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Conformational Polymorphism and Thermorearrangement of 2,2'-Bis-O-(N,N-dimethylthiocarbamato)-1,1'-binaphthalene. A Facile Synthesis of 1,1'-Binaphthalene-2,2'-dithiol.

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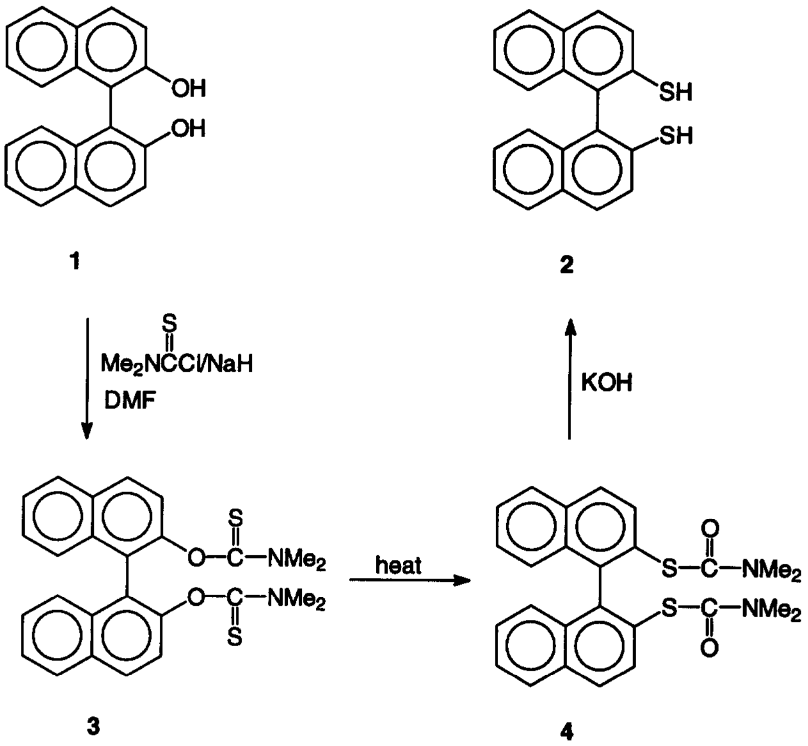
Abstract:. *The title compound was found to exhibit conformational polymorphism which greatly influenced the efficiency of the thermorearrangement to 2,2'-bis-S-(N,N-dimethylthiocarbamato)-1,1'-binaphthalene. Recognition of this phenomenon has allowed a reproducible synthesis of 1,1'-binaphthalene-2,2'-dithiol.*

INTRODUCTION

The field of binaphthalene chemistry has developed into a large and diversified discipline in recent years and the binaphthalene moiety has been involved in many successful synthetic procedures especially involving chiral compounds[1]. Much activity in this field has been based on 1,1'-binaphthalene-2,2'-diol (**1**) which is readily available in enantiomerically pure form[2,3]. Although the chemistry of sulfur containing binaphthalene compounds has been investigated by only a relatively small number of researchers some notable results have been recorded[4]. In an extension of our previous work with dithiocarbocations[5] and anions[6] we had need for significant amounts of 1,1'-binaphthalene-2,2'-dithiol (**2**) and related compounds. This paper reports some observation on the synthesis of **2** and the conformational polymorphism of an intermediate compound. The synthesis of **2** has been described by several authors[7,8] and the most attractive of the various synthetic routes involves Newman-Kwart thermorearrangement of the dimethylthiocarbamoyl ester **3** into **4** as a key step (Scheme). The substrate **3** which is required for this reaction can be readily derived from **1** (Scheme). Several reports on the conversion of **3** to **4** have appeared. Cram and coworkers[8] obtained **4** in 40% yield without comment, but De Lucchi *et.al.*[9] obtained **4** in variable (0-70%) yields[10]. Our initial experience with this reaction under a variety of conditions supported the latter observation and hence invited a more thorough examination.

RESULTS AND DISCUSSION

The substrate **3** was obtained from **1** as an analytically pure, white powder. Thermolysis of samples of **3** either neat or in solution at various temperatures gave no significant amounts of **4** (Table 1, entries 1-3). The only product that could be isolated from these reactions in a pure form was shown to be 1,1'-binaphthothiophene (**5**)* which had previously been identified from this reaction[9] and utilized to some profit[12]. The remaining material from these reactions proved to be an inseparable mixture of compounds which was unreactive towards further thermolysis. Elemental analysis of this residual mixture showed a N/S ratio of 2:1 consistent with the removal of one sulfur from the binaphthalene framework. In addition, ^1H and ^{13}C NMR spectra of the mixture indicated similar functionality to that in both **3** and **4**. Alkaline hydrolysis of the mixture gave 1,1'-binaphthalene-2-ol-2'-thiol (**6**) in *ca* 50% mass recovery whose ^1H NMR spectrum showed two exchangeable one-proton singlets at δ3.34 and 4.89 assigned to the SH and OH groups respectively, together with aromatic hydrogen resonances. Compound **6** was characterized by methylation to **7**. The ^{1}H NMR spectrum of **7** showed two three-proton singlets at δ 2.38 and 3.78, assigned to the SMe and OMe groups respectively. Apart from **5**, definite structural assignments could not be made for the remainder of the material formed during these thermolyses.



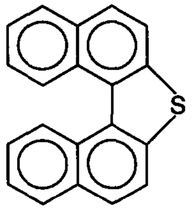
Scheme

Table 1. Thermolysis of 2,2'-Bis-O-(N,N-dimethylthiocarbamato)-1,1'-binaphthalene (**3**).

entry	Method	Temperature/°C	Products(%)[a] 3	4	5	6[b]
1	[c]neat, 40 min	285	-	-	30	55
2	[c]neat, 40 min	310	-	-	40	50
3	[c]glycerol solution	280	-	-	30	45
4	[c]gas phase ex toluene solution 0.36 cm^3 min^{-1}	400	-	50	36	-
5	[c]gas phase ex toluene solution 0.60 cm^3 min^{-1}	400	10-15	35	20	-
6	[d]neat, 40 min	285	-	70-75	20	-

[a] all products were isolated by flash chromatography.
[b] isolated following KOH treatment of the crude reaction mixture.
[c] powder.
[d] crystals.

Successful thermal rearrangements of 2-naphthyl[13] and 2'-methoxy-2-(1,1'-binaphthalene)[14] N,N-dimethylthiocarbamates have been achieved. These results indicated that the naphthalene moiety itself seemed unlikely to be the cause of the difficulties observed in the reaction with **3**. Intramolecular reaction between the two thiocarbamate groups in **3** can obviously occur, and clearly this must be involved in the formation of **5**. Any interaction of this type must require conformations such that the pendant groups are close together in space. These arrangements would be determined by the relative conformations of the thiocarbamoyl units and also the rotational energetics of the biaryl single bond. A model for some of these conformational effects is the biphenyl analogue **8**[15], which was found to undergo facile thermorearrangement. Thus it became apparent that thermolysis of **3** presented some unique difficulties[16].



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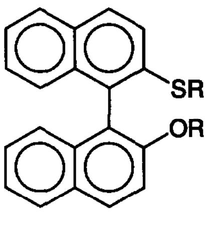
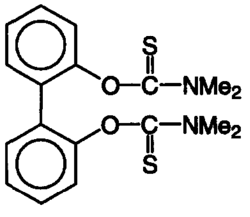


6 R = H

7 R = Me



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Therefore the reaction was examined using an inert gas flow system at 400°C with the reactant at low concentration. This protocol is similar to the original Kwart method[17]. The rationale of this approach was to expose the diluted reactant to relatively high temperatures for a short time to promote independent, intramolecular rearrangement of the thiocarbamoyl groups. It was gratifying to find that these experiments gave some of the desired material **4** together with lesser amounts of **5** (Table 1, entry 4). In contrast to the earlier results from condensed phase reactions, unsymmetrically substituted materials convertible into **6** were not formed to any appreciable extent. Increasing the flow rate of **3** through the pyrolysis tube gave some unreacted **3** and lesser amounts of **4** (Table 1, entry 5). A further restriction was the observation that the effectiveness of the gas phase thermolysis decreased with usage of the apparatus and increasingly larger amounts of **5** were obtained. This trend could be reduced by thoroughly cleaning the apparatus and replacing the quartz column packing.

The formation of the thiophene byproduct **5** can be rationalized by evoking an intramolecular displacement reaction similar to that described for the Newman-Kwart rearrangement[18]. Thiophene ring formation is possible after rearrangement of both thiocarbamate units or subsequent to the rearrangement of only one pendant group. An attempt to differentiate these mechanistic possibilities was made by heating purified **4** to 280°C for 40 min. Some (10-15%) of **5** was produced and, as a consequence of this observation, prolonged heating of the rearrangement reaction mixture after all the reactant had been consumed was avoided.

The most efficient gas phase protocol for the conversion of **3** into **4** involved carefully maintaining **3** in an inert environment at the required thermolysis temperature. This implied that "thermal pretreatment" of **3** may be a factor in the success or otherwise of this reaction. Relatively low temperature thermal treatment was effected by successive crystallizations of the powder form of **3** from hot toluene and this process produced a shiny crystalline solid. This material showed identical IR and NMR spectral data, melting point and elemental analysis to the original powder. Condensed phase thermolysis of this crystalline form of **3** gave a pale brown glassy oil which solidified at room temperature. After chromatography, significant amounts of **4** were obtained together with some **5**. Thermolysis of mixtures of powder and crystalline **3** gave variable, generally low yields of **4**. Eventually it was found (Table 1, entry 6) that the optimal yield of **4** could be *reproducibly* obtained by the thermolysis of crystalline **3** at 285°C for 40 min under nitrogen on a multigram scale.

The observed differences in properties between the two solid forms of **3** with respect to chemical reactivity was also apparent in X-ray powder diffraction patterns (Figure 1). An X-ray crystal structure of crystalline **3** was obtained in order to confirm the molecular structure and also to examine the solid state conformation. A general view of **3** is given in Figure 2 and, as expected, shows that the two naphthalene rings

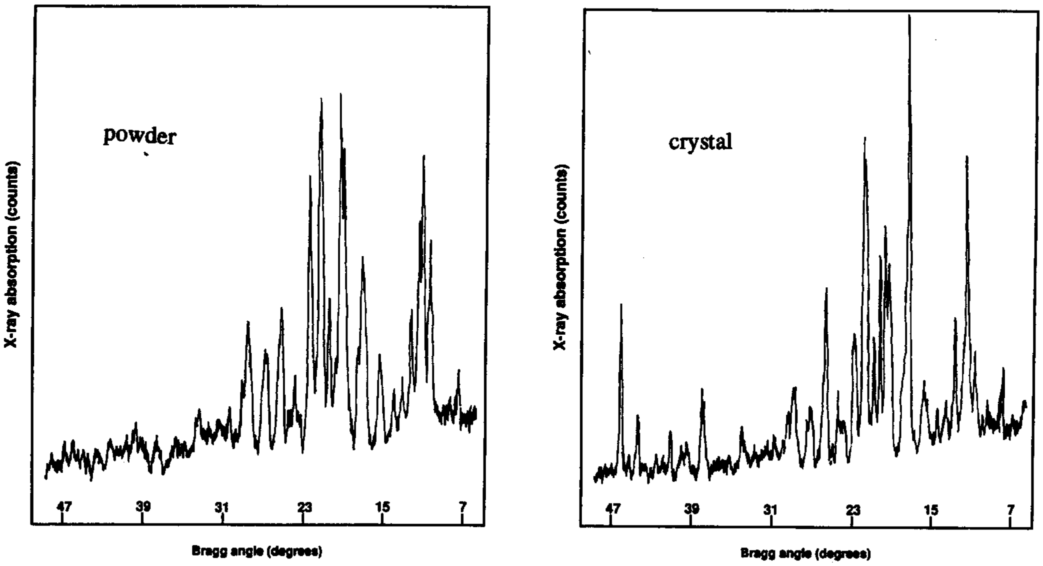

Figure 1. X-ray Powder Diffraction Patterns of Powdered and Crystalline Forms of 3

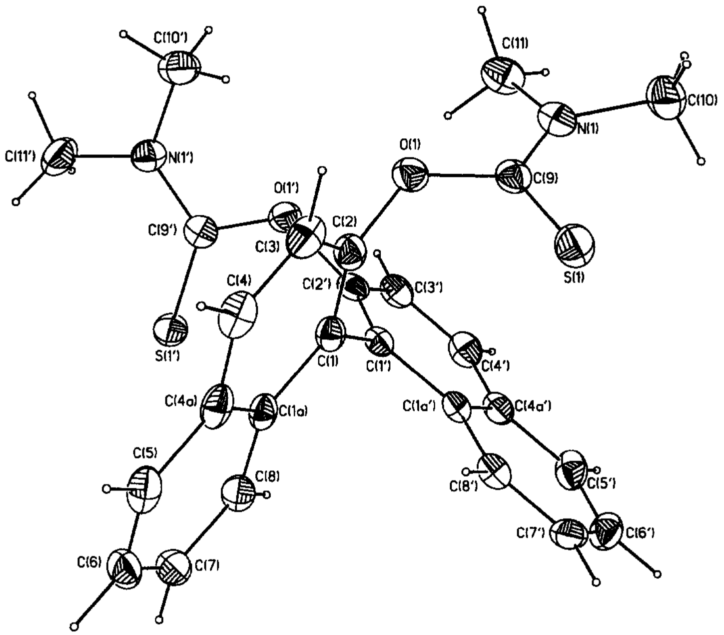

Figure 2. X-ray Crystal Structure of 3.

are not coplanar. The molecule has a *cisoid* arrangement around the central biaryl bond with an interplanar dihedral angle of 74°. The two thiocarbamoyl groups are extended away from each other and, although there are slight differences in bond lengths and bond angles between the corresponding bonds in the separate heteroatom fragments (Table 2), the distance between the sulfur and carbon reaction centres are comparable (S_1-C_2 = 2.977 Å and S_1'-C_2' = 2.971 Å).

The success of the thermorearrangement is therefore demonstrably dependent on the crystalline nature of dimethylthiocarbamoyl ester **3**. It seems that there are at least two forms of **3** which are isostructural but conformationally different in solid state, *i.e.* displaying the phenomenon of conformational polymorphism[19]. Conformational polymorphism has been observed with other biaryl derivatives and is considered to be a result of restricted rotation of aryl groups about the biaryl single bond producing several possible stable conformations. 1,1'-Binaphthalene itself can exist as two independently stable conformers, with interplanar dihedral angles of 67.7° and 101.4°[20].

Molecular mechanics energy minimisation calculations were performed on **3** in order to obtain some indication for more than one preferred conformation separated by a significant energy barrier. The integrity of this approach was tested with 1,1'-binaphthalene and two minima were found with interplanar angles comparable to those observed in the solid state although the energy barrier to interconversion could not be well established[21]. Calculations on **3**, with the side chain conformations fixed and the naphthalene rings treated as separate π-systems, indicated two energy minimized structures with dihedral angles of 76° and 113°. As noted with 1,1'-binaphthalene, attempts to determine the rotational barrier between the two conformers were unproductive. Similar calculations with **8** showed many possible conformations with relatively low energy barriers to interconversion. Despite the limitations implicit in these molecular structure calculations, they do provide support for the notion that, unlike **8**, **3** can probably exist in at least two different stable spatial arrangements. Thus a feasible explanation for the variable thermochemical properties of different solid forms of **3** is offered based on differing mixtures of several conformers being contained in the various solid samples. A study of the solution dynamics of **3** using variable temperature ^{1}H and ^{13}C NMR showed no evidence for more than one separate solution conformation.

Conversion of **4** to **2** was readily achieved by reduction with LAH or alternatively by hydrolysis with aqueous KOH. Alkaline hydrolysis proved convenient, especially for large scale production, as it gave **2** without the necessity for chromatographic purification of the intermediate compound.

CONCLUSION

Recognition of the conformational polymorphism of **3** has allowed for the development of a reliable protocol for the intramolecular thermal rearrangement to **4**. The structural requirements for this phenomenon appear to be related to the restriction of rotation about the biaryl bond. Related compounds with similar bond rotation restrictions could be expected to show similar chemistry[16].

EXPERIMENTAL

General

General experimental conditions have been described previously[5].

2,2'-Bis-O-(N,N-dimethylthiocarbamato)-1,1'-binaphthalene (3)

Sodium hydride (50% mineral oil dispersion, 20.2 g, 420 mmol) was added in small portions over 2 hr to a stirred solution of 1,1'-binaphthalene-2,2'-diol **1**[22] (60 g, 210 mmol) in dry DMF (450 cm^3) at 0°C under N_2. After the addition was complete, N,N-dimethylthiocarbamoyl chloride[13] (52 g, 420 mmol) was added in one portion and the mixture was stirred at 85°C under N_2 for 1 hr. The resulting brown suspension was cooled and shaken with 1% aqueous KOH (1.5 dm^3). The precipitate was filtered and dried in air at 25°C overnight. Crude **3** (110 g) was dissolved in hot toluene (250 cm^3) and the water which separated was removed by decantation. The organic solution was cooled in an ice bath to give **3** (91 g, 94%) as a powder, m.p. 208°C (Lit. 208-209.5°C)[8]. IR (KBr, cm^{-1}) ν_{max} 1661 (Ar-O-C=S). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.51 (s, 6H, NCH_3); 3.07 (s, 6H, NCH_3); 7.25 - 7.31 (m, 2H, Ar); 7.41 - 7.46 (m, 4H, Ar); 7.62 (d, J = 9.0 Hz, 2H, Ar); 7.90 (d, J =

9.0 Hz, 2H, Ar); 7.96 (d, *J* = 9.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.98 (CH_3), 42.67 (CH_3), 123.62 (CH), 123.86 (C), 125.66 (CH), 126.27 (CH), 126.69 (CH), 127.68 (CH), 128.23 (CH), 131.32 (C), 133.20 (C), 149.39 (C-2), 186.04 (C=S). Anal: calcd. for $C_{26}H_{24}N_2O_2S_2$: C, 67.79; H, 5.25; N, 6.08; S, 13.92. Found: C, 67.43; H, 5.36; N, 6.11; S, 13.96%.

The powder (50 g) was refluxed in toluene (500 cm^3) for *ca* 10 min then allowed to cool slowly to room temperature. After standing at room temperature for *ca* 12hr, the precipitate of shiny crystalline plates of **3** (35 - 40 g) was collected by filtration, m.p. 208-210°C. Identical NMR spectra to those described above. Anal: calcd. for $C_{26}H_{24}N_2O_2S_2$: C, 67.79; H, 5.25; N, 6.08; S, 13.92. Found: C, 68.03; H, 5.43; N, 6.21; S, 13.80%. On some occasions the product was obtained from the toluene solution as a fine powder/crystalline mix. In these cases the recystallization process was repeated until highly defined reflective plates were obtained.

Typical Experiments for the Thermolysis of 3

a. Powdered samples:

(i) Powder **3** (1.5 g, 3.25 mmol) was contained in a 1.8 cm i.d. pyrex tube and held in a boiling sulfolene bath (285°C) for 40 min under N_2. After cooling to room temperature, the dark brown opaque material was dissolved in hot $CHCl_3$ (25 cm^3) and chromatographed on silica gel (60g). Elution with $CHCl_3$ gave dinaphtho(2,1-b:1′,2′-d)thiophene **5** (0.185 g, 30%) m.p. 203°C (Lit m.p. 202°C)[7]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.55 - 7.88 (m, 4H); 7.93 - 8.05 (m, 6H); 8.85 - 8.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 120.92 (CH), 124.93 (CH), 125.27 (CH), 126.13 (CH), 127.45 (CH), 128.73 (CH), 129.95 (C), 131.45 (C), 132.19 (C), 138.53 (C-2). Anal. calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.10. Found: C, 84.56; H, 4.70; S, 10.70 %. Further elution with $CHCl_3$ gave a mixture of unidentified products (0.60 g) with similar t.l.c. R_f to **4**, m.p. *ca* 190°C.

(ii) A solution of **3** (1 g, 2.17 mmol) in dry toluene (25 cm^3) was pumped into a heated N_2 stream which then passed through a 1 cm id x 15 cm silica tube packed with quartz wool held at 400°C . The rate of addition was maintained at 0.36 cm^3 min^{-1} with a metering pump and the effluent from the tube was collected in an ice cooled vessel. The solvent was removed from the pyrolysate *in vacuo* to give a crude product which was chromatographed on silica gel (30g) in $CHCl_3$ to give **5** (0.23 g, 36%) and 2,2′-bis-S-(N,N-dimethylthiocarbamato)-1,1′-binaphthalene **4** (0.5 g, 50%), m.p. 249°C (Lit. 245-247°C)[8]. IR (KBr, cm^{-1}) ν_{max} 1657 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.76 (bs, 12H, NCH_3); 7.08 (d, *J* = 8.4 Hz, 2H, Ar); 7.22 (m, 2H, Ar); 7.45 (m, 2H, Ar); 7.79 (d, *J* = 8.7 Hz, 2H, Ar); 7.90 (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): 36.77 (CH_3), 126.39 (CH), 126.59 (CH), 126.87 (CH), 127.80 (CH), 128.15 (CH), 128.34 (C), 133.14 (CH), 140.81 (C-2), 166.22 (C=O).

b. Crystalline samples:

Crystalline 2,2′-bis-O-(N,N-dimethylthiocarbamato)-1,1′-binaphthalene **3** (5 g, 10.85 mmol) contained in a pyrex tube was heated in a boiling sulfolene bath (285°C) for 40 min under N_2 as for *a.(i)* above. After cooling to room temperature, the pale brown, clear, glassy solid was dissolved in hot $CHCl_3$ (25 cm^3) and chromatographed on silica gel to give **5** (0.7 g, 20%), m.p. 203°C and **4** (3.75 g, 75%), m.p. 249°C. Reactions in the same apparatus with smaller samples (approx. 0.5 g) gave optimal yields after heating for 25 - 30 min.

2′-Hydroxy-1,1′-binaphthalene-2-thiol (6)

A suspension of the unidentified material from thermolysis of **3** as in *a.(i)* above (0.5 g) and KOH (0.5 g) in methanol and THF (1:1, 10 cm^3) was refluxed under N_2 for 3 hr, then cooled to room temperature and added with vigorous stirring to cold degassed water (15 cm^3). The aqueous layer was acidified with concentrated H_2SO_4 producing a white precipitate which was extracted with ether (3 x 10 cm^3). The ether extract was dried over $MgSO_4$, filtered, and evaporated *in vacuo* to give the crude product which was purified by p.l.c. (1:1 CH_2Cl_2/hexanes) to give **6** (0.25 g) m.p. 150-152°C. IR (KBr, cm^{-1}) ν_{max} 3412 (O-H), 2563.5 (S-H). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.34 (s, SH); 4.89 (s, 1H, OH); 7.00 (d, *J* = 8.3 Hz, 1H); 7.10 (d, *J* = 8.4 Hz, 1H); 7.30 (m, 5H); 7.50 (d, *J* = 8.6 Hz, 1H), 7.83 (m, 3H); 7.92 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 116.57 (C), 117.83 (CH), 123.86 (CH), 124.25 (CH), 125.06 (CH), 125.68 (CH), 126.97 (CH), 127.21 (CH), 127.68 (CH), 128.33 (CH), 129.35 (C), 129.65 (CH), 130.80 (CH), 131.84 (C), 132.73 (C), 133.71 (C), 151.08 (C). Anal: calcd. for $C_{20}H_{14}SO$: C, 79.40; H, 4.70; S, 10.60. Found: C, 79.42; H, 4.70; S, 10.24%.

2-Methoxy-2'-methylthio-1,1'-binaphthalene (**7**)

Iodomethane (0.071 g, 0.5 mmol) was added to a solution of **6** (0.060 g, 0.2 mmol) in 1:1 10% aqueous NaOH/ethanol (5 cm^3). A precipitate was observed after stirring 5 min. The yellow coloured solution containing a white precipitate was stirred at room temperature overnight. Dichloromethane (25 cm^3) was then added and the organic layer was separated, washed with 10% NaOH (5 cm^3), water (5 cm^3) and dried over $MgSO_4$. Filtration and evaporation of solvents *in vacuo* gave a crude product which was separated by radial chromatography on a Chromatotron with 1:1 CH_2Cl_2/hexanes to give **7** (0.036 g, 55%), m.p. 154-156°C. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.38 (s, 3H, SCH_3); 3.78 (s, 3H, OCH3); 6.99 (d, $J = 8.4$ Hz, 1H, Ar); 7.22 (m, 2H, Ar); 7.35 (m, 2H, Ar); 7.46 (d, $J = 9.1$ Hz, 1H, Ar), 7.57 (d, $J = 9.0$ Hz, 1H); 7.86 (d, $J = 8.4$ Hz, 2H); 7.94 (d, $J = 8.4$ Hz, 1H); 8.01 (d, $J = 9.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 15.97 (SCH_3), 56.92 (OCH_3), 114.07 (CH), 120.89 (C), 123.41 (CH), 123.80 (CH), 124.83 (CH), 125.01 (CH), 125.38 (CH), 126.66 (CH), 126.77 (CH), 128.08 (CH), 128.12 (CH), 128.43 (CH), 129.25 (C), 136.12 (CH), 131.39 (C), 133.23 (C), 133.46 (C), 136.35 (C). Anal: calcd. for $C_{22}H_{18}SO$: C, 79.96; H, 5.49; S, 9.70. Found: C, 79.65; H, 5.87; S, 9.40.

2,2'-Bis-S-(N,N-dimethylthiocarbamato)biphenyl (**8**)

A sample of *2,2'-bis-O-(N,N-dimethylthiocarbamato)biphenyl*[15] (6 g, 16.6 mmol) as held in a 100 cm^3 round bottomed flask and immersed in a molten Wood's metal bath (310°C) for 25 min. The melt was cooled and triturated with hexane to give brown solid which was recrystallized from toluene/petroleum ether (40-60°C) to give **8** (3 g, 50%), m.p. 94°C (Lit. 94-96°C)[15]. IR ($CHCl_3$, cm^{-1}) ν_{max} 1670 (S-C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.88 (s, 12H, NCH_3); 7.30 - 7.48 (m, 6H, Ar); 7.64 - 7.68 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 36.96 (CH_3), 128.07 (CH), 128.86 (CH), 130.77 (CH), 136.93 (CH), 145.67 (C).

1,1'-Binaphthalene-2,2'-dithiol (**2**)

a. A suspension of purified **4** (5 g, 10.85 mmol) in 1:1 methanol/THF (60 cm^3) was heated to reflux under N_2. When the solid had dissolved, solid KOH (5 g) was added slowly. The mixture was then refluxed for 3 hr by which time no **4** remained (t.l.c.). The mixture was then cooled to room temperature and added with vigorous stirring to cold, degassed water (75 cm^3). The aqueous layer was separated and acidified with concentrated sulfuric acid producing a white precipitate which was extracted with ether (3 x 25 cm^3). The ether layer was dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo* to give crude product which was flash chromatographed on silica gel with 1:9 CH_2Cl_2/hexanes to give **2** (3.11 g, 90%). m.p. 155-156°C (Lit. 152-153.5°C)[8]. IR (KBr, cm^{-1}) ν_{max} 2565 (S-H). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.25 (s, 2H, SH); 7.00 (d, $J = 8.1$ Hz, 2H, Ar); 7.25 (m, 2H, Ar); 7.39 (m, 2H, Ar), 7.50 (d, $J = 9.0$ Hz, 2H, Ar); 7.84 (d, $J = 4.2$ Hz, 2H, Ar), 7.87 (d, $J = 3.3$ Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 124.90 (CH), 125.54 (CH), 127.23 (CH), 127.94 (CH), 128.32 (CH), 129.10 (CH), 131.39 (C), 131.85 (C), 131.96 (C), 132.65 (C-2).

b. Unpurified product (35 g) from the thermolysis of **3** as in *b* above was suspended in 1:1 methanol/THF (400 cm^3) and refluxed under N_2. When the solid had dissolved, solid KOH (35 g) was added slowly and the mixture was then refluxed for 3 hr . The mixture was cooled to room temperature and added to well stirred cold degassed water (500 cm^3). After 10 min, precipitated **5** was filtered and the filtrate was washed with CH_2Cl_2 (3 x 100 cm^3). The aqueous layer was then acidified with concentrated sulfuric acid producing white precipitate which was extracted with ether (3 x 100 cm^3). The combined ether extracts were dried over $MgSO_4$, filtered and evaporated *in vacuo* to give crude product which was chromatographed on silica gel column with 1:1 CH_2Cl_2/hexanes to give **2** (16 g).

Molecular Mechanics Calculations on **3**

Molecular mechanics calculations were carried out with the MMX force field using the PC-MODEL-Pi program, version 3.2 (Serena Software, Bloomington, Indiana, USA). The two naphthalene ring systems were treated as independent π-electron systems for preliminary RHF SCF calculations. Calculations starting from a completely planar structure or with the two naphtahlene rings orthogonal invariably gave one of two conformations with interplanar angles of 76° or 113°. The MMX energies of these two arrangements were found to vary greatly depending upon the conformation of the side chains, so for comparative studies they were fixed. Typical results for these constrained structures were MMX energies of 281.4 kJ mol^{-1} and 268.8 kJ mol^{-1} for the *cisoid* and *transoid* conformers respectively. The minimum energy barrier for interconversion between these two conformations could be depicted by stepwise calculation of the MMX energy as a function of the interplanar angle using a rigid rotor approximation. The minimum energy barrier to interconversion was found to be at an interplanar angle of *ca* 95°. As noted for the structures at energy minima, calculations of the height of the rotation barrier were dependent on the conformation of the side chains and could not be estimated with any confidence.

X-ray Powder Diffraction Patterns of 3

Samples of the powder and crystalline forms of **3** were prepared by spreading a fine slurry of the solids onto glass microscope slides. The powder diffraction patterns were obtained with a Philips X-Ray generator using CuK$_\alpha$ radiation and are shown in the discussion section as Figure 1.

Single Crystal X-ray Diffraction Analysis of 3

Crystals of **3** were grown from toluene as described above and a colourless block was selected and used for data collection. The unit-cell dimensions and orientation matrices were calculated from 25 accurately centred reflections on a Nicolet R3M fully automated diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Data were collected in ω scan mode, in the range $4 < 2\theta < 48°$. The intensities of 3 standard reflections, (4 0 0) (0 6 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 - 0.756 (maximum), 0.704 (minimum)] using programs from the SHELXTL package[23]. The structure was solved using the TREF option of the program SHELXS-86[24] with the E-map revealing the coordinates of all non-hydrogen atoms. Weighted least-squares refinement using SHELX-76[25] followed by a difference Fourier synthesis showed electron density maxima in reasonable locations for the hydrogen atoms and these were input in calculated positions with $r_{C\text{-}H}$ = 0.98Å and fixed isotropic temperature factors. All non-hydrogen atoms were assigned anisotropic temperature factors and the model refined to convergence with R = 0.0427, R_w = 0.0545. The weighting scheme $w = [0.8526/(\sigma^2F + 0.001593F^2)]$ was used. The final difference Fourier map was essentially flat with the highest peak corresponding to 0.25e Å^{-3}. *Crystal Data* - $C_{26}H_{24}N_2O_2S_2$, *M* = 460.62 g mol^{-1}, monoclinic, space group: $P2_1/n$[26], a = 9.136 (2) Å, b = 18.196 (7) Å, c = 13.885(5)Å, β = 97.13 (3)°, V = 2290 (1) Å^3, D_C = 1.34 g cm^{-3}, Z = 4, μ(Mo-Kα) = 2.57 cm^{-1}. *Data Collection* - Scan speed: 5.00 deg min^{-1}, $4 < 2\theta < 48°$, 3973 data collected, unique data 2636 with $I > 2\sigma I$ considered observed. *Structure Refinement* - Number of parameters = 301, $R(\Sigma\Delta F/\Sigma|F_o|)$ = 0.0427, $Rw[\Sigma w^{½}(\Delta F)/\Sigma w^{½}F_o]$ = 0.0545. A diagram of the final structure is given as Figure 2 and selected bond lengths and angles are in Table 2. A unit cell diagram and lists of positional parameters, thermal parameters, hydrogen atom coordinates, torsion angles and distances from atomic planes are available from the authors on request.

Table 2. Selected bond lengths and angles for **3**.

Bond lengths (Å).

N(1) ---C(10)	1.464(4)	C(4a) ---C(1a)	1.422(4)	C(6') ---C(5')	1.365(5)
N(1) ---C(11)	1.464(4)	C(6) ---C(7)	1.419(5)	C(5') ---C(4a')	1.411(4)
N(1) ---C(9)	1.328(4)	C(7) ---C(8)	1.366(4)	C(4') ---C(4a')	1.421(4)
C(9) ---S(1)	1.655(3)	C(8) ---C(1a)	1.417(4)	C(4') ---C(3')	1.368(5)
C(9) ---O(1)	1.373(4)	C(1)---C(1a)	1.437(4)	C(3') ---C(2')	1.411(4)
O(1) ---C(2)	1.406(4)	C(1) ---C(1')	1.487(4)	C(2') ---O(1')	1.406(4)
C(2) ---C(3)	1.406(4)	C(8') ---C(1a')	1.424(4)	O(1') ---C(9')	1.365(4)
C(2) ---C(1)	1.363(4)	C(8') ---C(7')	1.362(4)	C(9') ---S(11)	1.666(3)
C(3) ---C(4)	1.363(5)	C(1') ---C(1a')	1.439(4)	C(9') ---N(11)	1.326(4)
C(4) ---C(4a)	1.424(5)	C(1') ---C(2')	1.367(4)	N(11) ---C(10')	1.463(4)
C(5) ---C(4a)	1.421(4)	C(1a')---C(4a')	1.423(4)	N(11) ---C(11')	1.465(4)
C(5) ---C(6)	1.360(5)	C(7')---C(6')	1.403(5)		

Bond angles (degrees).

C(10)-N(1)-C(11)	117.6(3)	C(8)-C(1a)-C(1)	122.8(3)	C(4a)-C(1a)-C(1)	118.8(3)
C(10)-N(1)-C(9)	119.3(3)	C(1)-C(1')-C(1a')	120.1(3)	C(4a)-C(1a)-C(8)	118.4(3)
C(11)-N(1)-C(9)	123.1(3)	C(1)-C(1')-C(2')	122.1(3)	C(1a')-C(8')-C(7')	120.7(3)
N(1)-C(9)-S(1)	126.3(2)	C(1a')-C(1')-C(2')	117.8(3)	C(1a)-C(1)-C(1')	121.4(3)
N(1)-C(9)-O(1)	110.4(3)	C(8')-C(1a')-C(1')	121.9(3)	C(2)-C(1)-C(1')	120.1(3)
S(1)-C(9)-O(1)	123.3(2)	C(8')-C(1a')-C(4a')	118.3(3)	C(2)-C(1)-C(1a)	118.4(3)
C(9)-O(1)-C(2)	118.3(2)	C(1')-C(1a')-C(4a')	119.8(3)	C(7)-C(8)-C(1a)	121.1(3)
O(1)-C(2)-C(3)	118.4(3)	C(8')-C(7')-C(6')	120.6(3)	C(6)-C(7)-C(8)	120.2(3)
O(1)-C(2)-C(1)	118.1(3)	C(7')-C(6')-C(5')	120.4(3)	C(5)-C(6)-C(7)	120.3(3)
C(3)-C(2)-C(1)	123.4(3)	C(6')-C(5')-C(4a')	120.7(3)	C(1')-C(2')-O(1')	118.8(3)
C(2)-C(3)-C(4)	119.1(3)	C(4a')-C(4')-C(3')	120.8(3)	C(3')-C(2')-O(1')	117.5(3)
C(3)-C(4)-C(4a)	120.7(3)	C(1a')-C(4a')-C(5')	119.2(3)	C(2')-O(1')-C(9')	118.8(2)
C(4a)-C(5)-C(6)	120.6(3)	C(1a')-C(4a')-C(4')	119.1(3)	O(1')-C(9')-S(1')	123.4(2)
C(4)-C(4a)-C(5)	121.0(3)	C(5')-C(4a')-C(4')	121.7(3)	O(1')-C(9')-N(1')	110.8(3)
C(4)-C(4a)-C(1a)	119.6(3)	C(4')-C(3')-C(2')	119.2(3)	S(1')-C(9')-N(1')	125.8(2)
C(5)-C(4a)-C(1a)	119.4(3)	C(1')-C(2')-C(3')	123.3(3)	C(9')-N(1')-C(10')	122.9(3)
C(9')-N(1')-C(11')	119.9(3)	C(10')-N(1')-C(11')	117.2(3)		

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