Pergamon

Tetrahedron, Vol. 53, No. 17, pp. 6073-6084, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00268-8

Synthesis of Structurally Modified Atropisomeric Biaryl Dithiols. Observations on the Newman-Kwart Rearrangement

Sergio Cossu,[a] **Ottorino De Lucchi,**[a]* **Davide Fabbri,**[b] **Giovanni Valle**[c]#
[a]Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy
[b]Istituto CNR, IATCAPA, via Vienna 2, I-07100 Sassari, Italy
[c]Centro Studi Biopolimeri del CNR, via Marzolo 1, I-35131 Padova, Italy

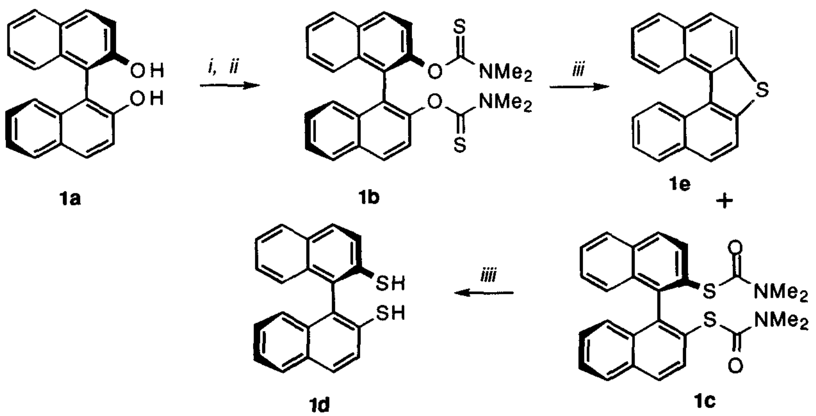
Gavin F. Painter, Robin A. J. Smith*
Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand

Abstract: The preparation of a number of biaryldithiols from biaryldiols is discussed. A key reaction is the Newman-Kwart thermorearrangement of bisthiocarbamates and crucial variables of temperature and reaction time have been identified. Alternative approaches to 3,3'-disubstituted dithiols via ortho metallation are presented. The benefit of using such disubstituted compounds is illustrated with representative examples of the stereochemical features of the derived carbanions in reactions with prochiral electrophiles. © 1997 Published by Elsevier Science Ltd.

As resolution procedures have improved in the recent past, so has the use of synthetic chiral auxiliaries in asymmetric synthesis. Some of the advantages of synthetic chiral auxiliaries over auxiliaries derived from the natural chiral pool include the ready availability of both enantiomers in most cases and the ability to design an auxiliary for a specific task. A well known example is 1,1'-binaphthalene-2,2'-diol (**1a**)[§] which has been used widely for asymmetric synthesis.[1]

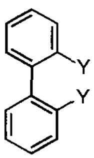
The related dithiol (**1d**) offers some contrasting chemistry compared with the oxygen analogue (**1a**) and has also been used in asymmetric synthesis to a limited extent.[2] The full potential of this compound and structural analogues for asymmetric synthesis is under development (*e.g. vide infra*) and as part of this effort, a variety of modified biaryldithiols are required.

Scheme 1[§]

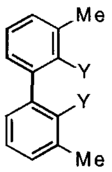


Reagents and Conditions: *i.* NaH, DMF, 1 h, 0 °C. *ii.* Me$_2$NC(S)Cl, DMF, 1 h, 80 °C. *iii.* 20 min, 270 °C. *iiii.* LiAlH$_4$, THF

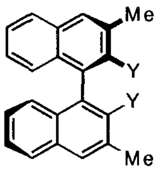
Efficient syntheses of **1d** from **1a** have been reported[3,4] and in this paper the general nature of the diol to dithiol transformation (Scheme 1) *via* a Newman-Kwart rearrangement is addressed. In the work described in this report, diols **1a**-**6a** were considered.



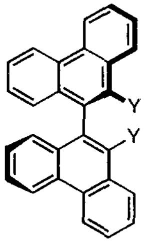
2a-d



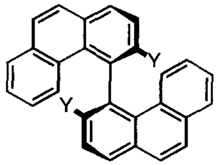
3a-d



4a-d



5a-d



6a-d

a: Y = OH **b**: Y = OC(S)NMe$_2$ **c**: Y = SC(O)NMe$_2$ **d**: Y = SH

The production of the bis-*O*-thiocarbamate esters **1b**,[3,4] **2b**,[5] **3b**-**6b** was routine with the isolated yields in the 70-90% range. In contrast to reports of other bis-*O*-thiocarbamate esters, the ^{1}H-NMR spectra of compounds **4b** and **5b** in CDCl$_3$ solution at room temperature were not trivial. For example, the ^{1}H-NMR spectrum of **4b** displayed eleven separate resonances in the 2-3 ppm range and also **5b** behaves similarly. As both materials were colorless crystalline solids with a sharp melting point and a correct analytically derived empirical formula, it was concluded that **4b** and **5b** exist as a series of relatively long-lived conformations on the NMR time scale in CDCl$_3$ solution at room temperature. An X-ray crystal analysis of **5b** (Figure 1) confirmed the molecular structure and showed a cisoid arrangement with a biaryl interplanar angle of 69.8° comparable to that (74°) of **1b**.[3] In addition, it is noted that the thiocarbamoyl groups are almost perpendicular (82.8°) with respect to the attached aromatic rings.

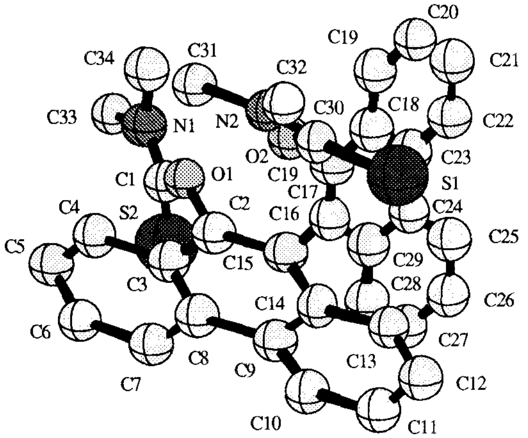
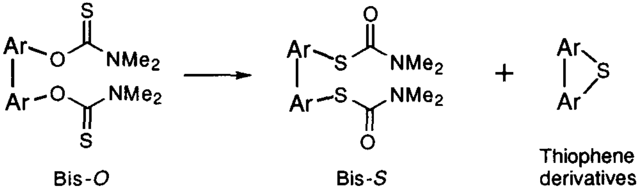


Figure 1. Perspective Ball & Stick drawing of the X-ray structure of **5b** with numbering used in the text. Hydrogen atoms omitted.

The key step in the reaction sequence (Scheme 1) is the Newman-Kwart thermorearrangement of bis-*O*-thiocarbamates to bis-*S*-thiocarbamates which is usually performed on the neat material. The results from this study are presented in the Table 1 along with comparative data for **1b**,[3,4] (*R*)-**6b**[5] and the 1,1'-biphenyl analogue **2b**.[6]

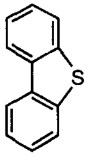
In accord with the literature,[6] we have found that thermorearrangement of **2b** (entry 1) gives the bis-*S* product **2c** in good yields. The capricious nature of this reaction with the binaphthyl substrate (**1b**) has been reported[3,7] with the major by-product being the intramolecular dinaphthothiophene. Provided the sample of **1b** was highly crystalline, then good returns of the bis-*S* product **1c** are obtained (entry 2), however if the substrate is not sufficiently crystalline, lower conversions to the bis-*S* material are noted (entry 3). Optimization of experimental conditions with the lower quality crystals of **1b** showed that improved returns can be achieved by relatively small changes in the reaction conditions. The product distribution from the thermorearrangement reaction is particularly sensitive to small changes in temperature and reaction time. Higher temperatures and longer reaction times provoke the formation of greater quantities of the thiophene derivatives. The optimum reaction conditions achieved with **1b** (entry 4) were similar to those found for optically active (*R*)-**1b** (entry 5).[4]

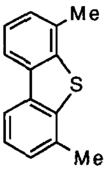
Table 1. Thermorearrangement of Biaryl Bis-*O*-thiocarbamates

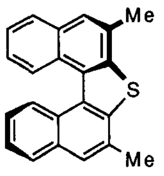


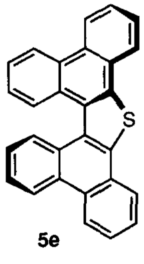
Entry	Reagents	Products (%)		Reaction Conditions	
	Bis-*O*	Bis-*S*	Thiophene	Temp (°C)	Time (min)
1 (ref 6)	**2b**	**2c** (72)	-	310	25
2 (ref 3)	**1b**	**1c** (70-75)	**1e** (20)	285	40
3	**1b**	**1c** (50)	**1e** (47)	285	40
4	**1b**	**1c** (82)	**1e** (15)	271	22
5 (ref 4)	(*R*)-**1b**	(*R*)-**1c** (70)	**1e** (20)	285	22
6	**3b**	**3c** (80)	**3e** (20)	285	22
7	**4b**	**4c** (84)	-	270	20
8	**5b**	**5c** (89)	-	270	20
9	**6b**	**6c** (73)	**6e** (11)	270	20
10	**6b**	-	**6e** (85)	285	40
11	**6b**	**6c** (51)*	**6e** (17)*	262	15
12	**6b**	**6c** (62)	**6e** (21)	265	20
13 (ref 5)	(*R*)-**6b**	(*R*)-**6c** (70-75)	**6e** (20-25)	280-285	22

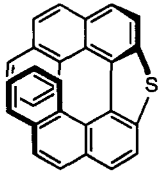
* 10% starting material also recovered.


2e


3e


4e


5e

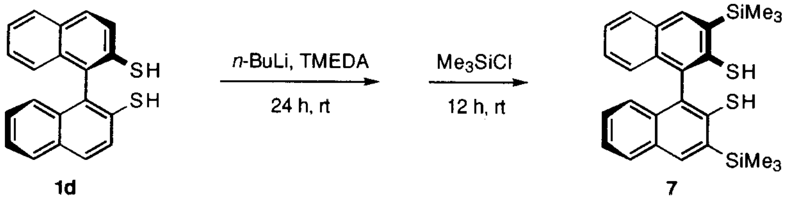

6e

These reaction parameters were also effective when applied to **3b**-**5b** (entries 6-8). Dramatic time and temperature dependent results were obtained for the the thermolysis of **6b**. As with **1b** (entry 4), a reaction time of around 20 min and temperature of 270 °C gave the best yield of the bis-*S* compound **6c** from **6b** (entry 9). An increase in the reaction time and temperature lead to increased amounts of thiophene **6e** with only trace amounts of the bis-*S* compound **6c** detected after 40 min at 285 °C (entry 10). Operation at lower temperatures and shorter times (entries 11, 12) gave lower conversions and no improvement in the ratio of bis-*S* to thiophene. A reaction with (*R*)-**6b** has been recently reported[5] (entry 13) which confirms the optimum conditions for rearrangement of this substance and produced optically active bis-*S* product. In summary the rearrangement of bis(thiocarbamates) can be effected provided empirical optimisation of the reaction time and temperature is carried out with the recognition that these are very sensitive parameters.

The ^1H and ^{13}C-NMR spectral properties of the bis-*S* compounds **4c, 5c** derived from **4b** and **5b** were comparable to those of previously characterised biaryl bis-*S*-thiocarbamates,[3,6] apart from peaks assigned to occluded dichloromethane solvent. This type of compound has been reported earlier.[2a] The syntheses of the dithiols **1d-5d** from the bis-*S*-thiocarbamate esters *via* alkaline hydrolysis[3] or $LiAlH_4$ reduction[4-6] were also routine with yields in the 80-90% range. Some of the dithiols readily oxidized to the internal disulfides on standing in solution in air.

An alternative to developing optimum thermolysis conditions for each biaryl system of interest is to prepare substituted biaryldithiols from readily available and established dithiols. An example of this approach is the production of 3,3'-disubstituted binaphthyls from **1d** using ortho metallation techniques.[8]

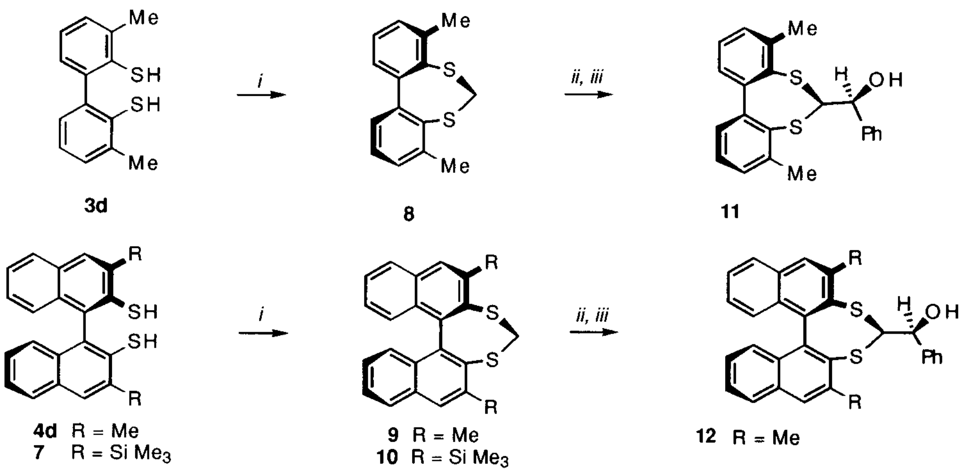
Scheme 2



As outlined in Scheme 2 the 3,3'-bis(trimethylsilyl) dithiol **7** can be conveniently prepared in this manner.

An example of the variable reactivity of 3,3'-substituted biaryldithiols is illustrated in the reactions of the carbanions derived from the dithiepine with prochiral electrophiles. This reaction sequence is outlined in Scheme 3 with benzaldehyde as the electrophile.

Scheme 3



Reagents and conditions: *i.* $CH_2(OMe)_2$, BF_3 Et_2O *ii.* *n*-BuLi, THF, -78 °C *iii.* PhCHO

The carbanion of the dithiepine derived from **1d** reacts with benzaldehyde to give a 4:1 mixture of diastereoisomers[9] whereas the comparable reactions with anions based on **8** or **9** give only one stereoisomer. In contrast, the anion derived from **10** is unreactive towards this electrophile. The relative stereochemistry of the adducts **11** and **12** is drawn as determined in the binaphthyl case.[9] These results reflect a mere segment of the synthetic avenues which await to be explored in this area of chemistry and establish the need for a library of biaryldithiols as discussed in this paper.

EXPERIMENTAL SECTION

^{1}H-NMR and ^{13}C-NMR spectra were obtained, in $CDCl_3$ solutions, on Varian Gemini 200, VXR 300 and Unity 400 spectrometers operating at 200/50 MHz, 300/75 MHz and 400/100 MHz respectively. Spectral data, relative to internal tetramethylsilane $\delta = 0$ ppm, is presented as: Chemical shift (number of protons, multiplicity, coupling constant). IR spectra were recorded in KBr pellets on a Perkin Elmer 983 spectrophotometer. Electron impact high resolution mass spectra (HRMS) were obtained from the Chemistry Department, University of Canterbury (New Zealand). Melting points were determined either on a Gallenkamp heating block apparatus in open capillary tubes or on a Büchi 535 apparatus and are uncorrected. Column chromatography was carried out at atmospheric pressure on Silica gel 60 (Merck Art 9385). PreparativeTLC chromatography was carried on 1.25 mm thick layers of Silica gel 60 PF254 (Merck, Art 7747). Radial chromatography was carried under nitrogen on a Chromatotron model 7924T using Kieselgel 60 PF254 (Merck, Art 7749).

3,3'-Dimethyl-1,1'-dibenzo-2,2'-diol (3a). A solution of BBr_3 (22.58 g, 90.2 mmol) and dichloromethane (70 mL) was added dropwise to a solution of 2,2'-dimethoxy-3,3'-dimethyl-1,1'-biphenyl[10] (10.7 g, 4.42 mmol) in the same solvent (100 mL) stirred at -78 °C. The stirred solution was allowed to reach room temperature during 4 h. Water (100 mL) was carefully added to the reaction mixture and the organics were extracted with diethyl ether (4 x 100 mL), dried over sodium sulfate, filtered and concentrated. The resulting solid was recrystallised from methanol to furnish **3a** (18.35 g, 95%) as a colorless solid: mp 84-6 °C. ^{1}H-NMR (300 MHz) δ 2.31 (s, 6 H, CH_3), 5.18 (bs, 2 H, OH), 6.95 (2 H, t, J = 8.3 Hz), 7.08 (2 H, d, J = 8.3 Hz), 7.40 (2 H, t, J = 8.3 Hz). ^{13}C-NMR (100 MHz) δ 16.0, 120.8, 122.0, 125.4, 128.1, 131.3, 151.4. Anal. calcd for $C_{14}H_{14}O_2$: C, 78.5; H, 6.6. Found: C, 78.7; H, 6.4%.

2,2'-Bis-(*N*,*N*-dimethylthiocarbamoyloxy)-3,3'-dimethyl-1,1'-biphenyl (3b). NaH (2.05 g of a 60% dispersion in mineral oil, 51.34 mmol) was added during 20 min to a stirred solution of **3a** (15 g, 23.33 mmol) and dry DMF (70 mL) under nitrogen at 0 °C. After 1 h, *N*,*N*-dimethylthiocarbamoyl chloride (6.35 g, 51.34 mmol) was added in portions and the resulting mixture was heated at 85 °C for 1 h, then cooled to room temperature and treated with 1% KOH solution (300 mL). The solid that separated was collected by filtration, dissolved in dichloromethane (250 mL) washed with water, dried over sodium sulfate, filtered and concentrated to give **3b** (7.70 g, 85%) as a colorless solid: mp 140-1 °C (ethyl acetate-light petrol). ^{1}H-NMR (300 MHz) δ 2.24 (s, 6 H, CH_3), 3.00 (s, 6 H, N-CH_3), 3.17 (s, 6 H, N-CH_3), 7.09-7.23 (series of m, 6 H, Ar). ^{13}C-NMR (300 MHz) δ 16.8, 37.9, 43.0, 124.8, 125.8, 129.0, 129.4, 129.4, 131.4. Anal. calcd for $C_{20}H_{24}N_2O_2$: C, 61.8; H, 6.2; N, 7.2. Found: C, 62.0; H, 6.4; N, 7.2%.

2,2'-Bis(*N*,*N*-dimethylcarbamoylthio)-3,3'-dimethyl-1,1'-biphenyl (3c) and 3,3'-dibenzo[2,1-*b*:1':2'-*d*]thiophene (3e). A crystalline sample of **3b** (7.70 g, 19.85 mmol) was placed into a pyrex tube and heated at 285 °C for 22 min under nitrogen. After cooling to room temperature, the solid was dissolved in dichloromethane (150 mL) and chromatographed on a silica gel column. Elution with a 1:1

dichloromethane-light petrol gave **3e** (0.84 g, 20%): mp 153-4 °C (dichloromethane-light petrol); ^{1}H-NMR (300 MHz) δ 2.58 (s, 6 H, CH_3), 7.23 (2 H, d, *J* = 7.5 Hz, Ar), 7.35 (2 H, t, *J* = 7.5 Hz, Ar), 7.92, (2 H, d, *J* = 7.5 Hz, Ar). ^{13}C-NMR (100 MHz, 1 C atom omitted) δ 20.3, 119.0, 124.5, 126.6, 132.0, 136.0. Anal. calcd for $C_{14}H_{12}S$: C, 79.2; H, 5.7. Found: C, 79.5; H, 5.4%.

Elution with ethyl acetate gave **3c** (6.16 g, 80%): mp 124-5 °C (dichloromethane-light petrol). ^{1}H-NMR (300 MHz) δ 2.47 (6 H, s, CH_3), 2.88 (12 H, bs, N-CH_3), 7.08-7.11, 7.26-7.31 (series of m, 6 H, Ar). ^{13}C-NMR (100 MHz) δ 21.9, 37.0, 127.7, 128.3, 128.7, 129.5, 143.4, 147.9, 166.1. IR (KBr pellets) 3011, 2916, 1652, 1578, 1449, 1432, 1358, 1256, 788, 775, 735 cm^{-1}. Anal. calcd for $C_{20}H_{24}N_2O_2$: C, 61.8; H, 6.2; N, 7.2. Found: C, 61.9; H, 6.4; N, 7.2%.

3,3'-Dimethyl-1,1'-dibenzo-2,2'-dithiol (3d). A solution of **3c** (6.16 g, 15.88 mmol) and dry THF (100 mL) was added dropwise during 1 h to a suspension of $LiAlH_4$ (0.62 g, 79.4 mmol) in the same solvent (50 mL), stirred under nitrogen at 0 °C. The reaction mixture was gently refluxed for 3 h, then cooled at 0 °C, quenched with water and made acidic with 10% hydrochloric acid. The organics were extracted with diethyl ether, dried over sodium sulfate, filtered and concentrated. The solid obtained was recrystallised from ethanol to furnish **3d** (3.65 g, 95%) as a colorless solid: mp 97-8 °C. ^{1}H-NMR ($CDCl_3$) δ 2.43 (6 H, s, CH_3), 3.28 (2 H, s, SH), 7.00-7.32 (6 H, series of m, Ar). ^{13}C-NMR (100 MHz) δ 21.3, 124.7, 125.7, 127.1, 127.4, 129.2, 129.5. IR (KBr pellets) 3466, 3046, 2921, 1448, 1382, 790, 783, 729 cm^{-1}. Anal. calcd for $C_{14}H_{14}S_2$: C, 68.2; H, 5.7. Found: C, 68.4; H, 5.9%.

A solution of **3d** standing in air gave **3,3'-dimethyldibenzo[2,1-*c*:1',2'-*e*][1,2]dithiin** (100%): mp 126-7 °C (light petrol); ^{1}H-NMR (300 MHz) δ 2.52 (6 H, s, CH_3), 7.20 (2 H, d, *J* = 7.8 Hz), 7.28 (2 H, t, *J* = 7.8 Hz), 7.51 (2 H, d, *J* = 7.8 Hz). ^{13}C-NMR (100 MHz) δ 20.8, 125.9, 127.4, 129.4, 136.6, 137.1, 139.0. Anal. calcd for $C_{14}H_{12}S_2$: C, 68.8; H, 4.9. Found: C, 68.7; H, 4.9%.

2,2'-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-3,3'-dimethyl-1,1'-binaphthalene (4b). As described for the preparation of **3b** above, **4b** was prepared from of 3,3'-dimethyl-1,1'-binaphthalene-2,2'-diol (**4a**)[11] (873 mg, 2.78 mmol), NaH (60% dispersion in mineral oil, 265 mg, 6.63 mmol) and *N*,*N*-dimethylthiocarbamoyl chloride (840 mg, 6.80 mmol) in DMF (15 mL). Crystallisation from toluene gave **4b** (1.14 g, 84%) as colorless crystals, mp 279-281 °C. ^{1}H-NMR (300 MHz) δ 2.00-3.15 (18 H, m, 4 x N-CH_3, 2 x Ar-CH_3), 7.10-7.45 (6 H, m, Ar), 7.75-7.95 (4 H, m, Ar). Anal. calcd for $C_{28}H_{28}N_2O_2S_2$: C, 68.8; H, 5.8; N, 5.7; S, 13.1. Found: C, 68.7; H, 5.9; N, 5.8; S, 13.4%.

2,2'-Bis(*N*,*N*-dimethylcarbamoylthio)-3,3'-dimethyl-1,1'-binaphthalene (4c). Compound **4b** (64.0 mg, 0.131 mmol) was thermolysed as described above for **3b** to give **4c** as a white solid (63.1 mg, 84%), mp 118-122 °C. ^{1}H-NMR (200 MHz) δ 2.66 (18 H, s, 4 x N-CH_3, 2 x Ar-CH_3), 7.02 (2 H, d, *J* = 8.7 Hz, Ar), 7.13 (2 H, ddd, *J* = 7.9, 6.6, 1.3 Hz, Ar), 7.40 (2 H, ddd, *J* = 8.1, 6.6, 1.5 Hz, Ar), 7.80 (2 H, d, *J* = 8.2 Hz, Ar), 7.87 (2 H, s, Ar). ^{13}C-NMR (50 MHz) δ 22.1, 36.8, 125.2, 126.8, 126.9, 127.5, 128.5, 128.7, 132.1, 133.9, 139.8, 144.3, 165.8 (C=O). Anal. calcd for $C_{29}H_{30}Cl_2N_2O_2S_2$: C, 60.7; H, 5.3; N, 4.9; S, 11.2. Found: C, 60.5; H, 5.4; N, 4.6; S, 11.2%.

3,3'-Dimethyl-1,1'-binaphthalene-2,2'-dithiol (4d). Compound **4d** was prepared as for **3d** above from **4c** (1.24 g, 2.54 mmol) and $LiAlH_4$ (1.00 g, 26.3 mmol) in THF (55 mL) and was obtained as a yellow solid (0.83 g, 94%), mp 234-8 °C. ^{1}H-NMR (300 MHz) δ 2.64 (6 H, s, 2 x Ar-CH_3), 3.29 (2 H, s, 2 x

SH), 6.93 (2 H, d, *J* = 8.3 Hz, Ar), 7.22 (2 H, ddd, *J* = 8.3, 6.8, 1.5 Hz, Ar), 7.41 (2 H, ddd, *J* = 8.1, 6.8, 1.2 Hz, Ar), 7.80-7.87 (4H, m, Ar). ^{13}C-NMR (100 MHz) δ 21.9, 125.1, 125.5, 126.5, 127.6, 128.6, 131.1, 131.9, 132.2, 133.2, 133.8. HRMS found: $(M)^+$, 346.0852. $C_{22}H_{18}S_2$ requires $(M)^+$, 346.0850.

On standing in air a solution of **4d** gave **3,3'-dimethylbinaphtho[2,1-*c*:1',2'-*e*][1,2]dithiin** (100%): mp 130-1 °C. ^{1}H-NMR (300 MHz) δ 2.66 (6 H, s, CH_3), 6.96 (2 H, d, *J* = 7.5 Hz), 7.05 (2 H, t, *J* = 7.0 Hz), 7.34 (2 H, t, *J* = 7.0 Hz), 7.65 (2 H, s), 7.75 (2 H, d, *J* = 7.5 Hz). ^{13}C-NMR (100 MHz, 1 C atom omitted) δ 20.8, 125.9, 127.4, 129.4, 129.8, 136.6, 137.1, 137.8, 139.0, 143.2. Anal. calcd for $C_{22}H_{16}S_2$: C, 76.7; H, 4.7. Found: C, 76.5; H, 4.4%.

10,10'-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-9,9'-biphenanthrene (5b). NaH (60% dispersion in mineral oil, 230 mg, 5.75 mmol) was added portion wise to a stirred solution of 9,9'-biphenanthrene-10,10'-diol (**5a**)[12] (1.0 g, 2.59 mmol) in DMF (25 mL) at 0 °C under an argon atmosphere equipped with a pressure release system. After 1 h *N*,*N*-dimethylthiocarbamoyl chloride (0.76 g, 6.14 mmol) was added and the reaction mixture was stirred at 85-90 °C for 2 h. After cooling to 0 °C, the product was precipitated with the addition of 5% KOH (100 mL). The precipitate was washed with 5% KOH (2 x 100 mL) and H_2O (5 x 200 mL). The solid was dissolved in dichloromethane and dried ($MgSO_4$). After filtration the solvent was removed *in vacuo* to give a crude product which was exposed to refluxing toluene (75 mL). Removal of the supernatant after cooling gave **5b** (1.30 g, 90%) as a colorless solid, mp 295 °C. ^{1}H-NMR (200 MHz) δ 2.07-3.20 (12 H, m, N-CH_3), 7.26-8.16 (12 H, m, Ar), 8.70-8.86 (4 H, m, Ar). HRMS found: $(M)^+$, 560.1598. $C_{34}H_{28}N_2O_2S_2$ requires $(M)^+$, 560.1592.

Table 2 - Crystal Data and Summary of Intensity Data Collection and Structure Refinement for **5b**. The reflections were phased by SHELX 86 direct methods. Refined with least squared with all non hydrogen atoms anisotropic. The hydrogen atoms were refined isotropically.

Cell chemical composition	$C_{272}S_{16}O_{16}N_{16}H_{224}$	Cell wt	4485.82
Space group	Monoclinic	Cell vol. [Å^3]	5710.13
Crystal system	C2/c	*Z*	8
Cell constants:		F(000) (elec.)	2352.00
a [Å]	19.278(2)	$D_{calc.}$[g cm^{-3}]	1.3
b [Å]	9.051(2)	Diffractometer	Siemens R3m/V
c [Å]	33.600(2)	Radiation	Mo Kα
β	103.10(1)	Monochromator	graphite
Crystal size [mm]	0.4 x 0.6 x 0.6	Theta range [deg]	1.75 - 27.5
Recip. latt. segment:		Readen Reflections	6982
h	-25 - 24	2Theta:	4.3 - 56.0
k	0 - 11	Reflections observed [$F > 4s(F)$]	3748
l	0 - 44	Unique refl.	6876
Lin. abs. coeff. [mm^{-1}]	0.38	Abs. correction	ψ-scan
R_i	0.042	R_w [$w=1/s^2(F)$]	0.064
R	0.066		

Table 3 - Interatomic Distances (Å) with Standard Deviations for **5b**.

S(1)-C(30)	1.632(4)	S(2)-C(1)	1.635(5)	O(1)-C(1)	1.383(4)	O(1)-C(2)	1.397(4)
O(2)-C(17)	1.403(4)	O(2)-C(30)	1.364(4)	N(1)-C(1)	1.327(5)	N(1)-C(33)	1.457(5)
N(1)-C(34)	1.456(6)	N(2)-C(30)	1.345(5)	N(2)-C(31)	1.457(7)	N(2)-C(32)	1.461(6)
C(2)-C(3)	1.421(6)	C(2)-C(15)	1.359(5)	C(3)-C(4)	1.413(6)	C(3)-C(8)	1.406(6)
C(4)-C(5)	1.374(8)	C(5)-C(6)	1.385(9)	C(6)-C(7)	1.367(8)	C(7)-C(8)	1.403(7)
C(8)-C(9)	1.468(6)	C(9)-C(10)	1.413(6)	C(9)-C(14)	1.416(6)	C(10)-C(11)	1.361(7)
C(11)-C(12)	1.381(7)	C(12)-C(13)	1.366(6)	C(13)-C(14)	1.406(5)	C(14)-C(15)	1.451(5)
C(15)-C(16)	1.501(5)	C(16)-C(17)	1.344(5)	C(16)-C(29)	1.448(5)	C(17)-C(18)	1.441(5)
C(18)-C(19)	1.406(5)	C(18)-C(23)	1.409(5)	C(19)-C(20)	1.365(7)	C(20)-C(21)	1.398(6)
C(21)-C(22)	1.356(6)	C(22)-C(23)	1.409(6)	C(23)-C(24)	1.450(5)	C(24)-C(25)	1.407(5)
C(24)-C(29)	1.413(6)	C(25)-C(26)	1.356(6)	C(26)-C(27)	1.386(7)	C(27)-C(28)	1.365(5)
C(28)-C(29)	1.406(5)						

Table 4 - Atomic Parameters (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2) for **5b**.

Atom	x	y	z	U(eq)[a]	Atom	x	y	z	U(eq)[a]
S(1)	236(7)	1558(1)	67191(3)	0.0689(5)	S(2)	-14930(5)	8386(1)	57145(3)	0.0598(4)
O(1)	-522(1)	7120(3)	63058(7)	0.0454(9)	O(2)	324(1)	4389(3)	65306(6)	0.0449(8)
N(1)	-87(2)	8700(3)	59241(9)	0.053(1)	N(2)	708(2)	3903(4)	71835(9)	0.061(1)
C(1)	-683(2)	8089(4)	5980(1)	0.043(1)	C(2)	-1067(2)	6233(4)	6386(1)	0.041(1)
C(3)	-1484(2)	6800(4)	6650(1)	0.045(1)	C(4)	-1358(3)	8222(5)	6825(1)	0.060(2)
C(5)	-1772(3)	8761(6)	7076(1)	0.078(2)	C(6)	-2332(3)	7922(7)	7147(1)	0.077(2)
C(7)	-2465(2)	6542(6)	6981(1)	0.064(2)	C(8)	-2038(2)	5933(4)	6736(1)	0.048(1)
C(9)	-2128(2)	4413(4)	6579(1)	0.046(1)	C(10)	-2633(2)	3421(6)	6674(1)	0.059(2)
C(11)	-2679(2)	1998(6)	6540(1)	0.063(2)	C(12)	-2225(2)	1471(5)	6308(1)	0.057(2)
C(13)	-1728(2)	2392(4)	6210(1)	0.048(1)	C(14)	-1666(2)	3872(4)	6340(1)	0.041(1)
C(15)	-1134(2)	4836(4)	62339(9)	0.039(1)	C(16)	-0662(2)	4313(4)	59633(9)	0.038(1)
C(17)	31(2)	4042(4)	61199(9)	0.037(1)	C(18)	0526(2)	3575(4)	5881(1)	0.040(1)
C(19)	1247(2)	3292(4)	6060(1)	0.050(1)	C(20)	1696(2)	2788(5)	5829(1)	0.060(2)
C(21)	1439(2)	2585(5)	5409(1)	0.061(2)	C(22)	0748(2)	2871(4)	5232(1)	0.051(2)
C(23)	259(2)	3347(4)	5459(1)	0.041(1)	C(24)	-0491(2)	3591(4)	52824(9)	0.041(1)
C(25)	-799(3)	3308(5)	4868(1)	0.057(2)	C(26)	-1502(2)	3523(5)	4707(1)	0.063(2)
C(27)	-1944(2)	4037(5)	4949(1)	0.062(2)	C(28)	1670(2)	4326(4)	5353(1)	0.049(1)
C(29)	946(2)	4083(4)	5531(1)	0.042(1)	C(30)	0424(2)	3296(4)	6818(1)	0.046(1)
C(31)	830(3)	5486(6)	7238(1)	0.088(2)	C(32)	0920(2)	2945(7)	7540(1)	0.090(2)
C(33)	121(3)	9922(5)	5638(1)	0.074(2)	C(34)	614(2)	8294(5)	6165(1)	0.068(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5 - Bond Angles (Deg) with Standard Deviations for **5b**.

C(1)-O(1)-C(2)	118.3(4)	C(17)-O(2)-C(30)	119.6(3)	C(33)-N(1)-C(34)	117.2(5)	C(1)-N(1)-C(34)	122.7(4)
C(1)-N(1)-C(33)	119.9(6)	C(31)-N(2)-C(32)	118.3(4)	C(30)-N(2)-C(32)	119.2(4)	C(30)-N(2)-C(31)	122.4(4)
O(1)-C(1)-N(1)	109.2(4)	S(2)-C(1)-N(1)	127.3(3)	S(2)-C(1)-O(1)	123.5(5)	O(1)-C(2)-C(15)	118.2(5)
O(1)-C(2)-C(3)	118.1(3)	C(3)-C(2)-C(15)	123.5(5)	C(2)-C(3)-C(8)	119.3(4)	C(2)-C(3)-C(4)	121.3(5)
C(4)-C(3)-C(8)	119.4(4)	C(3)-C(4)-C(5)	120.5(5)	C(4)-C(5)-C(6)	119.7(5)	C(5)-C(6)-C(7)	120.8(7)
C(6)-C(7)-C(8)	121.1(6)	C(3)-C(8)-C(7)	118.3(4)	C(7)-C(8)-C(9)	122.7(5)	C(3)-C(8)-C(9)	118.9(5)
C(8)-C(9)-C(14)	119.3(4)	C(8)-C(9)-C(10)	23.1(4)	C(10)-C(9)-C(14)	117.5(4)	C(9)-C(10)-C(11)	121.6(6)
C(10)-C(11)-C(12)	120.7(5)	C(11)-C(12)-C(13)	119.7(5)	C(12)-C(13)-C(14)	121.4(6)	C(9)-C(14)-C(13)	119.1(5)
C(13)-C(14)-C(15)	120.8(4)	C(9)-C(14)-C(15)	120.1(4)	C(2)-C(15)-C(14)	118.6(4)	C(14)-C(15)-C(16)	121.2(3)
C(2)-C(15)-C(16)	120.2(4)	C(15)-C(16)-C(29)	120.7(5)	C(15)-C(16)-C(17)	120.4(3)	C(17)-C(16)-C(29)	118.9(5)
O(2)-C(17)-C(16)	119.1(4)	C(16)-C(17)-C(18)	124.1(4)	O(2)-C(17)-C(18)	116.3(5)	C(17)-C(18)-C(23)	117.7(6)
C(17)-C(18)-C(19)	122.1(4)	C(19)-C(18)-C(23)	120.1(5)	C(18)-C(19)-C(20)	120.8(4)	C(19)-C(20)-C(21)	119.5(7)
C(20)-C(21)-C(22)	120.4(5)	C(21)-C(22)-C(23)	122.1(4)	C(18)-C(23)-C(22)	117.0(5)	C(22)-C(23)-C(24)	123.4(4)
C(18)-C(23)-C(24)	119.6(4)	C(23)-C(24)-C(29)	120.1(4)	C(23)-C(24)-C(25)	122.4(5)	C(25)-C(24)-C(29)	117.5(5)
C(24)-C(25)-C(26)	122.0(5)	C(25)-C(26)-C(27)	120.4(4)	C(26)-C(27)-C(28)	119.8(6)	C(27)-C(28)-C(29)	121.0(5)
C(24)-C(29)-C(28)	119.2(4)	C(16)-C(29)-C(28)	121.2(4)	C(16)-C(29)-C(24)	119.6(5)	O(2)-C(30)-N(2)	108.3(3)
S(1)-C(30)-N(2)	127.2(3)	S(1)-C(30)-O(2)	124.5(3)				

10,10'-Bis-(*N*,*N*-dimethylcarbamoylthio)-9,9'-biphenanthrene (5c) and diphenanthro-[10,9-*b*:9',10'-*d*]thiophene (5e). 10,10'-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-9,9'-biphenanthrene (**5b**) (400 mg, 0.713 mmol) contained in a Pyrex tube under a nitrogen atmosphere was immersed into a sulfolane bath refluxing at 270 °C. After 20 min the Pyrex tube was removed from the heating bath. After cooling to rt the crude material was chromatographed on silica gel (elution with dichloromethane followed by 10% ether/dichloromethane) to give **5c** (356 mg, 89%) as a white solid, mp 298-301 °C. ^{1}H-NMR (200 MHz) δ 2.64 (12 H, s, 4 x N-CH$_3$), 7.24-7.37 (4 H, m, Ar), 7.56-7.79 (6 H, m, Ar), 8.48-8.56 (2 H, m, Ar), 8.73-8.85 (4 H, m, Ar). ^{13}C-NMR (50 MHz) δ 36.9, 122.5, 122.8, 126.8, 127.0, 127.1, 127.3, 127.7, 127.8, 128.7, 130.9, 131.2, 131.7, 133.1, 144.4, 165.5 (C=O). Anal. calcd for $C_{35}H_{30}Cl_2N_2O_2S_2$: C, 65.1; H, 4.7; N, 4.3; S, 9.9. Found: C, 64.9; H, 4.8; N, 4.3; S, 9.9%.

In some thermolyses of **5b** small amounts of **5e** could be isolated by chromatography as above, mp 254-6 °C (toluene). ^{1}H-NMR (300 MHz) δ 7.58 (2 H, t, *J* = 8.7 Hz), 7.64-7.75 (6 H, m), 8.12-8.15 (2 H, m), 8.65-8.80 (6 H, m). ^{13}C-NMR (100 MHz) δ 123.4, 123.8, 124.6, 125.3, 126.0, 126.8, 127.0, 127.4, 128.12, 129.1, 129.7, 130.0, 131.7, 137.3. Anal. calcd for $C_{28}H_{16}S$: C, 87.5; H, 4.2. Found: C, 87.5; H, 4.4%.

9,9'-Biphenanthrene-10,10'-dithiol (5d). A solution of **5c** (800 mg, 1.43 mmol) in THF (40 mL) was treated with $LiAlH_4$ (400 mg, 10.5 mmol) as for **3d** above. The reaction mixture was made slightly acidic (pH~6) with 1% HCl under an argon atmosphere and extracted with ether (2 x 100 mL) followed by dichloromethane (2 x 100 mL). The combined organic extract was washed with H_2O (2 x 300 mL) and dried ($MgSO_4$). After filtration, evaporation of the solvent *in vacuo* gave the crude product (610 mg) which was purified by radial chromatography. Elution with hexane/dichloromethane, 4:1, gave **5d** (506 mg, 85%) as a yellow solid: mp 249-253 °C. ^{1}H-NMR (200 MHz) δ 3.58 (2 H, s, 2 x SH), 7.15 (2 H, dd, J = 8.3, 1.2 Hz), 7.33 (2 H, ddd, J = 8.2, 7.0, 1.2 Hz), 7.60 (2 H, ddd, J = 8.3, 7.0, 1.3 Hz), 7.70-7.87 (4 H, m, Ar), 8.32-8.38 (2 H, m, Ar), 8.75-8.89 (4 H, m, Ar). Anal. calcd for $C_{28}H_{18}S_2$: C, 80.3; H, 4.3; S, 15.3. Found: C, 80.0; H, 4.4; S, 15.2%.

3,3'-Bis(*N*,*N*-dimethylthiocarbamoyloxy)-4,4'-biphenanthrene (6b). In a similar procedure as described for the preparation of **4b, 6b** was prepared from **6a**[13] (140 mg, 0.362 mmol), NaH (60% dispersion in mineral oil, 35.0 mg, 0.875 mmol) and *N*,*N*-dimethylthiocarbamoyl chloride (125 mg, 1.01 mmol) in DMF (3 mL). Crystallisation from toluene gave **6b** (162 mg, 80%) as tan coloured crystals, mp 252 °C; lit.[5] 242-3 °C. ^{1}H-NMR (300 MHz) δ 2.01 (6 H, s, 2 x N-CH_3), 2.81 (6 H, s, 2 x N-CH_3), 7.02 (2 H, t, J = 7.9 Hz, Ar), 7.43 (2 H, t, J = 7.9 Hz, Ar), 7.61 (2 H, d, J = 8.6 Hz, Ar), 7.79-7.88 (6 H, m, Ar), 8.01 (2 H, d, J = 8.6 Hz, Ar), 8.35 (2 H, d, J = 8.5 Hz, Ar). ^{13}C-NMR (100 MHz) δ 37.3, 42.4, 124.8, 126.3, 126.6, 126.8, 127.0, 127.1, 127.6, 128.2, 128.6, 130.7, 130.8, 131.3, 133.1, 149.4, 185.1 (C=S). Anal. calcd for $C_{34}H_{28}N_2O_2S_2$: C, 72.8; H, 5.0; N, 5.0; S, 11.4. Found: C, 72.6; H, 5.0; N, 5.2; S, 11.6%.

3,3'-Bis(*N*,*N*-dimethylcarbamoylthio)-4,4'-biphenanthrene (6c) and biphenanthro[4,3-*b*;3',4'-*d*]thiophene (6e). Crystalline **6b** (0.053 g, 0.094 mmol) contained in a Pyrex tube under a nitrogen atmosphere was immersed in a sulfolane bath which was refluxing at 270 °C for 20 min. After cooling to rt under nitrogen the reaction mixture was chromatographed on silica gel. Elution with dichloromethane afforded **6e** (0.005 g, 14%) as a yellow solid which was crystallised from toluene to give yellow crystals, mp 248-250 °C; lit.[5] 241°C. ^{1}H-NMR (300 MHz) δ 6.35 (2 H, t, J = 8.3 Hz, Ar), 7.09 (2 H, t, J = 7.9 Hz, Ar), 7.52 (2 H, d, J = 8.5 Hz, Ar), 7.65 (2 H, d, J = 7.9 Hz, Ar), 7.81 (2 H, d, J = 8.6 Hz, Ar), 7.95 (2 H, d, J = 8.6 Hz, Ar), 8.04 (2 H, d, J = 8.3 Hz, Ar), 8.15 (2H, d, J = 8.3 Hz, Ar). ^{13}C-NMR (100 MHz) δ 121.1, 123.6, 126.2, 126.3, 126.4, 126.7, 127.5, 128.5, 129.8, 130.1, 130.7, 131.1, 139.5. Anal. calcd for $C_{28}H_{16}S$: C, 87.5; H, 4.2; S, 8.3. Found: C, 87.8; H, 4.4; S, 8.3%.

Continued elution with 10% ether/dichloromethane gave **6c** (0.042 g, 0.071 mmol, 75%) as a colorless solid which crystallised from toluene, mp 248-249 °C; lit.[5] 243 °C. ^{1}H-NMR (200 MHz) δ 2.47 (12 H, broad s, 4 x N-CH_3), 6.91 (2 H, dt, J = 7.9, 1.50 Hz, Ar), 7.34 (2 H, dt, J = 7.9, 0.9 Hz, Ar), 7.80 (6 H, m, Ar), 7.89 (2 H, d, J = 8.7 Hz, Ar), 7.90 (2 H, d, J = 8.2 Hz, Ar), 8.05 (2 H, d, J = 8.3 Hz, Ar). ^{13}C-NMR (100 MHz) δ 36.6, 126.3, 126.4, 126.7, 127.4, 128.3, 128.7, 128.9, 129.2, 130.5, 130.9, 133.3, 133.8, 136.0, 144.3, 165.5 (C=O). Anal. calcd for $C_{34}H_{28}N_2O_2S_2$: C, 72.8; H, 5.0; N, 5.0; S, 11.4. Found: C, 72.6; H, 5.0; N, 5.0; S, 11.2%.

4,4'-Biphenanthrene-3,3'-dithiol (6d). In a similar procedure as described for the preparation of **4d**, **6d** was prepared from **6c** (0.468 g, 0.835 mmol) and $LiAlH_4$ (0.407 g, 10.7 mmol) in THF (30 mL). **6d** was obtained as a yellow solid (0.307 g, 88.0%), mp 191-2 °C; lit.[5] 196 °C. ^1H-NMR (200 MHz) δ 3.11 (2 H, s, 2 x SH), 6.91 (2 H, dt, J = 7.8, 1.6 Hz, Ar), 7.36 (2 H, t, J = 6.5 Hz, Ar), 7.68 (2 H, d, J = 8.3 Hz, Ar), 7.73-7.84 (6 H, m, Ar), 7.91 (4 H, t, J = 8.4 Hz, Ar). ^{13}C-NMR (100 MHz) δ 124.1, 125.4, 125.8, 126.5, 126.8, 127.6, 127.7, 128.8, 129.2, 130.1, 132.2, 133.3, 133.6, 136.8.

3,3'-Bis(trimethylsilyl)-1,1'-binaphtho-2,2'-dithiol (7). A solution of **1d** (1 g, 3.14 mmol), cyclohexane (20 mL) and TMEDA (20 mL) was added dropwise by syringe at 0 °C, to a solution of cyclohexane (10 mL), TMEDA (10 mL) and *n*-BuLi (50 mmol, 20 mL of a 2.5 *M* solution in hexanes) while stirring under argon. The resulting solution was stirred at rt for 24 h, cooled at 0 °C and treated with trimethylsilyl chloride (5.4 g, 50 mmol). After 12 h the reaction was quenched with water, made acidic with 10% HCl, extracted with diethyl ether (3 x 70 mL) and dried (Na_2SO_4). The residue was purified by flash chromatography to give **7** (1.04 g, 72%): mp 161-2 °C (EtOH). ^1H-NMR (300 MHz) δ 0.52 (18 H, s, $SiCH_3$), 3.39 (2 H, s, SH), 6.88 (2 H, d, J = 8.1 Hz, Ar), 7.24 (2 H, td, J = 8.1, 1.2 Hz, Ar), 7.41 (2 H, td, J = 8.1, 1.2 Hz, Ar), 7.88 (2 H, d, J = 8.1 Hz, Ar), 8.09 (2 H, s, Ar). Anal. calcd for $C_{26}H_{30}S_2Si_2$: C, 67.5; H, 6.5. Found: C, 67.3; H, 6.4%.

3,3'-Dimethyl-dibenzo[2,1-*d*;1',2'-*f*][1,3]dithiepine (8). A dichloromethane (15 mL) solution of **3d** (1.0 g, 4.06 mmol) and dimethoxymethane (0.4 g, 4.06 mmol) was treated with a dichloromethane (5 mL) solution of boron trifluoride diethyl etherate (0.2 mL) at rt while stirring and monitoring by TLC. After 12 h the crude reaction mixture was concentrated at reduced pressure and purified by flash chromatography on silica gel. Elution with 1:1 dichloromethane: light petrol gave **8** (1.0 g, 100%): mp 102-4 °C. ^1H-NMR (300 MHz) δ 2.40 (6 H, s, CH_3), 3.26 (2 H, s), 7.02 (2 H, d, J = 8.4 Hz), 7.13 (2 H, t, J = 8.4 Hz), 7.20 (2 H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz) δ 21.62, 43.4, 125.1, 127.8, 129.9, 132.1, 135.9, 139.3. Anal. calcd for $C_{15}H_{14}S_2$: C, 69.7; H, 5.5. Found: C, 69.4; H, 5.7%.

3,3'-Dimethylbinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (9). A dichloromethane (15 mL) solution of **4d** (0.8 g, 2.31 mmol) and dimethoxymethane (0.19 g, 2.31 mmol) was treated with a dichloromethane (5 mL) solution of boron trifluoride diethyl etherate (0.31 mL, 2.31 mmol) as for 3,3'-dimethyldibenzo[2,1-*d*:1',2'-*f*][1,3]dithiepine above. After 12 h the crude reaction mixture was concentrated at reduced pressure and purified by flash chromatography on silica gel. Elution with 1:1 dichloromethane : light petrol gave **9** (0.78 g, 95%) mp 240-1 °C (dichloromethane-light petrol); ^1H-NMR (300 MHz) δ 2.74 (6 H, s, CH_3), 4.20 (2 H, s), 6.98 (2 H, d, J = 7.8 Hz, Ar), 7.13 (2 H, td, J = 7.8, 1.2 Hz, Ar), 7.42 (2 H, td, J = 7.8, 1.2 Hz, Ar), 7.83 (2 H, d, J = 7.8 Hz, Ar), 7.89 (2 H, s, Ar). ^{13}C-NMR (100 MHz) δ 22.3, 46.8, 125.2, 125.4, 126.5, 126.7, 127.4, 128.6, 129.8, 130.8, 133.9, 138.0, 143.7. Anal. calcd for $C_{23}H_{18}S_2$: C, 77.0; H, 5.1. Found: C, 76.8; H, 5.2%.

3,3'-Bis(trimethylsilyl)binaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (10). This compound was prepared as for 3,3'-dimethylbinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (**9**) above starting from **7** (1 g, 21.6 mmol) in 95% yield. mp 188-9 °C (dichloromethane-diethyl ether): ^1H-NMR (300 MHz) δ 0.57 (18 H, s, $SiCH_3$), 4.22 (2 H, s), 6.86 (2 H, d, J = 8.7 Hz), 7.10 (2 H, td, J = 7.0, 1.5 Hz), 7.35 (2 H, td, J = 7.0, 1.5 Hz), 7.82 (2 H, d, J = 8.7 Hz), 8.06 (2 H, s). ^{13}C-NMR (100 MHz) δ 0.6, 49.0, 126.5, 126.7, 127.2, 128.4, 132.4, 132.7, 133.0, 134.1, 136.5, 142.1, 143.0. Anal. calcd for $C_{27}H_{30}S_2Si_2$: C, 68.3; H, 6.4. Found: C, 68.6; H, 6.3%.

Reaction of 3,3'-dimethyldibenzo[2,1-*d*:1',2'-*f*][1,3]dithiepine and 3,3'-dimethylbinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine with benzaldehyde. General procedure. A THF (10 mL) solution of 3,3'-dimethyldibenzo[2,1-*d*:1',2'-*f*][1,3]dithiepine (**8**) or 3,3'-dimethylbinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (**9**) (0.56 mmol) was cooled under argon at -78 °C and treated with *n*-BuLi (0.98 mL, 0.62 mmol of a 1.6 *M* solution in hexanes) while stirring. After 2 h the resulting pale yellow solution was treated with benzaldehyde (0.62 mmol) and gently warmed to rt during 3 h. The solution was treated with water (4 mL), extracted with diethyl ether (3 x 30 mL) and dried (Na_2SO_4).

2-(Hydroxyphenylmethyl)-3,3'-dimethyldibenzo[2,1-*d*:1',2'-*f*][1,3]dithiepine (11). (96% yield): mp 154-5 °C (dichloromethane-hexane). ^{1}H-NMR (300 MHz) δ 2.41 (3 H, s, CH_3), 2.70 (3 H, s, CH_3), 3.50 (1 H, bs, OH, exchange with D_2O), 4.43 (1 H, d, J = 9.3 Hz), 4.84 (1 H, d, J = 9.3 Hz), 7.18-7.46 (11 H, m, Ar). ^{13}C-NMR (100 MHz, 2 C atom omitted) δ 22.5, 29.7, 72.1, 75.6, 127.1, 127.1, 127.2, 127.7, 128.5, 128.7, 129.3 (2C), 129.7, 129.9, 130.1, 136.8, 142.3, 149.0. Anal. calcd for $C_{22}H_{20}OS_2$: C, 72.5; H, 5.5. Found: C, 72.6; H, 5.3%.

2-(Hydroxyphenylmethyl)-3,3'-dimethylbinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (12). (96% yield): mp 201-2 °C (dichloromethane-hexane): ^{1}H-NMR (300 MHz) δ 2.43 (3 H, s, CH_3), 2.78 (3 H, s, CH_3), 3.40 (1 H, bs, OH, exchange with D_2O), 4.22 (1 H, d, J = 10.5 Hz), 4.80 (1 H, d, J = 10.5 Hz), 6.92 (1 H, d, J = 8.4 Hz), 7.02 (1 H, d, J = 8.4 Hz), 7.13 (1 H, t, J = 7.6 Hz), 7.17 (1 H, t, J = 7.6 Hz), 7.29-7.36 (5 H, m), 7.42 (1 H, t, J = 7.6 Hz), 7.48 (1 H, t, J = 7.6 Hz), 7.82 (1 H, d, J = 8.4 Hz), 7.83 (1 H, s), 7.89 (1 H, d, J = 8.4 Hz), 7.95 (1 H, s). ^{13}C-NMR (100 MHz, 1 C atom omitted) δ 22.2, 23.0, 74.4, 75.5, 125.4, 125.6, 126.7, 127.0, 127.1, 127.4, 127.4, 127.4, 127.6, 128.4, 128.6, 128.7, 128.7, 131.0, 131.1, 133.9, 134.0, 135.8, 138.2, 138.6, 139.2, 143.2, 144.3. Anal. calcd for $C_{30}H_{24}OS_2$: C, 77.6; H, 5.2. Found: C, 77.7; H, 5.3%.

Acknowledgements. Mr. A. Canu (Department of Chemistry, University of Sassari) is thanked for microanalytical determinations. Mr. Neil Beare (University of Otago) is thanked for assistance with some of the reactions involving **5b**. This research has been assisted by grants and scholarships from the Research Committee of the University of Otago and from the New Zealand Universities Postgraduate Scholarships Committee. The work was also partially supported by CNR (Rome).

REFERENCES AND NOTES

Author to whom inquires concerning the X-ray structure analysis should be addressed.

§ The materials used in this study were all racemic. The stereochemistry reported in the drawings indicates that the molecule is chiral and does not represent its absolute configuration.

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(*Received in UK* 31 *December* 1996; *revised* 12 *March* 1997; *accepted* 13 *March* 1997)