Pergamon

Tetrahedron Vol. 51, No. 3, pp. 787-800, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00951-1

Synthesis and Structural Characterization of Dithiacyclophanes Derived From Biaryldithiols.

Upul K. Bandarage, Lyall R. Hanton and Robin A.J. Smith*

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

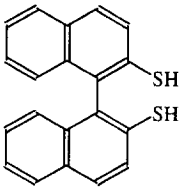
Abstract:. *The relative efficiencies of the reaction of dibromides with biphenyl-2,2'-dithiol and 1,1'-binaphthalene-2,2'-dithiol to produce dithiacyclophanes have been examined as a potential route to chiral biaryl dithiols. Reaction of the resolvable dibromide 2,2'-bis(bromomethyl)-1,1'-binaphthalene with 1,1'-binaphthalene-2,2'-dithiol gave a diastereoisomeric mixture of dithiacyclophanes. Reaction of 1,1´-binaphthalene-2,2´-bis(methylenethiol) with 2,2'-bis(bromomethyl)-1,1'-binaphthalene gave a mixture including dinaphtho[2,1-c:1´,2´-d]thiepin and the racemic diastereoisomer of 11,13,26,28-tetrahydrotetranaphtho[2,1-c:1´,2´-e:2´´,1´´-j:1´´´,2´´´-l][1,8]dithiacyclotetradecin.*

INTRODUCTION

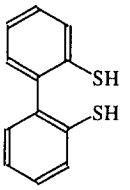
The chemistry of 2,2'-disubstituted-1,1'-binaphthalenes has been widely investigated in recent times. A significant driving force for this effort is the application of chiral binaphthalenes to enantioselective synthesis. The predominant heteroatom substituents used in this work have been O- or P-based and the field has been well reviewed recently[1]. In contrast, relatively few reports have appeared concerning S-substituted binaphthalenes although some notable results have been recorded[2]. In an extension of our previous work with dithiocarbocations[3] and anions[4] we have investigated the synthesis and properties of S-substituted binaphthalenes related to 1,1'-binaphthalene-2,2'-dithiol (**1**)[5]. As part of our research in this area we prepared some dithiacyclophane derivatives and this paper reports the results of this activity. Biaryl-fused thiacyclophanes are potentially chiral and are of interest for utilization as macrocyclic polydentate ligands[6], intermediates for the synthesis of chiral macrocyclic alkenes[7] , and also as a potential route to chiral biaryl dithiols *(vide infra)*.

Dithiacyclophanes are usually prepared by the reaction of a dithiol with a dihalide under basic conditions; incorporation of biaryl components in either or both reactant moieties is possible. The relative efficiency of the cyclization mode compared to undesired reactions such as linear polymerization are presumably determined by factors such as the relative orientation of the residual groups after the initial halide displacement by sulfur and also the strain energetics of the ring which is being created. In addition the choice of solvent and metal cation can influence the efficiency of these cyclization reactions[8]. The structural features of the reactants were

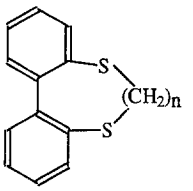
considered to be important to our research and were initially examined with the simple dithiol, biphenyl-2,2'-dithiol (**2**) and a series of dibromides. Subsequent reactions with 1,1'-binaphthalene-2,2'-dithiol (**1**) were then undertaken.



1



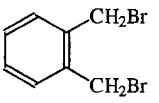
2



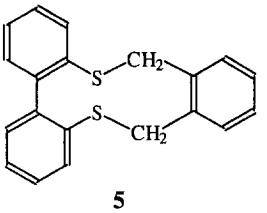
3 *(n=1 - 5)*

RESULTS AND DISCUSSION

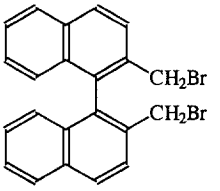
The reaction of **2** with a series of dihalides in basic ethanol solution has been reported previously[9]. The results recorded are in good agreement with similar reactions carried out in this study (Table 1) and are listed for comparison. From these data it is evident that insertion of a single carbon between the two sulfur functions in **2** to give **3**(n=1) is best achieved under acidic conditions and, for polymethylene dihalides, the efficiency of ring formation is increased with increasing ring size. Reaction of **2** with the necessarily *cisoid* bis benzyl halide **4** proceeded well to produce the dithiacyclophane **5** incorporating three benzene rings. However, reaction of **2** with the biaryl bis benzyl halide, 2,2'-bis(bromomethyl)-1,1'-binaphthalene (**6**)[10], gave no recognizable products resulting from dithiacyclophane formation. The reaction mixture consisted of intractable polymeric material and repetition of the reaction under high dilution conditions did not provide a more amenable product mixture. A relatively planar, *cisoid* conformation is required from the residues of both **2** and **6** for intramolecular cyclization to occur in preference to intermolecular reactions. It is evident from the result of the reaction of **2** with **4** that the biphenyl dithiol has little problem in this regard so the difficulty in obtaining high cyclization efficiencies is presumably related to **6**.



4



5



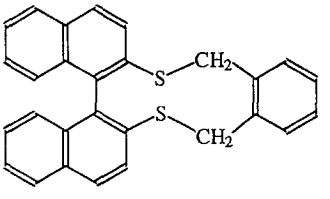
6

Table 1. Preparation of Dithiacyclophanes from Biphenyl-2,2´-dithiol (**2**)

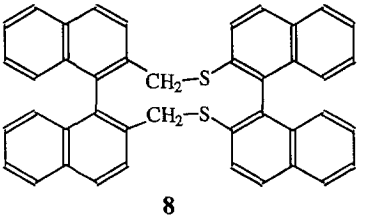
Reactant	*Dithiacyclophane*	*Yield (%)*[a]
dibromomethane	**3**(n=1)	0
diiodomomethane	**3**(n=1)	-- (39)
dimethoxymethane[b]	**3**(n=1)	71
1,2-dibromoethane	**3**(n=2)	34 (41)
1,3-dibromopropane	**3**(n=3)	-- (36)
1,4-dibromobutane	**3**(n=4)	64 (66)
1,5-dibromopentane	**3**(n=5)	-- (81)
4	**5**	67 (69)
6		0

[a]values in parentheses are from previous work[9] [b]using BF_3OEt_2/CH_2Cl_2

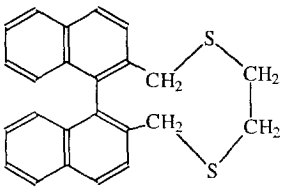
Having established some ideas of the scope and limitation of dithiacyclophane formation with **2** attention was then turned to the binaphthalene system by using **1**. Reaction of the demonstrably effective dibromide **4** with the disodium salt of **1** gave dithiacyclophane **7** in 72% yield. The ^1H NMR of **7** showed a four-proton AB system at δ 3.70 and 3.82 (J = 14.2 Hz) assigned to the methylene protons. The high symmetry of this compound was apparent by observing only thirteen aromatic carbon resonances in the ^{13}C NMR spectrum. In general we found little difference in the cyclization reactivity between **1** or **2** and simple aliphatic electrophiles[11] and this similarity of reactivity is retained in dithioacetalization reactions[12]. However, in contrast to the results with **2**, reaction of dibromide **6** and the disodium salt of **1** gave dithiacyclophane **8** in moderate (21%) yield together with polar, unidentified material. The ^{13}C NMR of **8** showed it to be a 1:4.3 mixture of two diastereoisomers. These diastereoisomers could not be separated, despite extensive chromatography. The ^1H NMR of **8** showed a four-proton AB pattern at δ 3.94 and 4.38 (J = 15.4 Hz) assigned to methylene protons of the major diastereoisomer. The yield and diastereoisomeric ratio of **8** was not altered by carrying out the reaction under high dilution conditions. Molecular mechanics calculations[13] on **8** showed the R*,R* diastereoisomer was favoured by *ca.* 7 kcal/mol although the structure of the major diastereoisomer could not be ascertained from the available data.



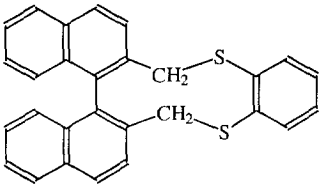
7



8



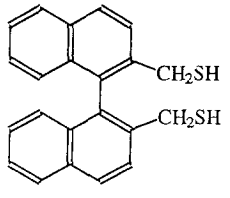
9



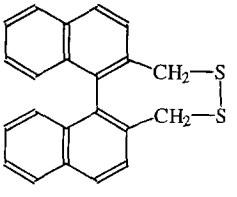
10

The reaction of **6** with **1** was of particular interest as **6** has been obtained in high enantiomeric purity[10,14]. The resolution of **1** has been achieved by other methodologies[15] but if this cyclization reaction could be carried out efficiently and with some level of selectivity then reaction with one enantiomer of **6** would produce two optically pure diastereoisomers of **8** which, after reductive elimination, lead to separate enantiomers of **1.** These considerations invited further investigation of the reactivity of dibromide **6** with simple dithiols. Reaction of the disodium salt of 1,2-ethanedithiol with **6** gave the dithiacylophane **9** in 70% yield. While reaction with the disodium salt of benzene-1,2-dithiol give a lower yield (57%) of dithiacyclophane **10**. The ^{1}H NMR of **9** showed aliphatic resonances as a four-proton mutiplet at δ 3.00 - 3.15 and a four-proton apparent singlet at δ 3.41. The ^{13}C NMR spectrum of **9** showed three sharp aliphatic resonances in an intensity ratio of 2:1:1. These spectra indicate that the preferred conformation of **9** is such that the ring methylene groups are nonequivalent. The determination of the preferred solution conformation for macroheterocycles is not a trivial problem and usually requires a combination of several techniques for satisfactory results[16]. In contrast to **9**, the ^{1}H NMR of **10** showed a four-proton AB pattern at δ 3.65 and 4.16 (J = 13.2 Hz), assigned to the benzylic methylene protons and a single aliphatic ^{13}C NMR resonance all of which is indicative of a symmetrical conformation. These results showed that the cyclization reactivity of **6** was not unusual and dithiacylophanes could be obtained satisfactorily with simple dithiols with the exception of biaryldithiols.

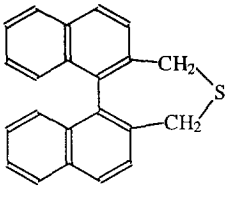
Incorporation of presumably more flexible alkylthiol functionality and retention of the desired biaryl structure was the impetus for cyclization studies with 1,1′-binaphthalene-2,2′-bis(methylenethiol) (**11**). The corresponding reactions in the biphenyl series had been reported previously[17] and while this work was in progress a paper describing extensions to binaphthalenes appeared[7]. Reaction of dibromide **6** with **11** gave a mixture containing at least four products which was partially separable by radial chromatography. The least polar compound product was identified as the disulfide **12**. This compound was inevitably obtained in minor amounts from various preparations of **11**. The ^{1}H NMR of **12** showed a four-proton AB pattern at δ 3.54 and 4.03 (J = 12.3 Hz), while the ^{13}C NMR showed only one aliphatic resonance and ten ^{13}C aromatic resonances.



11



12



13

This simple spectral display indicated the complete equivalence of the two naphthalene rings. The second nonpolar compound isolated was identified as the thiacyclophane **13**. The ^{1}H NMR of **13** showed four-proton broad singlet at δ 3.41 assigned to methylene protons while ^{13}C NMR showed one resonance in the aliphatic region and ten aromatic resonances. Elemental analysis of **13** gave an empirical formula of $C_{22}H_{16}S$ and the structure was confirmed by X-ray crystal diffraction analysis. The X-ray crystal structure of **13** (Figure 1) showed the expected *cisoid* arrangement around the C(4)-C(5) bond with an interplanar dihedral angle C(15)-C(5)-C(4)-C(16) of 66.1°. The torsion angles C(7)-S(1)-C(2)-C(3) and C(2)-S(1)-C(7)-C(6) were found to be 45.9° and 43.8°, respectively, indicating the C-S-C-C bonds adopt the expected gauche arrangement[18]. The solid-state structure (Supplementary material) consists of molecules held together in sheets in the (101) plane by a number of different interactions. There are close S···H contacts (2.919, 2.944 Å), edge-to-face π-π interactions and CH_2···arene interactions; close C···H contacts are in the range 2.67-3.10Å . Adjacent sheets are held together by edge-to-face π-π interactions only. Compound **13** was most probably formed during the reaction *via* the monoanion of **11** which can be conceived as undergoing an intramolecular nucleophilic substitution with the ejection of bisulfide ion. A recent paper has described an independent synthesis of **13** in high yields by treatment of **6** with sulfide anion[19] and a notable feature of this report was the resolution of **13** by chromatography on a chiral stationary phase.

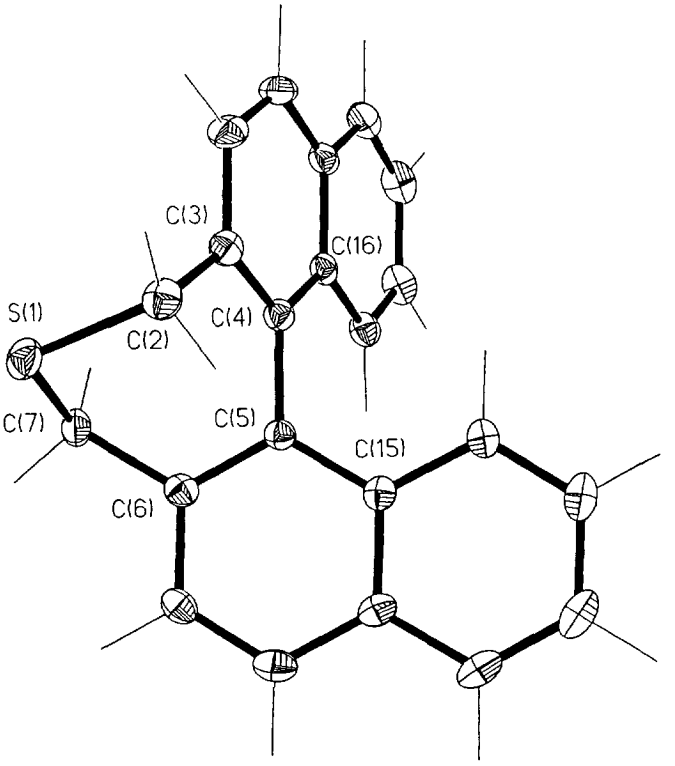
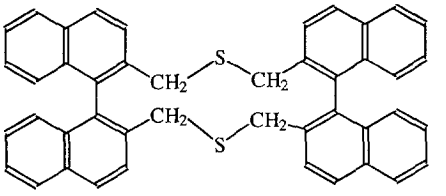


Figure 1. X-ray Crystal Structure of **13**

The major (41%) compound isolated from reaction *between* **6** and **11** was **14.** Elemental analysis of **14** gave an empirical formula of $C_{22}H_{16}S$ but on this basis and from the spectroscopic data it was not possible to assign the structure with certainty. The structure for **14** was unambiguously established by X-ray diffraction analysis which showed a [3,0,3,0]-*ortho*dithiacyclophane arrangement with the relative configuration of each binaphthalene unit as R^*,R^* (Figure 2). This arrangement of binaphthalene rings clearly indicated the racemic diastereoisomer. One binaphthalene ring in **14** showed a *cisoid* conformation with an interplanar dihedral angle C(22)-C(4)-C(5)-C(23) of 81.8°.



14

The other ring showed a *transoid* conformation with an interplanar dihedral angle C(38)-C(11)-C(12)-C(39) of 102.2°. In contrast to the *exo* arrangement of S atoms in most dithiacyclophanes[16,20], **14** has one S atom in an *endo* orientation while the other has an *exo* arrangement. Analysis of the crystal structure and CPK models of **14** shows S(1) adopts an *endo* arrangement apparently to minimize the interactions between the protons on C(7) and C(14). The torsion angles about the C-S-C-C bonds have pairs of values indicating approximate gauche and anti arrangements. The values for the gauche arrangements C(14)-S(1)-C(2)-C(3) and C(7)-S(8)-C(9)-C(10) were found to be -45.8° and 69.2°, respectively. While, the values for the anti C(2)-S(1)-C(14)-C(13) and C(9)-S(8)-C(7)-C(6) were 160.2° and -170.6° respectively. Each S atom has one carbon sulfur bond in a gauche arrangement and the other in an anti arrangement, regardless of whether the S atom is *exo* or *endo*.

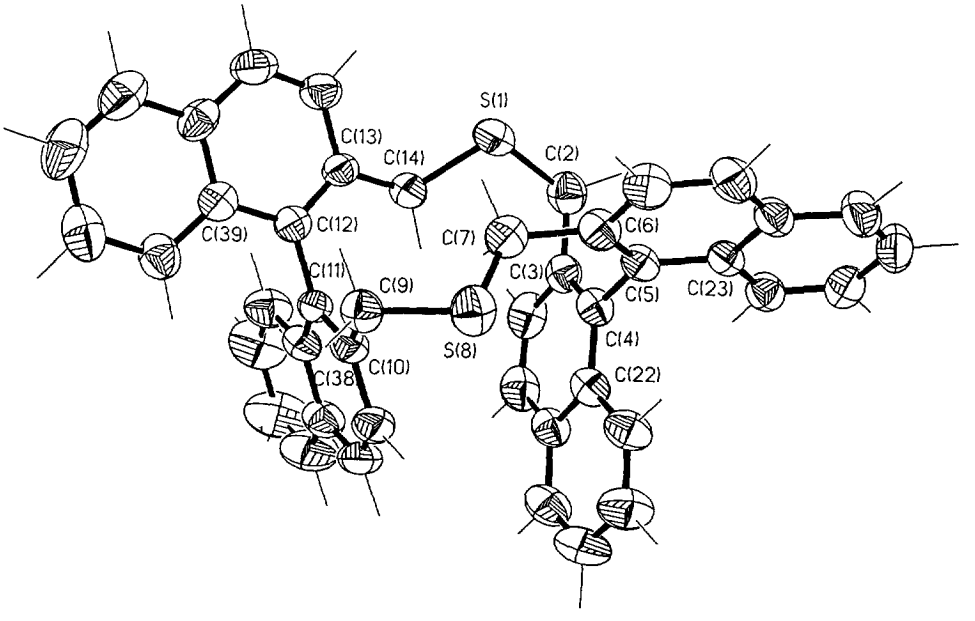


Figure 2. X-ray Crystal Structure of **14**

This is in contrast to most simple dithiacyclophanes[16,20] and crown thioethers[18] which display a strong preference for the gauche arrangement about C-S bonds, regardless of the disposition of the S atom. The unusual anti arrangement is probably necessitated by the short CH_2-S-CH_2 arrays that link the arene rings on different, twisted binaphthalene units. The nonplanar binaphthalene units require the linked arene rings to be approximately orthoganal to each other and hence anti arrangements about the C-S bonds are necessary to create the 14-membered ring. The S-C bond lengths in **14** are longer than in **13** or in other dithiacyclophanes[20]. This bond lengthening reflects the conformational strain present in **14**. The distance between the *exo* and *endo* S atoms is 5.04 Å. This distance is shorter than that found in simpler dithiacyclophanes where the S atoms are exclusively *exo* and distances are >5.3 Å[20]. CPK models indicate that only a small rearrangement of **14** is required to bring the *exo* S into an *endo* configuration. Thus, since only one S must alter its conformation, it is expected that **14** will bind readily to a variety of transition metal ions. The solid-state structure of **14** consists of chains of 'dovetailed' molecules held by edge-to-face π-π interactions (Supplementry material). Each binaphthalene unit has an edge and a face interaction with the binaphthalene on the adjacent molecule. Close intermolecular C···H contacts are in the range 2.94-3.07 Å. Sheets of molecules, in the (101) plane, are formed by close S···H interactions (2.807 Å) between neighbouring chains. The solid-state structure is completed by edge-to-face π-π interactions between adjacent sheets.

In contrast to the lack of symmetry evident in the solid state, the solution spectroscopic data for **14** indicated a more regular structural array. The ^{1}H NMR spectrum showed an eight-proton AB pattern at δ 3.01 and 3.45 (J = 12.6 Hz) assigned to the benzylic methylene protons while the ^{13}C NMR spectrum showed one aliphatic resonance together with ten aromatic resonances. At elevated temperatures (100°C) the ^{1}H NMR AB pattern for the benzylic methylene protons remained well resolved. This compound appears to be identical[21] with that isolated previously and assigned as racemic[7]. An impure sample of another, polar product from the reaction was obtained which gave a ^{1}H NMR spectrum displaying an AB pattern at δ 3.55 and 3.69 (J = 14.4 Hz) and a complex aromatic region. The relative intensities of these two spectral regions was 1:3. The ^{13}C NMR spectrum showed one aliphatic resonance together with ten aromatic resonances. The structure for this product can not be assigned with confidence however possible structures are the meso diastereoisomer of **14**[7] or alternatively a higher molecular weight product resulting from the incorporation of three or more binaphthalene units. In summary, the utilization of the biaryl bisbenzylthiol **11** did indeed create greater amounts of intermolecular cyclized products although a rather complex mixture was still evident.

CONCLUSION

From this work it seems that in some reactions there is little difference in reactivity between **1** and **2** towards cyclization. Given the considerable difference in the rotational energetics about the biaryl single bond in these two dithiols it appears therefore dithiacyclophane formation is not significantly influenced by restricted bond rotation. The efficiencies and diastereoselectivities observed in these reactions are encouraging but will require further study and refinement if they are to provide an attractive route to chiral biaryl dithiols. The use of biaryl moieties to pre-organize thiacyclophanes for metal complexation is being investigated.

EXPERIMENTAL

General experimental conditions have been described previously[5].

Dibenzo[d,f][1,3]dithiepin **3**(n=1)

A solution of dimethoxymethane (0.076 g, 1 mmol) in dry CH_2Cl_2 (4 cm^3) was added to a stirred solution of biphenyl-2,2′-dithiol (**2**)[22] (0.108 g, 0.5 mmol) and $BF_3.OEt_2$ (3 drops) in CH_2Cl_2 (20 cm^3) at room temperature under nitrogen. After stirring overnight at room temperature, the reaction mixture was poured into water (25 cm^3) and extracted with CH_2Cl_2 (3 x 10 cm^3). The combined extracts were washed with 10% NaOH (10 cm^3), water, then dried ($MgSO_4$) and filtered. Evaporation of the solvent *in vacuo* gave a crude product which was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **3**(n=1) (0.082 g, 71.4%), m.p. 96°C (Lit. 95 - 96°C)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.35 (s, 2H, CH_2); 7.34 - 7.41 (m, 4H, Ar); 7.47 -7.54 (m, 2H, Ar); 7.66 (d, J = 7.6 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 46.58 (CH_2), 128.69 (CH), 129.72 (CH), 129.98 (CH), 130.87 (C), 135.52 (CH), 147.39 (C). Anal: calcd. for $C_{13}H_{10}S_2$: C, 67.79; H, 4.38; S, 27.84. Found: C, 67.80; H, 4.34; S, 27.73%.

6,7-Dihydrodibenzo[e,g][1,4]dithiocin **3**(n=2)

A solution of 1,2-dibromoethane (0.075 g, 0.4 mmol) in alcohol (25 cm^3) was added slowly over 5 min to a stirred solution of biphenyl-2,2′-dithiol (**2**) (0.109 g, 0.5 mmol) in 10% NaOH (2 cm^3) and alcohol (10 cm^3) under nitrogen at room temperature. After stirring for one hour at room temperature the white suspension was dissolved in CH_2Cl_2 (50 cm^3). The CH_2Cl_2 layer was separated and washed with water, dried ($MgSO_4$) and filtered. Evaporation of solvent gave crude product which was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **3**(n=2) (0.033 g, 34%), m.p. 180°C (Lit. 179-180°C)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.92 - 3.28 (A_2B_2 m, 4H, CH_2); 7.26 -7.32 (m, 2H, Ar); 7.36 - 7.46 (m, 4H, Ar); 7.79 -7.86 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 38.44 (CH_2), 128.85 (CH), 128.91 (CH), 129.04 (CH), 134.26 (C), 136.77 (CH), 148.28 (C). Anal: calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95; S, 26.24. Found: C, 68.81; H, 4.94; S, 25.77%.

6,7,8,9-Tetrahydrodibenzo[b,d][1,6]dithiecin **3**(n=4)

This compound was prepared as for **3**(n=2) using 1,4-dibromobutane (0.086 g, 0.4 mmol) and biphenyl-2,2′-dithiol (**2**) (0.109 g, 0.5 mmol). The crude product was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **3**(n=4) (0.070 g, 64%), m.p. 144°C (Lit. 143-144°C)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.45 - 1.60 (m, 4H, CH_2); 2.29 (dis.t, J = 13.2 and 12.2 Hz, 2H, CH_2); 3.15 (d, J = 13.4 Hz, 2H, CH_2); 7.12 - 7.19 (m, 2H, Ar); 7.25 - 7.41 (m, 4H, Ar); 7.65 -7.71 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 22.79 (CH_2), 37.25 (SCH_2), 127.25 (CH), 128.44 (CH), 131.05 (CH), 132.17 (C), 135.25 (CH), 148.19 (C). Anal: calcd. for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92; S, 23.54. Found: C, 70.22; H, 6.19; S, 23.27%.

10,15-Dihydrotribenzo[b,d,h][1,6]dithiecin **5**

This compound was prepared as for **3**(n=2) using α,α′-dibromo-*o*-xylene (**4**) (0.106 g, 0.4 mmol) and biphenyl-2,2′-dithiol (**2**) (0.109 g, 0.5 mmol). The crude product was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **5** (0.086 g, 67%), m.p. 101°C (Lit. 102-103°C)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.58 and 3.74 (ABq, J = 14.3 Hz, 4H, CH_2); 7.00 - 7.06 (m, 2H, Ar); 7.17 - 7.33 (m, 8H, Ar); 7.54 - 7.59 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.84 (CH_2), 126.94 (CH), 128.05 (CH), 128.19 (CH), 130.17 (CH), 130.89 (CH), 133.40 (C), 136.32 (CH), 137.77 (C), 146.52 (C). Anal: calcd. for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03; S, 20.01.

Found: C, 75.20; H, 5.06; S, 20.00%.

4.9-Dihydrodinaphtho[2,1-b:1′,2′-d]benzo[h][1,6]dithiecin **7**

A solution of α,α′-dibromo-*o*-xylene (**4**) (0.109 g, 0.4 mmol) in alcohol (25 cm^3) was added slowly over 5 min to a stirred solution of 1,1′-binaphthalene-2,2′-dithiol (**1**) (0.159 g, 0.5 mmol) in 10% NaOH (3 cm^3) and absolute alcohol (10 cm^3) under nitrogen at room temperature. A white precipitate formed after the addition was complete. After stirring for 2 hr at room temperature t.l.c. showed some reactants were still present and the mixture was heated under reflux for 30 min then cooled to room temperature and the suspension was dissolved in CH_2Cl_2 (50 cm^3). The CH_2Cl_2 layer was separated and washed with water, dried ($MgSO_4$) and filtered. Evaporation of the solvents gave a crude product which was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **7** (0.125 g, 72%), m.p. 220°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.70 and 3.82 (ABq, J = 14.2 Hz, 4H, CH_2); 6.90 - 7.04 (m, 2H, Ar); 7.10 (d, J = 8.4 Hz, 2H, Ar); 7.15 - 7.23 (m, 4H, Ar); 7.36 - 7.43 (m, 2H, Ar); 7.67 (d, J = 8.7 Hz, 2H, Ar); 7.76 - 7.83 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.98 (CH_2), 126.37 (CH), 126.55 (CH), 126.78 (CH), 126.90 (CH), 128.00 (CH), 128.62 (CH), 130.24 (CH), 131.98 (C), 132.81 (CH), 133.13 (C), 133.36 (C), 138.25 (C), 142.71 (C). Anal: calcd. for $C_{28}H_{20}S_2$: C, 79.96; H, 4.79. Found: C, 79.92; H, 5.12%.

11,26-Dihydrodinaphtho[2,1-b:1′,2′-d:2″,1″-h:1‴,2‴-j] [1,6]dithiacyclododecin **8**

(a) This compound was prepared as for **7** using 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**)[10] (0.176 g, 0.4 mmol). The crude product was purified by p.l.c. (1:1, CH_2Cl_2/hexanes). Compound **8** was obtained as a inseparable diastereoisomeric mixture in 1:4.3 ratio (0.051 g, 21%), m.p. 305°C (with decomposition). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): major isomer 3.89 and 4.46 (ABq, J = 11.7 Hz); 6.78 - 7.45 (m, Ar); 7.64 - 8.05 (m, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 36.47 (CH_2, minor), 38.32 (CH_2, major). Anal: calcd. for $C_{42}H_{28}S_2$: C, 84.53; H, 4.73. Found: C, 84.33; H, 5.12%. In addition a complex mixture of polar material (0.1 g) was obtained which was not investigated further..

(b) A mixture of 1,1′-binaphthalene-2,2′-dithiol (**1**) (0.159 g, 0.5 mmol) and 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**) (0.176 g, 0.4 mmol) in dry benzene (50 cm^3) was added to a solution of 10% NaOH (10 cm^3) in ethanol (75 cm^3) using a metering pump over 2.5 hr at room temperature under nitrogen. After stirring overnight at room temperature, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 and purified by p.l.c. (1:1, CH_2Cl_2/hexanes) to give **8** (0.050 g, 21%) together with a mixture of polar material (0.095 g).

3,8-Dihydrodinaphtho[2,1-f:1′,2′-h][1,4]dithiecin **9**

This compound was prepared as for **7** using 1,2-ethanedithiol (0.047 g, 0.5 mmol) and 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**) (0.176 g, 0.4 mmol). The crude product was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **9** (0.105 g, 71%), m.p. 230°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.00 - 3.15 (m, 4H, CH_2); 3.41 (s, 4H, CH_2); 7.20 - 7.32 (m, 4H, Ar); 7.41 - 7.44 (m, 2H, Ar); 7.53 (d, J = 8.4 Hz, 2H, Ar); 7.92 (d, J = 8.4 Hz, 2H, Ar); 7.96 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 32.42 (2 x CH_2), 35.61 (CH_2), 41.87 (CH_2), 125.55 (CH), 126.15 (CH), 126.59 (CH), 126.89 (CH), 128.33 (CH), 129.41 (CH), 131.70 (C), 132.95 (C), 133.72 (C), 133.82 (C). Despite several attempts, satisfactory analytical data could not be obtained for this compound.

3,11-Dihydrobenzo[b]dinaphtho[2,1-f:1′,2′-h][1,6]dithiecin **10**

This compound was prepared compound as for **7** using 1,2-benzenedithiol (0.071 g, 0.5 mmol) and 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**) (0.176 g, 0.4 mmol). The crude product was purified by p.l.c. (3:7, CH_2Cl_2/hexanes) to give **10** (0.096 g, 57%), m.p. 174°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.65 and 4.16 (ABq, J = 13.2 Hz, 4H, CH_2); 6.96 (d, J = 8.4 Hz, 2H, Ar); 7.0 - 7.1 (m, 2H, Ar); 7.18 (t, J = 8.2 Hz, 2H, Ar); 7.37 (d, 2H, J = 7.2 Hz, Ar); 7.35 - 7.50 (m, 2H, Ar); 7.56 (d, J = 8.4 Hz, 2H, Ar); 7.8 - 7.9 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 40.48 (CH_2), 125.74 (CH), 125.88 (CH), 126.53 (CH), 127.50 (CH), 128.44 (CH), 128.26 (CH), 128.49 (CH), 132.65 (C), 132.90 (C), 136.62 (CH). Anal: calcd. for $C_{28}H_{20}S_2$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.88; H, 4.93; S, 15.40%.

1,1′-Binaphthalene-2,2′-bis(methylenethiol) **11**

A solution of 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**)[10] (1.70 g, 386 mmol) and thiourea (1 g, 13 mmol) in absolute alcohol (20 cm^3) was refluxed for 3 hr. The mixture was then cooled to room temperature and 10% KOH (40 cm^3) was slowly added. The mixture was then stirred at room temperature for 1 hr under nitrogen and the resulting suspension was washed with CH_2Cl_2(2 x 50 cm^3) and the CH_2Cl_2 extract was dried ($MgSO_4$), filtered and evaporated *in vacuo* to give crude product which was purified by silica gel column chromatography (1:1, CH_2Cl_2/H) to give pure **6** (1.06 g, 81%), m.p. 87-88°C (Lit. 97°C)[7]. ^{1}H nmr ($CDCl_3$, 300 MHz) δ (ppm): 1.60 - 3.53 (AXY[23], δ_A = 1.63, δ_X = 3.37, δ_Y = 3.48, J_{XY}= 13.4 Hz, J_{AX} = 8.8 Hz, J_{AY} = 7.0 Hz, 6H, CH_2, SH); 7.05 (d, J = 8.4 Hz, 2H, Ar); 7.18 (m, 2H, Ar); 7.39 (m, 2H, Ar); 7.68 (d, J = 8.7 Hz, 2H, Ar); 7.86 (d, J = 8.4 Hz, 2H, Ar); 7.95 (d, J = 8.7 Hz, 2H, Ar). ^{13}C nmr ($CDCl_3$, 75 MHz) δ (ppm): 27. 25 (CH_2), 125.99 (CH), 126.25 (CH), 126.65 (CH), 127.12 (CH), 128.12 (CH), 128.96 (CH), 132.66 (C), 133.0 (C), 137.47 (C). Anal: calcd. for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24; S, 18.50. Found: C, 76.40; H, 5.51; S, 18.20%.

Reaction of 2,2′-bis(bromomethyl)-1,1′-binaphthalene (**6**) *with 1,1′-binaphthalene-2,2′-bis(methylenethiol)* (**11**)

2,2′-Bis(bromomethyl)-1,1′-binaphthalene (**6**) (0.22 g, 0.5 mmol) in alcohol (10 cm^3)was added over 5 min to a stirred solution of 1,1′-binaphthalene-2,2′-bis(methylenethiol) (**11**) (0.22 g, 0.625 mmol) in absolute alcohol (10 cm^3) and 10% NaOH (2 cm^3). After stirring an additional hour at room temperature, the resulting white suspension was dissolved in CH_2Cl_2 (50 cm^3). The CH_2Cl_2 layer was then separated and washed with water, dried ($MgSO_4$), filtered. Evaporation of the solvent *in vacuo* gave crude product (0.3 g) whose t.l.c. (3:7, CH_2Cl_2/hexanes) showed the presence of at least four compounds R_f 0.5, 0.44, 0.36, 0.31. Partial separation was achieved by radial chromatography on a Chromatotron. Elution with hexanes gave dinaphtho[2,1-d:1′,2′-f][1,2]dithiocin (**12**) (0.036 g, 17% based on **11**), m.p. 175°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.54 and 4.03 (ABq, J = 12.3 Hz, 4H, CH_2); 7.03 (d, J = 8.1 Hz, 2H, Ar); 7.19 - 7.24 (m, 2H, Ar); 7.41 - 7.46 (m, 4H, Ar); 7.92 (d, J = 8.4 Hz, 2H, Ar); 7.97 (d, J = 8.7 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 41.42 (CH_2), 125.91 (CH), 126.48 (CH), 126.76 (CH), 128.13 (CH), 128.55 (CH), 129.12 (CH), 132.59 (C), 133.07 (C), 134.50 (C), 136.10 (C). Anal: calcd. for $C_{22}H_{16}S_2$: C, 76.71; H, 4.68; S, 18.61. Found: C, 77.02; H, 4.71; S, 18.40%. Elution with 1:9, CH_2Cl_2/hexanes gave dinaphtho[2,1-c:1′,2′-d]thiepin (**13**) (0.102 g, 52% based on **11**), m.p. 233°C (Lit 216-218°C)[19]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.41 (bs, 4H, CH_2); 7.21 - 7.30 (m, 4H, Ar); 7.42 - 7.47 (m, 2H, Ar); 7.53 (d, J = 8.4 Hz, 2H, Ar); 7.92 (d, J = 8.1 Hz, 2H, Ar); 7.96 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 32.41 (CH_2), 125.55 (CH), 126.15 (CH), 126.59 (CH), 126.89 (CH), 128.33 (CH), 129.41 (CH), 131.70 (C), 132.95 (C), 133.71 (C), 133.83 (C). Anal: calcd. for $C_{22}H_{16}S$: C, 84.58; H, 5.16; S, 10.26. Found: C, 84.75; H, 5.21; S, 9.97%. Elution with 1:4, CH_2Cl_2/hexanes

gave an impure sample of an unidentified compound (0.009 g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.55 and 3.69 (ABq, J = 14.4 Hz, 8H, CH_2); 6.78 (d, J = 8.1 Hz, 4H, Ar); 7.10 - 7.15 (m, 4H, Ar); 7.32 - 7.37 (m, 4H, Ar); 7.84 (d, J = 8.4 Hz, 4H, Ar); 7.44 (d, J = 8.7 Hz, 4H, Ar), 8.13 (d, J = 8.7 Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.02 (CH_2), 125.60 (CH), 125.61 (CH), 126.53 (CH), 126.99 (CH), 128.13 (2 x CH), 132.68 (C), 132.78 (C), 132.68 (C), 134.35 (C). Further elution with 1:4, CH_2Cl_2/hexanes gave *racemic* 11,13,26,28-tetrahydrotetranaphtho[2,1-c:1′,2′-e:2″,1″-j:1‴,2‴-l][1,8]dithiacyclotetradecin (**14**) (0.12 g, 41 % based on **6**), m.p. 252-254°C (Lit 264°C)[7]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.01 and 3.45 (ABq, J = 12.6 Hz, 8H, CH_2); 6.96 (d, J = 8.7 Hz, 4H, Ar); 7.16 (d, J = 8.1 Hz, 4H, Ar); 7.20 (t, J = 7.8 Hz, 4H, Ar); 7.44 (t, J = 7.8 Hz, 4H, Ar); 7.47 (d, J = 8.4 Hz, 4H, Ar); 7.84 (d, J = 7.8 Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 35.00 (CH_2), 125.59 (CH), 126.09 (CH), 126.29 (CH), 127.31 (CH), 127.87 (CH), 128.10 (CH), 132.54 (C), 132.67 (C), 133.92 (C), 134.26 (C). Anal: calcd. for $C_{44}H_{32}S_2$: C, 84.58; H, 5.16. Found: C, 84.11; H, 5.06%.

Crystallographic Data for **13**

Crystal Data - $C_{22}H_{16}S$, M = 312.44 g mol^{-1}, monoclinic, space group: $P2_1/n$ (No 14)[24], a = 8.334(4) Å, b = 19.064(9) Å, c = 9.773(5) Å, β = 95.20(4)°, V = 1546(1) Å^3, D_C = 1.34 g cm^{-3}, Z = 4, μ(Mo-Kα) = 2.05 cm^{-1}, crystal size: 0.7 x 1.1 x 0.2 mm. *Data Collection* - Scan speed: 15 deg min^{-1}, 4444 data collected, unique data 2905 with I > 2.5σI considered observed. Crystals of **13** were obtained by slow evaporation of a CH_2Cl_2/hexanes solution and a colourless rhomb was selected and used for data collection The unit-cell dimensions and orientation matrices were calculated from 25 accurately centred reflections on a Nicolet P3 diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Data were collected in ω-2θ scan mode, in the range 4 < 2θ < 60°. The intensities of 3 standard reflections, (6 0 0) (0 10 0) (0 0 4) measured after every 100 reflections, showed crystal decay of < 3%. Lorentz and polarisation corrections were applied together with empirical absorption corrections [transmission - 0.758 (maximum), 0.726 (minimum)] using programs from the SHELXTL package[25]. The structure was solved using the TREF option of the program SHELXS-86[26] with the E-map revealing the coordinates of all non-hydrogen atoms. The structure was refined by full matrix least-squares[27] with all non-hydrogen atoms anisotropic. Hydrogen atoms were placed in idealized positions, with fixed isotropic temperature factors, and constrained to ride 1.08 Å from the appropriate carbon atom. All non-hydrogen atoms were assigned anisotropic temperature factors and the model refined to convergence with R = 0.0537, R_w = 0.0574. The weighting scheme w = [1.209/(σ^2F + 0.001669F^2)] was used. The final difference Fourier map was essentially flat with the highest peak corresponding to 0.40, -0.34e Å^{-3}. *Structure Refinement* - Number of variables = 208, R($\Sigma\Delta F/\Sigma|F_o|$) = 0.0537, Rw[$\Sigma w^{½}(\Delta F)/\Sigma w^{½}F_o$] = 0.0574. A diagram of the final structure is given as Figure 1.

Selected Bond Lengths (Å) and Angles (°) :

S(1)---C(2)	1.828(3)	S(1)---C(7)	1.821(2)	C(6)---C(7)	1.504(3)
C(2)---C(3)	1.504(3)	C(3)---C(4)	1.386(3)	C(5)---C(6)	1.385(3)
C(4)---C(5)	1.491(3)				
C(2)-S(1)-C(7)	99.5(1)	S(1)-C(2)-C(3)	112.3(2)		
C(2)-C(3)-C(4)	120.0(2)	C(3)-C(4)-C(5)	118.6(2)		
C(4)-C(5)-C(6)	119.3(2)	C(5)-C(6)-C(7)	119.3(2)		
S(1)-C(7)-C(6)	113.0(2)				

Crystallographic Data for **14**

Crystal Data - $C_{44}H_{32}S_2$, M = 624.82 g mol^{-1}, monoclinic, space group: $P2_1/c$ (No 14)[24], a = 13.26(1) Å, b = 10.47(1)Å, c = 25.02(3) Å, β = 104.14(9)°, V = 3367(6) Å^3, D_C = 1.23 g cm^{-3}, Z = 4, μ(Mo-Kα) = 1.88 cm^{-1}, crystal size: 0.8 x 0.9 x 0.2 mm. *Data Collection* - Scan speed: 4.88 deg min^{-1}, 6450 data collected, unique data 3325 with I > 2.5σI considered observed. Crystals of **14** were obtained by slow evaporation of a CH_2Cl_2/hexanes solution and a colourless rhomb was selected and used for data collection The unit-cell dimensions and orientation matrices were calculated from 25 accurately centred reflections on a Nicolet P3 diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Data were collected in ω-2θ scan mode, in the range 4 < 2θ < 52°. The intensities of 2 standard reflections, (0 6 0) (0 0 8) measured after every 100 reflections, showed crystal decay of < 3%. Lorentz and polarisation corrections were applied together with empirical absorption corrections [transmission - 0.778 (maximum), 0.760 (minimum)] using programs from the SHELXTL package[25]. The structure was solved using the TREF option of the program SHELXS-86[26] with the E-map revealing the coordinates of all non-hydrogen atoms. The structure was refined by full matrix least-squares[27] with all non-hydrogen atoms anisotropic. Hydrogen atoms were placed in idealized positions, with fixed isotropic temperature factors, and constrained to ride 1.08 Å from the appropriate carbon atom. All non-hydrogen atoms were assigned anisotropic temperature factors and the model refined to convergence with R = 0.0587, R_w = 0.0555. The weighting scheme w = [2.185/(σ^2F + 0.000329F^2)] was used. The final difference Fourier map was essentially flat with the highest peak corresponding to 0.32, -0.30 e Å^{-3}. *Structure Refinement* - Number of variables = 415, R($\sum\Delta F/\sum|F_o|$) = 0.0587, Rw[$\sum w^{½}(\Delta F)/\sum w^{½}F_o$] = 0.0555. A diagram of the final structure is given as Figure 2.

Selected Bond Lengths (Å) and Angles (°) :

S(1)---C(2)	1.857(4)	S(1)---C(14)	1.844(4)	C(5)---C(6)	1.401(5)
C(6)---C(7)	1.552(5)	C(9)---C(10)	1.522(5)	C(4)---C(5)	1.519(5)
S(8)---C(7)	1.812(4)	S(8)---C(9)	1.866(4)	C(3)---C(4)	1.381(5)
C(2)---C(3)	1.512(5)	C(10)---C(11)	1.383(5)	C(11)---C(12)	1.498(5)
C(12)---C(13)	1.394(5)	C(13)---C(14)	1.552(5)		

C(2)-S(1)-C(14)	103.9(2)	C(7)-S(8)-C(9)	97.3(2)
S(1)-C(2)-C(3)	114.3(3)	C(2)-C(3)-C(4)	123.0(4)
C(3)-C(4)-C(5)	122.8(4)	C(4)-C(5)-C(6)	119.6(4)
C(5)-C(6)-C(7)	122.8(4)	S(8)-C(7)-C(6)	112.9(3)
S(8)-C(9)-C(10)	113.7(3)	C(9)-C(10) -C(11)	123.5(4)
C(10)-C(11) -C(12)	121.1(3)	C(11)-C(12) -C(13)	119.4(4)
C(12)-C(13) -C(14)	123.3(3)	S(1)-C(14) -C(13)	112.9(3)

Acknowledgements. This research has been assisted by grants from the Research Committees of the University of Otago and the New Zealand Universities Grants Committee. The authors thank Professor H.J. Bestmann for providing information prior to publication and Professor W.T. Robinson, University of Canterbury, for data collection.

REFERENCES and NOTES

1. Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503-517.
2. e.g. De Lucchi, O. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *74*, 195-213. De Lucchi, O.; Fabbri, D.; Cossu, S.; Valle, G. *J. Org. Chem.* **1991**, *56*, 1888-1894. Delogu, G.; De Lucchi, O.; Maglioli, P.; Valle, G. *J. Org. Chem.* **1991**, *56*, 4467-4473. De Lucchi, O.; Fabbri, D.; Lucchini, V. *Synlett* **1991**, 565-568. De Lucchi, O.; Fabbri, D.; Lucchini, V. *Tetrahedron* **1992**, *48*, 1485-1496.
3. Gamage, S.A.; Smith, R.A.J. *Tetrahedron* **1990**, *46*, 2111-2128. Gamage, S.A.; Smith, R.A.J. *Australian Journal of Chemistry* **1990**, *43*, 815-824. Abdul-Rahman, B.M.; Smith, R.A.J. *Tetrahedron* **1987**, *43*, 1847-1856. Smith, R.A.J.; Abdul-Rahman, B.M. *Synthesis* **1984**, 166-168.
4. Smith, R.A.J.; Lal, A.R. *Australian Journal of Chemistry* **1979**, *32*, 353-360. Smith, R.A.J.; Abdul-Rahman, B.M. *J. Chem. Soc. Chem. Commun.* **1975**, 216-217.
5. Bandarage, U.K.; Simpson, J.; Smith, R.A.J.; Weavers, R.T. *Tetrahedron* **1994**, *50*, 3463-3472.
6. Hanton, L.R.; Kemmitt, T. *J. Chem. Soc. Chem. Commun.* **1991**, 700-702.
7. Bestmann, H.J.; Schaper, W.; Holzmann, H.G.; Zimmermann, R. *Chem. Ber.* **1991**, *124*, 2773-2779.
8. *e.g.* Buter, J.; Kellog, R.M.; van Bolhuis, F. *J. Chem. Soc. Chem. Commun.* **1990**, 282-284.
9. Allen,D.W.; Braunton, P.N.; Miller, I.T.; Tebby, J.C. *J. Chem. Soc. (C)* **1971**, 3454-3466.
10. Bestmann, H.J.; Both, W. *Chem Ber.* **1974**, *107*, 2926-2930. Jung, M.E.; Hogan, K.E. *Tetrahedron Letters* **1988**, *29*, 6199-6202.
11. An exception to this may be the comparative reactivity of **1** and **2** with 1,3-dibromopropane: *c.f.* Dore, A.; Cossu, S.; De Lucchi, O. *Tetrahedron Letters* **1991**, *36*, 4771-4774.
12. Bandarage, U.K. *An Investigation of the Chemistry of Biaryl Dithiols*, PhD thesis, University of Otago 1992.
13. PC-MODEL-Pi version 3.2 available from Serena Software, Box 3076, Bloomington, Indiana, USA.
14. Hall, D.; Turner, E.E. *J. Chem. Soc.* **1955**, 1242-1251. Maigrot, N.; Mazaleyrat, J.P. *Synthesis* **1985**, 317-320. Colletti, S.; Halterman, R.L. *Tetrahedron Letters* **1989**, *27*, 3513-3516.
15. Di Furia, F.; Furlani, M.; Licini, G.; Modena, G. *Phosphorus, Sulfur, Silicon Relat. Elem.*, **1993**, *74*, 399-400. Fabbri, D.; Delogu, G.; De Lucchi, O. J. *Org. Chem.* **1993**, *58*, 1748-1750. Di Furia, F.; Licini, G.; Modena, G.; Valle, G. *Bull. Soc. Chim. Fr.* **1990**, 734-744. Di Furia, F.; Licini, G.; Modena, G.; De Lucchi, O. *Tetrahedron Letters* **1989**, *30*, 2575-2576.
16. e.g. Bodwell,G.J.; Ernst, L.; Hopf, H.; Jones, P.G., McNally, J.P.; Schomburg, D. *Chem. Ber.* **1990**, *123*, 2381-2386. Okajima, T.; Wang, Z.-H.; Fukazawa, Y. *Chem. Letters* **1991**, 37-40.
17. Bestmann, H.J.; Schaper, W. *Tetrahedron Letters* **1975**, 3511-3512. Bangiu, M.; Pogany, I.; Mosora, D.; Rusu, P.; Stängiulescu, R.; Dezsö, M. *Rev. Roum. de Chim.* **1985**, *30*, 703-712.
18. Wolf, Jr., R.E.; Hartman, J.R.; Storey, J.M.E.; Foxman, B.M.; Cooper. S.R. *J. Am. Chem. Soc.* **1987**, *109*, 4328-4335. Desper, J.M.; Gellman, S.H.; Wolf, Jr., R.E.; Cooper. S.R. *J. Am. Chem. Soc.* **1991**, *113*, 8663-8671. Desper, J.M.; Vyvyan, J.R.; Mayer, M.J.; Ochrymowycz, L.A.; Gellman, S.H. *Inorg. Chem.* **1993**, *32*, 381-382.
19. Stará, I.G.; Starý, I.; Tichý, M.; Závada, J.; Fiedler, P. *J. Org. Chem.* **1994**, *59*, 1326-1332.

20. Okajima, T.; Wang, Z.-H.; Fukazawa, Y. *Tetrahedron Lett.* **1989**, *30*, 1551; Edema, J.J.H.; Thijs Stock, H.; Buter, J.; Kellogg, R.M.; Smeets, W.J.J.; Speak, A.L. *Tetrahedron* **1993**, *49*, 4355. Mitchell, R.H.; Anker, W.; Bushnell, G.W. *Can. J. Chem.*, **1979**, *57*, 3080. Chan, T.L.; Poon, C.D.; Mak, T.C.W. *Acta Crystallogr., Sect. C.*, **1986**, *42*, 897. Hanton, L.R.; Sikanyika, H. *J. Chem. Soc. Perkin Trans. 1* **1994** *in the press.*
21. Bestmann, H.J. *private communication.*
22. Sorrell, T.N.; Cheesman, E.H. *Synth. Commun.* **1981**, *11*, 909-912.
23. Garbisch, E.W. *J. Chem. Ed.* **1968**, *45*, 402-416.
24. Ibers, J.A.; Hamilton, W.C. eds: *International Tables for X-ray Crystallography* Vol 1; Kynoch Press: Birmingham, England 1966.
25. Sheldrick, G.M. SHELXTL: *An integrated system for solving, refining and displaying crystal structures from diffraction data.* University of Göttingen 1981.
26. Sheldrick, G.M. SHELXS-86: *A program for the solution of crystal structures from diffraction data.* University of Göttingen 1986.
27. Sheldrick, G.M. SHELX-76: *Program for crystal structure determination.* University of Cambridge 1976.

(*Received in UK* 25 *August* 1994; *revised* 21 *October* 1994; *accepted* 28 *October* 1994)