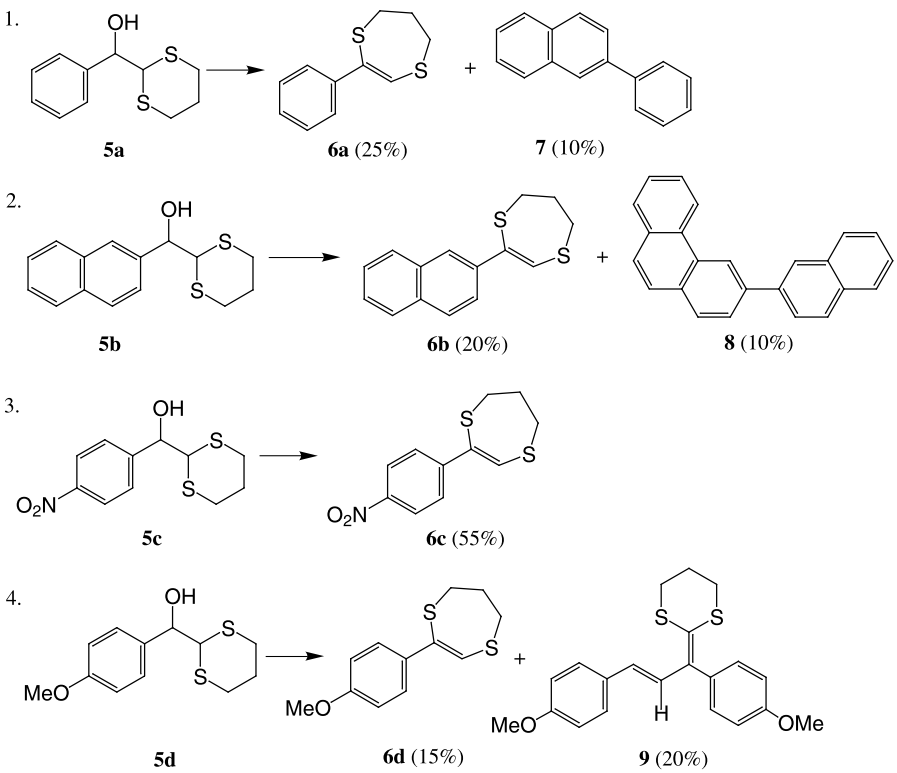


Scheme 2. Products from the reaction of **5a–d** under acid catalysis.

possible isomeric cyclization product, 2-naphthalen-2-yl-anthracene, since all the protons in this compound would be expected to resonate much higher up field, ca. δ 8.50. Our results are in good agreement with the fact that substitution at the 1-position of naphthalene is preferred over the 2-position,[15] thus favoring the formation of the phenanthrene ring over the anthracene ring. Although the yields of the cyclodimerization products **7** and **8** are low, their formation is important, as this reaction has not been described in the literature (Scheme 2).

There has been no data published concerning the electronic influence of substituents on the aryl ring in the reactions of aryl substituted 1,3-dithian-2-yl-arylmethanols. Therefore, we examined this issue. Acid treatment of 1,3-dithian-2-yl-4-nitrophenylmethanol **5c** gave the single product **6c** in 55% yield. Figure 1 shows the crystal structure of **6c**. Interestingly, this structure shows the aromatic ring twisting out of conjugation with the double bond of the dithiepine moiety. This observation may explain the reported ease by which 2-methyl-3-aryl-6,7-dihydro-5*H*-dithiepines undergo a photo-induced 1,3-proton shift to form the *exo*-methylene dithiepines.[10]

We next study the acid catalyzed reaction of a 1,3-dithian-2-yl-arylmethanol derivative having an electron-donating group on the aryl ring. Interestingly, the reaction of 1,3-dithian-2-yl-4-methoxy-phenylmethanol (**5d**) was

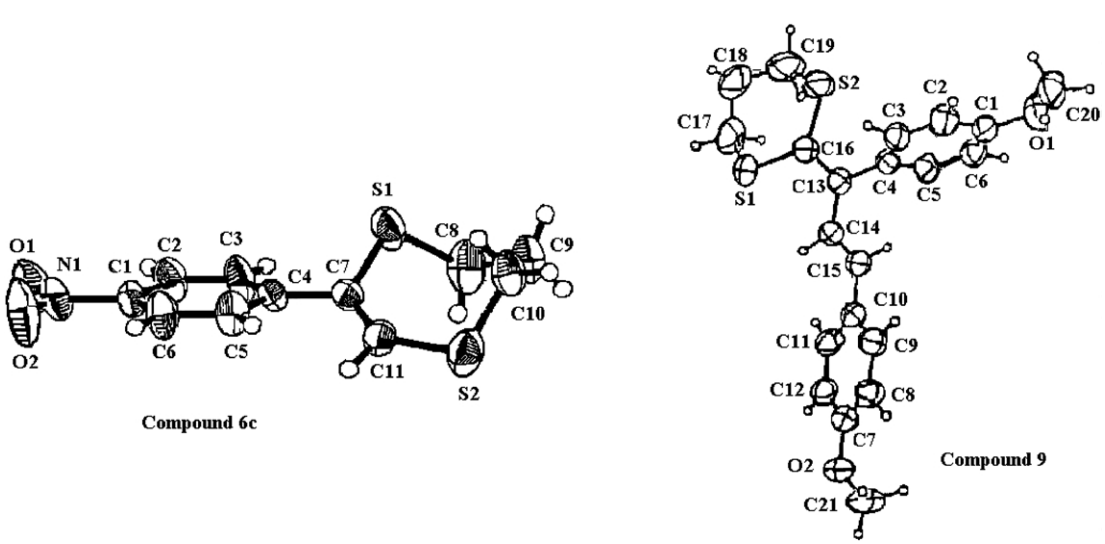
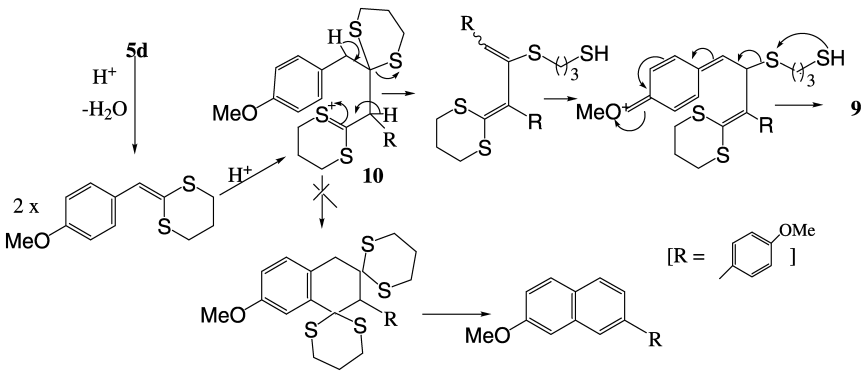


Figure 1. X-Ray structures for compound **6c** (brown prism crystal, triclinic) and **9** (yellow prism crystal, monoclinic).[16]



Scheme 3. Proposed mechanism for the formation of **9**.

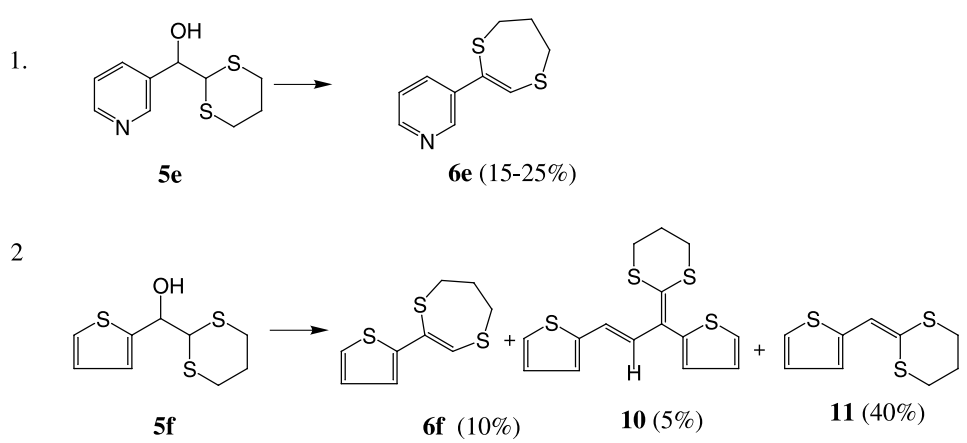
found to afford **6d** in 15% yield together with another new product isolated in 20% yield by chromatographic separation over silica gel. A substantial amount of polymerized material was also formed. The ^{1}H NMR of the new compound did not correlate to a naphthalene derivative. We were able to obtain a crystal of this product suitable for a X-ray crystallographic analysis of the new compound and determined its structure to be **9** (Fig. 1).[16]

The proposed mechanism for the formation of **9** is shown in Scheme 3. The acid catalyzed dehydration of **5d** would give the dithianylidene intermediate. Self-condensation of this would produce **10**. Friedel–Crafts cycloaromatization of **10** would yield the naphthalene derivative, while deprotonation of the dithiolium moiety followed by desulfuration of the dithioacetal group would yield **9**. Interestingly, the electron density in the aryl ring also controls the balance between the Friedel–Crafts and deprotonation–desulfuration reactions.

The electronic control by the aromatic ring was further examined by studying the rearrangement of 1,3-dithian-2yl-pyridylmethanol (**5e**) and 1,3-dithian-2yl-thiophenyl-methanol (**5f**) under the same reaction conditions (Scheme 4). Pyridine is an electron deficient aromatic heterocycle and the reaction of **5e** gave only rearrangement product **6e**, in low yield. Thus, **5e** was found to mimic the reactivity observed with **5c**. Similarly, the electron rich thiophene ring on **5f** was chosen to mimic electron rich group on the aryl ring of **5d**. Therefore, **5f** was found to afford the rearrangement product **6f** in 10% yield and **10** in 5% yield, together with dithianylidene derivative **11** in 40% yield. The formation of **10** was in good agreement with electron rich aryl ring. The structure of compound **10** was assigned based on the similarity between the ^{1}H NMR and ^{13}C NMR spectra of this compound to those of **9**. Compound **10** showed the presence of two conjugated vinylic protons in a trans-orientation (J=15 Hz). Furthermore, the parent ion peak in the mass spectrum at 322 corresponds to the dimer of **6f** less a molecule of 1,3-dimercaptopropane and two molecules of water. A substantial amount of 2-(2-thienylmethylene)-1,3-dithiane (**11**) formed also illustrate that it is less prone to dimerization. The formation of dithianylidenes by acid catalyzed dehydration has been reported (Scheme 1).[11]

3. Conclusion

In summary, all 1,3-dithian-2-yl-arylmethanol derivatives studied led to the familiar ring expansion products that have been widely reported. However, this reaction was found to proceed with a remarkable degree of product selectivity that was dictated by the electron density of the aromatic ring. This can be summarized as followed: (i) electron withdrawing groups favor rearrangement to form 2-aryl-6,7-dihydro-5*H*-[1,4]dithiepines, (ii) unsubstituted phenyl and naphthyl rings favor cycloaromatization products and (iii) electron donating groups lead to dimerization products. The low yields obtained with **5a**,**b** and **d** can be attributed to competing polymerization reactions. Heterocyclic **5e** and **5f** also afforded similar results.



Scheme 4. Products from the reaction heterocycle **5e** and **5f** under acid catalysis.

4. Experimental

Proton and carbon-13 NMR spectra were recorded using a 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Melting points were measured on a Fisher–John apparatus and are uncorrected. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen.

4.1. General procedure for the preparation of 1,3-dithian-2-yl-arylmethanols (5a–d)

These compounds were prepared from 2-lithio-1,3-dithiane and the corresponding arylaldehydes in a good yield according to reported procedures.[3,10,12] To a solution of 1,3-dithiane (33 mmol) in 50 mL THF at −40°C was added an equimolar amount of butyllithium (1.6 M in hexane) and stirred for 1.5 h. The calculated amount of arylaldehyde dissolved in THF was added slowly through a dropping funnel, after which the reaction mixture stirred at −20°C for a further 12–24 h. The THF was removed under vacuo and the product extracted with chloroform.

4.1.1. 1,3-Dithian-2-yl-phenylmethanol (5a).[3] Isolated in 85% yield (SiO_2, hexane/CH_2Cl_2, 1:2) as white solid, mp 72–73°C; ν_{max} ($CHCl_3$) 3450 (br), 1495, 1420, 1280 cm^{-1}; δ_H ($CDCl_3$) 7.39–7.28 (5H, m, Ar*H*), 4.88 (1H, d, *J*=7.4, 3.0 Hz, ArC*H*O), 4.05 (1H, d, *J*=7.4 Hz, SC*H*S), 3.35 (1H, br, O*H*), 2.88–2.81 (2H, m, CH_2S), 2.70–2.61 (2H, m, CH_2S), 1.95 (2H, m, CH_2); *m/z* (EI, 30 eV) 226 (15 M^+), 119 (100), 77 (58%).

4.1.2. 1,3-Dithian-2-yl-napthylmethanol (5b). Isolated in 80% yield (SiO_2, hexane/EA, 5:2) as light yellowish brown solid, mp 126–128°C; [Found: C, 65.05; H, 5.85. $C_{15}H_{16}OS_2$ requires C, 65.18; H, 5.83%]; ν_{max}($CHCl_3$) 3468 (br), 1411, 1354, 1240 cm^{-1}; δ_H ($CDCl_3$) 7.89–7.82 (4H, m, Ar*H*), 7.56–7.46 (3H, m, Ar*H*), 5.09 (1H, d, *J*=7.5 Hz, ArC*H*O), 4.20 (1H, d, *J*=7.5 Hz, SC*H*S), 3.20 (1H, br, O*H*), 3.00–2.93 (2H, m, CH_2S), 2.78–2.71 (2H, m, CH_2S), 2.06–2.01 (2H, m, CH_2); δ_C ($CDCl_3$) 137.5, 133.4, 133.1, 128.1, 127.8, 126.3, 126.2, 126.2, 124.3, 74.9, 52.8, 28.2, 27.6, 25.3; *m/z* (EI, 30 eV) 276 (8, M^+), 259 (16), 184 (78), 127 (48), 119 (100%).

4.1.3. 1,3-Dithia-2-yl-4-nitrophenylmethanol (5c). Isolated in 65% yield (SiO_2, hexane/EtOAc, 1:1) as a light brownish solid, mp 83–84°C; [Found: C, 48.88; H, 4.87. $C_{11}H_{13}NO_3S_2$ requires C, 48.69; H, 4.83%]; ν_{max} ($CHCl_3$) 3446 (br), 1522, 1349, 1176 cm^{-1}; δ_H ($CDCl_3$) 8.23 (2H, d, *J*=7.0 Hz, Ar*H*), 7.62 (2H, d, *J*=7.0 Hz, Ar*H*), 5.03 (1H, d, *J*=7.5 Hz ArC*H*O), 3.95 (1H, d, *J*=7.5 Hz, SC*H*S), 3.05 (1H, br, O*H*), 3.00–2.95 (2H, m, CH_2S), 2.76–2.72 (2H, m, CH_2S), 2.07–2.03 (2H, m, CH_2); δ_C ($CDCl_3$) 147.4, 127.8, 123.4, 73.5, 52.2, 27.8, 27.2, 25.1; *m/z* (EI, 30 eV) 271 (4, M^+), 259 (6), 121 (15), 119 (100%).

4.1.4. 1,3-Dithian-2-yl-4-methoxyphenylmethanol (5d). Isolated in 85% yield (SiO_2, hexane/EtOAc, 3:1) as a yellowish solid, mp 79–80°°C; [Found: C, 56.20; H, 6.21. $C_{12}H_{16}O_2S_2$ requires C, 56.22; H, 6.29]; ν_{max}($CHCl_3$) 3434 (br), 1513, 1249, 1169, 1026 cm^{-1}; δ_H ($CDCl_3$) 7.35 (2H, d, *J*=8.7 Hz, Ar*H*), 6.90 (2H, d, *J*=8.7 Hz, Ar*H*), 4.86 (1H, d, *J*=78.7 Hz, ArC*H*O), 4.07 (1H, d, *J*=8.7 Hz, SC*H*S), 3.82 (3H, s, O*Me*), 2.90 (1H, br, O*H*), 2.88–2.84 (2H, m, CH_2S), 2.76–2.73 (2H, m, CH_2S), 2.08–1.99 (2H, m, CH_2); δ_C ($CDCl_3$) 159.7, 132.2, 128.0, 113.7, 74.4, 55.2, 52.7, 28.3, 27.6, 25.4; *m/z* (EI, 30 eV) 256 (2, M^+), 137 (100), 119 (63%).

4.1.5. 1,3-Dithian-2-yl-pyridylmethanol (5e). Isolated in 55% yield (SiO_2, hexane/EA, 1:3) as light brown solid, mp 85–86°C; [Found: C, 52.82; H, 5.77. $C_{10}H_{13}ONS_2$ requires C, 52.83; H, 5.76]; ν_{max} ($CHCl_3$) 3458 (br), 1580, 1470, 1206 cm^{-1}; δ_H ($CDCl_3$) 8.66 (1H, s, Ar*H*), 8.56 (1 H, d, *J*=4.5 Hz, Ar*H*), 7.80 (1H, d, *J*=4.5 Hz, Ar*H*), 7.32 (1H, dd, *J*=7.8, 4.5 Hz, Ar*H*), 4.98 (1H, d, *J*=47.5 Hz, ArC*H*O), 3.96 (1H, d, *J*=7.5 Hz, SC*H*S), 3.65 (1H, br, O*H*), 3.02–2.94 (2H, m, CH_2S), 2.76–2.70 (2H, m, CH_2S), 2.08–2.03 (2H, m, CH_2); δ_C ($CDCl_3$) 149.2, 148.5, 136.0, 134.6, 123.3, 72.2, 52.1, 27,6, 27.0, 25.2; *m/z* (EI, 30 eV) 227 (2, M^+), 259 (16), 119 (100), 108 (6%).

4.1.6. 1,3-Dithian-2-yl-2-thienylmethanol (5f). Isolated in 95% yield (SiO_2, hexane/Et_2O, 1:1) as light brownish liquid; [Found: C, 46.47; H, 5.14. $C_9H_{12}OS_3$ requires C, 46.52; H, 5.20]; ν_{max} ($CHCl_3$) 3554 (br), 1417, 1381, 1225 cm^{-1}; δ_H ($CDCl_3$) 7.30 (1H, d, *J*=5.5 Hz, Ar*H*), 7.11 (1H, d, *J*=4.0 Hz, Ar*H*), 6.98 (1H, dd, *J*=5.5, 4.0 Hz, Ar*H*), 5.18 (1H, d, *J*=7.8 Hz, ArC*H*O), 4.05 (1H, d, *J*=7.8 Hz, SC*H*S), 3.24 (1H, br, O*H*), 3.00–2.92 (2H, m, CH_2S), 2.77–2.68 (2H, m, CH_2S), 2.04–2.00 (2H, m, CH_2); δ_C ($CDCl_3$) 143.5, 126.4, 125.8, 125,2, 52.5, 27.8, 27.3, 25.2; *m/z* (EI, 30 eV) 232 (3, M^+), 119 (100%).

4.2. General procedure for the reaction of (5a–f) under acid catalysis

Conc. H_2SO_4 (1–2 drops) was added to the 1,3-dithian-2-yl-arylmethanol (500 mg) in toluene under nitrogen and the solution heated under reflux for approx. 24 h. After cooling to room temperature, the solution was filtered through a celite cake to remove polymeric products and the cake was further washed twice with toluene. The toluene solution was washed with sodium bicarbonate, saturated brine, dried over sodium sulfate, and evaporated. The residue was purified by preparative thin layer chromatography (SiO_2, 20×20 cm).

4.2.1. 2-Phenyl-6,7-dihydro-5*H*-1,4-dithiepine (6a) and 2-phenylnaphthalene (7). Reaction of **5a** by the general procedure gave a mixture of **6a** as yellowish oil (25%) and **7** as pale yellowish solid (10%) (hexane/CH_2Cl_2, 5:1).

Compound **6a**.[3] δ_H ($CDCl_3$) 7.54–7.50 (2H, m, Ar*H*), 7.34–7.30 (3H, m, Ar*H*), 6.15 (1H, s, C=C*H*), 3.66–3.58 (4H, m, SCH_2×2), 2.27–2.21 (2H, m, CH_2); *m/z* (EI, 30 eV) 208 (100 M^+), 179 (45), 134 (72), 102 (42%).

Compound **7**. Mp 100–102°C (lit.[15,16] 101–103°C); δ_H ($CDCl_3$) 8.04 (1H, s, Ar*H*), 7.93–7.85 (3H, m, Ar*H*), 7.77–7.72 (3H, m, Ar*H*), 7.53–7.46 (4H, m, Ar*H*), 7.40–7.35 (1H, m, Ar*H*); *m/z* (EI 30 eV) 204 (100, M^+), 127 (8%).

4.2.2. 2-(2-Naphthyl)-6,7-dihydro-5*H*-1,4-dithiepine (6b) and 3-naphthalen-2-nyl-phenanthrene (8). Reaction of

5b by the general procedure gave a mixture of **6b** (20%) and **8** as yellowish solids (10%) (hexane/CH_2Cl_2, 1:7).

Compound **6b**. Mp 67–68°C; [Found: C, 69.77; H, 5.53. $C_{15}H_{14}S_2$ requires C, 69.72; H, 5.46]; ν_{max} ($CHCl_3$) 1597, 1533, 1408, 1294 cm^{-1}; δ_H ($CDCl_3$) 7.98 (1H s, Ar*H*), 7.80–7.74 (3H, m, Ar*H*), 7.65–7.60 (1H, m, Ar*H*), 7.49–7.44 (2H, m, Ar*H*), 6.27 (1H, s, C=C*H*), 3.76–3.68 (4H, m, SCH_2×2), 2.26–2.20 (2H, m, CH_2); δ_C ($CDCl_3$) 138.6, 135.4, 133.2, 133.1, 128.2, 127.7, 127.5, 126.3, 126.2, 126.1, 125.5, 118.9, 32.6, 31.0, 30.4; *m/z* (EI, 70 eV) 258 (96, M^+), 152 (100), 184 (86), 106 (48%).

Compound **8**. Mp 123–125°C; [Found: C, 94.43; H, 5.34. $C_{24}H_{16}$ requires C, 94.70; H, 5.30]; ν_{max}($CHCl_3$) 1595, 1495, 1447 cm^{-1}; δ_H ($CDCl_3$) 9.03 (1H, s, Ar*H*), 8.84 (1H, d, *J*=8.0 Hz, Ar*H*), 8.25, (1H, s, Ar*H*, 8.90–8.05 (7H, bs, Ar*H*), 7.95–7.53 (6H, m, Ar*H*); δ_C ($CDCl_3$) 139.3, 138.8, 133.7, 132.7, 132.3, 131.2, 130.6, 130.4, 129.1, 128.7, 128.6, 128.2, 127.7, 127.1, 126.7, 126.5, 126.4, 126.3, 126.2, 126.0, 125.9, 122.7, 121.4; *m/z* (EI, 30 eV) 304 (12, M^+), 178 (15%).

4.2.3. 2-(4-Nitrophenyl)-6,7-dihydro-5*H*-1,4-dithiepine (6c). Reaction of **5c** by the general procedure gave only **6c** as light brownish solid in 55% yield (hexane/Et_2O, 1:1). Mp 120–121°C; [Found: C, 52.01; H, 4.49. $C_{11}H_{11}NO_2S_2$ requires C, 52.15; H, 4.38]; ν_{max} ($CHCl_3$) 1578, 1510, 1341 cm^{-1}; δ_H ($CDCl_3$) 8.15 (2H, d, *J*=8 Hz, Ar*H*), 7.63 (2H, d, *J*=8 Hz, Ar*H*), 6.28 (1H, s, C=C*H*), 3.71–3.62 (4H, m, SCH_2×2), 2.28–2.22 (2H, d, CH_2); δ_C ($CDCl_3$) 147.5, 147.0, 132.4, 127.7, 123.5, 122.8, 33.0, 30.8, 30.0; *m/z* (EI, 30 eV) 253 (55, M^+), 106 (50%).

4.2.4. 2-(4-Methoxyphenyl)-6,7-dihydro-5*H*-1,4-dithiepine (6d) and (*E*)-3-(1,3-dithian-2-yliden)-1,3-di(4-methoxyphenyl)-1-propene (9). Reaction of **5d** by the general procedure gave a mixture of **6d** as yellowish oil (15%) and **9** as a pale yellowish solid (20%) (hexane/EtOAc, 4:1).

Compound **6d**. [Found: C, 60.34; H, 6.05. $C_{12}H_{14}OS_2$ requires C, 60.46; H, 5.92]; ν_{max} ($CHCl_3$) 1600, 1510, 1285, 1172 cm^{-1}; δ_H ($CDCl_3$) 7.40 (2H, d, *J*=8.8 Hz, Ar*H*), 6.80 (2H, d, *J*=8.8 Hz, Ar*H*), 6.00 (1H, s, C=C*H*), 3.78 (s, 3H), 3.78–3.49 (m, 4H), 2.52–2.26 (m, 2H); δ_C ($CDCl_3$) 159.48, 135.35, 133.76, 128.54, 116.30, 113.48, 55.31, 32.41, 31.11, 30.56; *m/z* (EI, 30 eV) 238 (90, M^+), 132 (98), 106 (85%).

Compound **9**. Mp 130–131°C; [Found: C, 68.15; H, 6.02. $C_{21}H_{22}O_2S_2$ requires C, 68.07; H, 5.98]; ν_{max} ($CHCl_3$) 1606, 1510, 1285, 1174 cm^{-1}; δ_H ($CDCl_3$) 7.57 (1H, d, *J*=15 Hz, C=C*H*), 7.29 (2H, d, *J*=8.7 Hz, Ar*H*), 7.12 (2H, d, *J*=8.7 Hz, Ar*H*), 6.96 (2H, d, *J*=8.7 Hz, Ar*H*), 6.80 (2H, d, *J*=8.7 Hz, Ar*H*), 5.93 (1H, d, *J*=15 Hz, C=C*H*), 3.85 (3H, s, O*Me*), 3.79 (3H, s, O*Me*), 3.02 (2H, t, *J*=6.5 Hz, SCH_2), 2.87 (2H, t, *J*=6.5 Hz, SCH_2), 2.19–2.12 (2H, m, CH_2); δ_C ($CDCl_3$) 158.9, 158.8, 139.5, 131.0, 130.6, 130.1, 129.7, 127.6, 125.8, 114.0, 113.9, 113.6, 55.3, 55.2, 29.8, 29.5, 24.4; *m/z* (EI, 30 eV) 370 (100, M^+), 309 (20), 237 (35%).

4.2.5. 2-(3-Pyridyl)-6,7-dihydro-5*H*-1,4-dithiepine (6e). Reaction of **5e** by the general procedure gave only **6e** as light brownish gum in 15–25% yield (hexane/Et_2O, 2:1); ν_{max} ($CHCl_3$) 1565, 1533, 1421, 1294 cm^{-1}; δ_H ($CDCl_3$) 8.67 (1H, s, Ar*H*), 8.48 (1H, d, *J*=4.6 Hz, Ar*H*), 7.76 (1H, d, *J*=8.6 Hz, Ar*H*), 7.22 (1H, dd, *J*=8.6, 4.6 Hz, Ar*H*) 6.13 (1H, s, C=C*H*), 3.64 (4H, m, SCH_2×2), 2.24 (2H, m, CH_2); δ_C ($CDCl_3$) 148.8, 148.2, 137.0, 134.6, 131.5, 122.9, 120.2, 32.7, 31.0, 30.3; *m/z* (EI, 30 eV) 209 (100, M^+), 135 (26), 106 (50), 103 (38%); HRMS: found: 209.0335. $C_{10}H_{11}NS_2$ requires 209.0333.

4.2.6. 2-(2-Thienyl)-6,7-dihydro-5*H*-1,4-dithiepine (6f), (*E*)-3-(1,3-dithian-2yliden)-1,3-di(2-thienyl)-1-propene (10) and 2-(2-thienylmethylene)-1,3-dithiane (11). Reaction of **5f** by the general procedure gave a mixture of **6f** as yellowish oil (10%), **10** (5%) as pale yellowish solid and **11** as brownish oil (40%), (hexane/CH_2Cl_2, 3:1).

Compound **6f**. [Found: C, 50.04; H, 4.62. $C_9H_{10}S_3$ requires C, 50.42; H, 4.70]; ν_{max} ($CHCl_3$) 1653, 1411, 1299 cm^{-1}; δ_H ($CDCl_3$) 7.18 (1H, d, *J*=5.2 Hz, Ar*H*), 7.14 (1H, d, *J*=3.6 Hz, Ar*H*), 6.95 (1H, dd, *J*=5.2, 3.6 Hz, Ar*H*), 6.31 (1H, s, C=C*H*), 3.58–3.52 (4H, m, SCH_2×2), 2.25–2.17 (2H, m, CH_2); δ_C ($CDCl_3$) 145.0, 128.4, 127.3, 124.9, 123.8, 116.8, 32.6, 30.9, 30.3; *m/z* (EI, 30 eV) 214 (70, M^+), 108 (45), 105 (30%). HRMS: found: 213.9942. $C_{10}H_{11}NS_2$ requires 213.9945.

Compound **10**. Mp 93–94°C. [Found: C, 55.95; H,.4.46. $C_{15}H_{14}S_4$ requires C, 55.86; H, 4.37]; ν_{max} ($CHCl_3$) 1614, 1557, 1423, 1285 cm^{-1}; δ_H ($CDCl_3$) 7.48–7.38 (2H, m, Ar*H*), 7.40 (1H, d, *J*=15.5 Hz, C=C*H*), 7.13–7.07 (2H, m, Ar*H*), 6.93–6.85 (2H, m, Ar*H*), 6.28 (1H, d, *J*=15.5 Hz, C=C*H*), 3.03 (2H, t, *J*=6.8 Hz, SCH_2), 2.90 (2H, t, *J*=6.8 Hz, SCH_2), 2.21–2.08 (2H, m, CH_2); δ_C ($CDCl_3$) 143.4, 138.6, 136.7, 129.8, 128.5, 127.6, 127.25, 126.9, 126.4, 125.9, 124.2, 123.2, 29.5, 29.3, 24.0; *m/z* (EI, 30 eV) 322 (100, M^+), 247 (45), 216 (30), 203 (96), 171 (60%).

Compound **11**. [Found: C, 50.46; H, 4.72. $C_9H_{10}S_3$ requires C, 50.42; H, 4.70]; ν_{max} ($CHCl_3$) 1562, 1428, 1419, 1300 cm^{-1}; δ_H ($CDCl_3$) 7.25 (1H, d, *J*=4.2 Hz, Ar*H*), 7.07 (1H, *J*=5.6 Hz, Ar*H*), 7.05 (1H, s, C=C*H*), 6.96 (1H, dd, *J*=5.6, 4.2 Hz, Ar*H*), 3.03–2.95 (4H, m, SCH_2×2), 2.24–2.12 (2H, m, CH_2); δ_C ($CDCl_3$) 139.3, 127.8, 127.5, 126.4, 125.6, 122.8, 30.0, 29.6, 24.2; *m/z* (EI, 30 eV) 214 (90, M^+), 140 (100%).

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16. The crytallographic data has been deposited at the Cambridge Database and assigned CCDC 187085 for compound **6c** and CCDC 187086 for compound **9**.