4-Acyl-1,2-dithiole-3-thiones and Their S-Oxides. Synthesis, Crystal Structures, and UV and Circular Dichroism Spectra

Agha Zul-Qarnain Khan,[a,†] Jan Sandström[a,*] and Sue-Lein Wang[b]
[a] Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden
[b] Department of Chemistry, The National Tsing-Hua University, Hsinchu, Taiwan 30043, Republic of China

When 6,6-dimethyl- and 6-phenyl-3-thioxo-6,7-dihydro-3H-1,2-benzodithiol-4(5H)-one was allowed to react with monomeric boron trisulphide under argon, the only products isolated after chromatography on silica were the corresponding S-oxides in up to 37% yield based on reacted starting material. The same S-oxides were obtained in good yields on oxidation of the thiones with m-chloroperbenzoic acid (MCPBA). The structures of the 6,6-dimethyl derivatives, thione and S-oxide, were established by X-ray crystallography. The S-oxide displays a very short intramolecular distance, 2.81 Å, between the S=O oxygen atom and the S-2 atom of the dithiole ring, which indicated an attractive interaction. The C$_6$ ring has a sofa conformation with one axial and one equatorial methyl group. Analysis of the ^{1}H NMR spectra of the 6-phenyl compounds leads to the same conformations with equatorial phenyl groups.

The 6-phenyl compounds are chiral and were able to be resolved into pure enantiomers by chromatography on triacetylcellulose. The UV spectra of all compounds and the CD spectra of the 6-phenyl derivatives are discussed in relation to the results of CNDO/S calculations. Bands in the CD spectrum of the thione S-oxide, which lack counterparts in the UV spectrum, are assigned to the S=O and C=O n ⟶ π* transitions.

Some years ago, two of us[1] described the formation of the 4-acyl-1,2-dithiole-3-thione **1a** in reaction between the ketene

a R^1 = R^2 = CH$_3$
b R^1 = Ph, R^2 = H
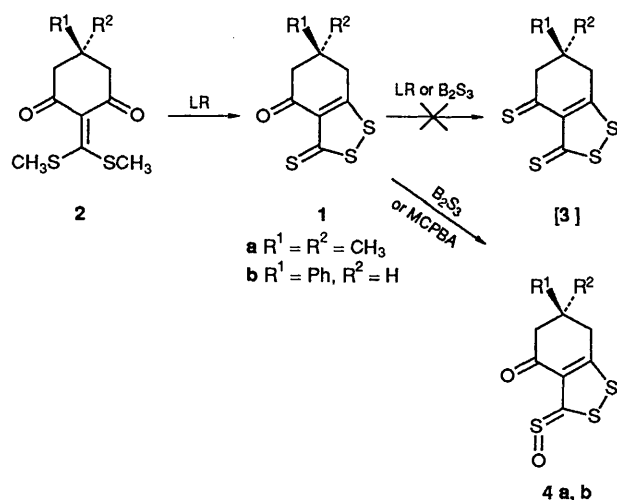
Scheme 1

dithioacetal **2a** and Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulphide, LR].[2,3] Compound **1a** appeared to be a promising starting material for the preparation of the 4-thioacyl analogue **3a**, which was expected to show degenerate no-bond–single-bond valence tautomerism.[4,5] However, reaction of **1a** with monomeric boron trisulphide (Steliou's reagent)[6] in toluene at ambient temperature for 60 h gave a 37% yield (based on reacted starting material) of a new compound, C$_9$H$_{10}$O$_2$S$_3$, together with unchanged **1a** (73%). Reaction at elevated temperatures (refluxing toluene) led to a lower yield and decreased recovery of

† On leave of absence from PCSIR, Karachi, Pakistan.

unchanged **1a**. Attempted thionation of **1a** with P$_4$S$_{10}$ or with LR at ambient temperature or in refluxing o-dichlorobenzene did not give any identifiable products.

The structure of the new compound was shown by single-crystal X-ray diffraction to be that of a thiocarbonyl S-oxide (sulphine)[7] of **1a** of Z configuration **4a**. The mechanism of formation of an oxidation product under the reaction conditions used remains obscure to us. Air oxidation during the reaction seems to be excluded. The reactions were performed under an argon atmosphere, and 1,2-dithiole-3-thiones are known to be very stable compounds with no tendency to undergo air oxidation. Possible sources of oxygen are a second molecule of **1a** in the reaction proper, or water or molecular oxygen during the chromatographic work-up. In the latter case oxygen must be transferred to a derivative of **1a** formed in the reaction with B$_2$S$_3$ or its precursors, since **1a** is unchanged under the work-up conditions. An analogue of **4a** (**4b**) was formed in the reaction of **1b** with Steliou's reagent. Both thione oxides were obtained in 82% yield on oxidation of the thiones with MCPBA in dichloromethane.

Although the original purpose of the study, the preparation of compounds **3**, was not fulfilled, the sulphines **4** are of sufficient interest to merit an investigation. In order to study the effect of S-oxidation on the bond lengths in the 1,2-dithiole ring, we determined the crystal structure of **1a** by X-ray diffraction. This confirmed the structure proposed earlier.[1] The synthesis of **1a** by a different route has recently been reported by Tominaga et al.[8]

Crystallographic Results.—The crystals of **1a**, orange plates, were found to have unit cells belonging to the monoclinic space group P2$_1$, containing two molecules. The final refinement indices were R = 0.0324 and R$_w$ = 0.0288. The crystals of the sulphine **4a** were orange-red prisms, and the unit cell was found to belong to the orthorhombic space group Pbca and to contain eight molecules. The final refinements indices were R = 0.0490 and R$_w$ = 0.0283.
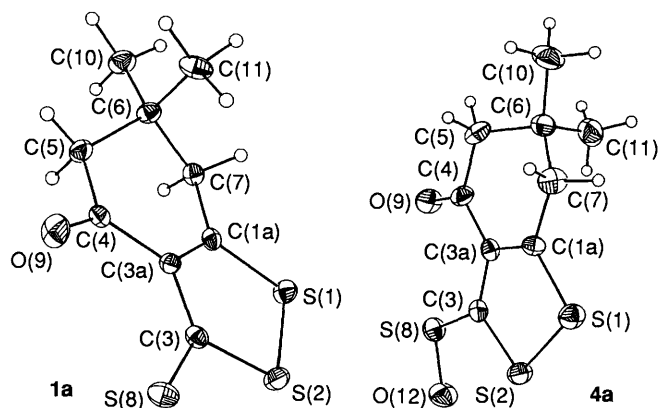
Fig. 1 ORTEP drawings of 1a and 4a

Table 1 Bond lengths (Å) in 1a and 4a

Bond	1a	4a
S(1)–S(2)	2.055(2)	2.070(3)
S(2)–C(3)	1.746(5)	1.722(8)
C(3)–C(3a)	1.439(7)	1.431(10)
S(1)–C(1a)	1.711(6)	1.695(8)
C(1a)–C(3a)	1.368(7)	1.358(11)
C(3a)–C(4)	1.484(8)	1.459(11)
C(4)–C(5)	1.507(9)	1.491(14)
C(5)–C(6)	1.533(7)	1.543(13)
C(6)–C(7)	1.526(9)	1.520(14)
C(1a)–C(7)	1.494(7)	1.499(13)
C(3)–S(8)	1.657(5)	1.668(7)
C(4)–O(9)	1.216(7)	1.224(12)
S(8)–O(12)	—	1.511(6)
C(6)–C(10)	1.530(10)	1.533(15)
C(6)–C(11)	1.506(10)	1.520(15)

Table 2 Bond angles (°) in 1a and 4a

Angle	1a	4a
S(1)–S(2)–C(3)	97.1(2)	94.6(3)
S(2)–C(3)–C(3a)	112.8(4)	116.0(5)
S(1)–C(1a)–C(3a)	118.9(4)	118.6(6)
S(2)–S(1)–C(1a)	94.1(2)	95.2(3)
C(1a)–C(3a)–C(3)	117.0(5)	115.6(7)
S(2)–C(3)–S(8)	114.2(3)	116.0(4)
C(3a)–C(3)–S(8)	133.0(4)	128.0(6)
C(3)–S(8)–O(12)	—	104.6(4)
C(3)–C(3a)–C(4)	123.5(4)	122.9(7)
C(3a)–C(4)–C(5)	116.2(5)	116.6(8)
C(4)–C(5)–C(6)	114.9(5)	116.8(8)
C(5)–C(6)–C(7)	107.2(5)	107.7(8)
C(1a)–C(7)–C(6)	113.0(5)	113.5(7)
S(1)–C(1a)–C(7)	116.9(4)	118.9(6)
C(3a)–C(1a)–C(7)	124.1(5)	122.5(7)
C(1a)–C(3a)–C(4)	119.4(5)	121.5(7)
C(3a)–C(4)–O(9)	122.3(5)	121.4(8)
C(5)–C(4)–O(9)	121.5(6)	121.9(8)
C(5)–C(6)–C(10)	109.0(5)	108.6(8)
C(5)–C(6)–C(11)	110.2(5)	109.1(8)
C(10)–C(6)–C(11)	109.6(6)	111.6(9)
C(7)–C(6)–C(10)	109.7(6)	109.9(8)
C(7)–C(6)–C(11)	111.1(5)	109.8(8)

The molecular structures of 1a and 4a are quite similar (Fig. 1). The carbocyclic parts assume 'sofa' conformations with one axial and one equatorial methyl group and with nearly planar 4-acyl-1,2-dithiole-3-thione parts. A least-squares best fit of the corresponding non-hydrogen atoms in the two molecules gave a

Table 3 [1]H Chemical shifts and coupling constants for 1b and 4b, solvent CDCl₃

Compd.	δ (ppm)		J/Hz				
1b	A 3.341			B	M	X	Y
	B 3.241	A	17.6		4.7	1.4	0.0
	M 3.575	B			11.5	0.0	0.0
	X 2.938	M				4.9	11.7
	Y 2.875	X					16.8
4b	A 3.210			B	M	X	Y
	B 3.126	A	17.8		4.9	1.4	0.0
	M 3.609	B			10.7	0.0	0.0
	X 2.935	M				4.7	12.2
	Y 2.881	X					17.2
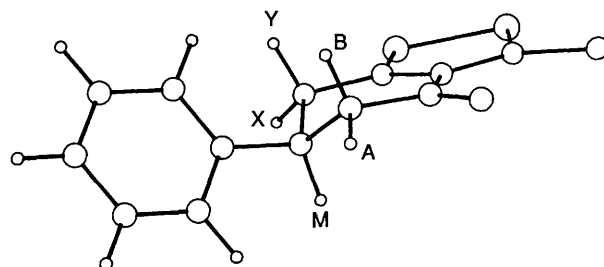
Fig. 2 Drawing of 1b, based on the X-ray crystal structure of 1a

mean deviation of only 0.07 Å. The corresponding bond lengths and angles in the 1,2-dithiole-3-thione parts are very similar (Tables 1 and 2), *i.e.* the introduction of an oxygen atom on the thiocarbonyl sulphur atom does not greatly affect the electronic ground state of the ring. The 4-oxo group also has a rather small effect, since the geometries of the 1,2-dithiole-3-thione parts of 1a and 4a are quite similar to that of the simple 4-methyl-1,2-dithiole-3-thione.[9]

The sulphine oxygen atom of 4a is in the plane of the dithiole ring. The bond lengths in the sulphine part do not differ much from those found for simple sulphines. The C=S bond in 4a is 1.669 Å compared with 1.610 Å in the unsubstituted sulphine[10] and 1.64 Å in ethylenetrithiocarbonate S-oxide.[11] The somewhat longer C=S bond in 4a can be ascribed to polarization due to the donor effect of the 1,2-dithiole ring. The corresponding bond in 1a is 1.657 Å. The SO bond in 4a is 1.512 Å compared with 1.469 and 1.50 Å, respectively, in the above-mentioned compounds. The CSO angle in 4a is 104.5°, considerably smaller than for the simple sulphine (114.7°)[10] or ethylene trithiocarbonate S-oxide (109.4°).[11] Consequently, the O-12–S-2 distance is only 2.807 Å, considerably shorter than the sum of oxygen and sulphur van der Waals' radii, 3.25[12] or 3.10 Å.[13] Short non-bonded S ··· O distances are quite common and have been discussed in depth by Kucsman and Kapovits.[14] No general explanation is given for 1,4-interactions, but an oxygen lone-pair–sulphur σ* orbital interaction is proposed. In the case of 4a coulombic attraction may also play a role, since according to CNDO/S calculations (*vide infra*) O-12 has a formal charge of −0.45 and S-2 one of +0.12 (in units of the electronic charge). It is worth noting that the corresponding distance in ethylene trithiocarbonate S-oxide is longer, 3.046 Å, and here the oxygen atom is forced 0.25 Å out of the CS₃ plane.[14]

^{1}H *NMR Spectra and Conformations of* 1b *and* 4b.—As expected, these compounds show very similar ^{1}H NMR spectra. The cyclohexenone proton resonances appear as an ABMXY system with a four-bond coupling ($^4J_{HH}$ 1.4 Hz) between two of them (A and X). Iterative analysis of the spectra gives the chemical shifts and coupling constants shown in Table 3.

Inspection of Newman projections along the C-5–C-6 and C-6–C-7 bonds (Fig. 2) show that the 6-phenyl group must be at

Table 4 UV–VIS and CD spectra[a]

Compound	Solvent	λ_{max}/nm (ε, $\Delta\varepsilon$)
1a, UV[b]	EtOH	490sh (170), 414 (7500), 332sh (6200), 308 (9000), 256 (11 000), 222 (19 000)
	$CH_2Cl_2:C_6H_{12}$ (1:9, v/v)	532 (93), 424 (5000), 341 (6100), 307 (7700), 257 (15 300), 220 (13 500)
1b, UV	EtOH	520sh (120), 414 (6000), 331sh (5200), 310 (7900), 265 (10 400), 222 (17 400), 205 (21 800)
1b, CD	EtOH	502 (+0.26), 400 (−0.76), 317 (+2.83), 272 (+5.48), 235 (−3.75), 220 (+1.33), 205 (−4.01)
4a, UV	EtOH	432 (6500), 357 (5900), 257 (6800), 214 (9800)
	$CH_2Cl_2:C_6H_{12}$ (1:9, v/v)	442 (4400), 354 (5400), 310sh (2000), 258 (6400), 208 (10 300)
4b, UV	EtOH	431 (7200), 356 (6950), 258 (9400), end absorption at 200 nm
4b, CD	EtOH	464 (+0.96), 390 (−0.71), 360 (−1.04), 348sh (−0.78), 313 (−1.08), 275 (−1.40), 246.5 (+1.48), 236.5 (+1.44), 224 (−1.06)

[a] First eluted enantiomer. [b] From ref. 1.

Fig. 3 CD spectra in ethanol of first eluted enantiomers of (a) **1b** and (b) **4b**

least predominantly equatorial, since the large J_{BM} and J_{MY} values (10.7–12.2 Hz) require dominant *anti* arrangement of the protons, which must all be axial. The lower vicinal coupling constants, J_{AM} and J_{MX} (4.7–4.9 Hz), are in agreement with a *gauche* arrangement of one axial (H-6) and one equatorial proton. The four-bond coupling between the A and X nuclei is between equatorial protons, as required for the nearly planar W arrangement of the protons and intervening carbon atoms.[15] For **1a**,[1] the CH_2 singlet at δ 2.52 was assigned to the CH_2CO moiety, *i.e.* to 5-H, based on the similarity in chemical shift with that found for similar structures, and the singlet at 2.94 to 7-H. In conformity with this, the protons designated A, B, M, X and Y in Table 2 are assigned to 5-H (eq), 5-H (ax), 6-H (ax), 7-H (eq) and 7-H (ax), respectively.

UV and CD Spectra of Compounds **1** *and* **4**.—The 6-phenyl compounds **1b** and **4b** are chiral, and it has been possible to resolve them into pure enantiomers by chromatography on swollen, microcrystalline triacetylcellulose[16–18] and subsequently to record their CD spectra. These spectra give an advantage in the analysis of the electronic transitions, since transitions of low probability in absorption spectra may show relatively strong CD bands.

The UV–VIS absorption spectra of **1a** and **1b** (Table 4) are quite similar, showing a weak band near λ = 520 nm, assigned to an n $\longrightarrow$ π^* transition, followed by five more or less well resolved, stronger bands with maxima in the range λ = 414 to 222 nm. The absorption due to the phenyl group in **1b** is overlapped by the dithiole–thione absorption and is only revealed by a weak fine structure near λ = 260 nm. The spectrum of **4a** in ethanol displays four medium–strong bands from λ = 432 to 208 nm, but no weak n $\longrightarrow$ π^* band. A fifth band appears as a shoulder at λ = 310 nm in a non-polar solvent. The spectrum of **4b** is quite similar, although the short-wavelength band is obscured by strong end absorption.

The CD spectrum of the first eluted enantiomer (E_1) of **1b** [Fig. 3(a), Table 3] shows absorption bands, which agree reasonably well with those of the UV–VIS absorption spectrum.
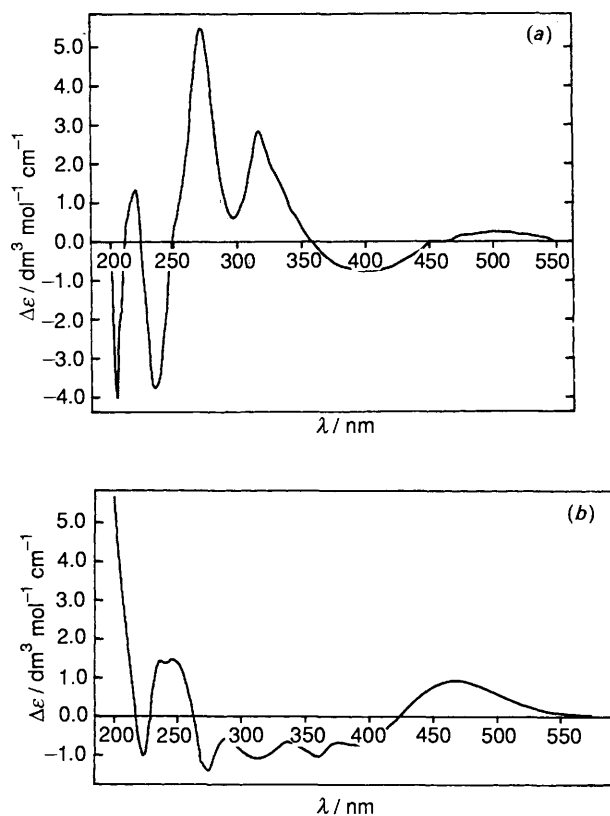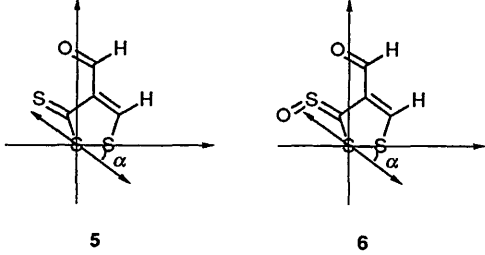
A weak, broad, positive band centred at λ = 502 nm is ascribed to the n $\longrightarrow$ π^* transition, followed by a stronger negative band at λ = 400 nm, positive bands at λ = 317 and 272 nm, and a negative band at λ = 235 nm. No strong band clearly assignable to the benzene p band can be observed. The two weak bands at λ = 220 and 205 nm may be residues of two oppositely signed stronger transitions in this region, the benzene p transition and the transition giving rise to a strong band at λ = 220 nm in the spectrum of **1a**.

The CD spectrum of the E_1 enantiomer of **4b** shows at least eight bands above λ = 200 nm, and the agreement with the UV–VIS spectrum is less evident than for **1b**. The appearance of the CD spectrum around λ = 425 nm indicates the presence of two rather strong transition with similar energies and opposite signs, which by overlap and elimination of intensity give rise to the maxima at λ = 390 and 464 nm. Resolution of the bands as Gaussians leads to a negative band centred at λ = 400 nm and halfwidth of *ca.* 50 nm, and a positive band centred at λ = 430 nm with halfwidth of *ca.* 75 nm. The latter corresponds to the UV band at λ = 431 nm, but the former lacks a counterpart in the UV spectrum. It may be due to the sulphoxy n $\longrightarrow$ π^* transition predicted by CNDO/S calculations to fall at λ = 391 nm (*vide infra*). The negative CD band at λ = 275 nm also lacks a counterpart in the UV spectrum, and it may be due to the 4-C=O n $\longrightarrow$ π^* transition, predicted to fall at λ = 268 nm.

In the schematic models, the rotational strengths of the transitions in **1b** and **4b** can be explained by one or more of three mechanisms: the one-electron, the coupled oscillator, and the magnetic–electric coupling mechanism.[19] In many cases with interaction between proximate chromophores with $\pi \longrightarrow \pi^*$ transitions the second mechanism is the most important one,[20] and sometimes the third gives important contributions. However, owing to the remote location of the phenyl group, the one-electron mechanism, which is based on a

Table 5 Calculated transition wavelengths (nm) oscillator strengths (f), and polarizations for **5** and **6**

Structure	λ_{max}/nm	f	Assignment	Orientation ($\alpha/°$)
5	901.9	0.0000	n $\longrightarrow$ π^* (C=S)	
	436.6	0.118	$\pi \longrightarrow \pi^*$	28
	343.7	0.056	$\pi \longrightarrow \pi^*$	26
	288.7	0.0004	n $\longrightarrow \pi^*$ (C=O)	
	271.4	0.044	$\pi \longrightarrow \pi^*$	87
	241.5	0.0516	$\pi \longrightarrow \pi^*$	18
	217.0	0.1175	$\pi \longrightarrow \pi^*$	49
6	408.0	0.3112	$\pi \longrightarrow \pi^*$	24
	390.8	0.0036	n $\longrightarrow \pi^*$ (S=O)	76
	290.8	0.0187	$\pi \longrightarrow \pi^*$	28
	268.0	0.0011	n $\longrightarrow \pi^*$ (C=O)	
	252.1	0.1329	$\pi \longrightarrow \pi^*$	27
	241.8	0.0547	$\pi \longrightarrow \pi^*$	56

mixing of n $\longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions in one chromophore by perturbations by chirally disposed static charges in the molecular skeleton,[21] becomes relatively more important. This mechanism is particularly efficient with degenerate or nearly degenerate transitions,[22,23] and may be responsible for a larger part of the rotational strengths of the two lowest-energy transitions in **4b**.

CNDO/S–CI calculations including d-orbitals have been performed on simplified models of **1a** and **4a** (structures **5** and **6**, Table 5). For **5** a thiocarbonyl n $\longrightarrow \pi^*$ transition is predicted at $\lambda = 902$ nm and a 4-formyl n $\longrightarrow \pi^*$ transition at $\lambda = 289$ nm. The first $\pi \longrightarrow \pi^*$ transition is predicted at $\lambda = 436$ nm, and other medium–strong $\pi \longrightarrow \pi^*$ transitions at $\lambda = 334$, 271, 241 and 217 nm.

The lowest-energy transition calculated for **6** is a strong $\pi \longrightarrow \pi^*$ transition at $\lambda = 408$ nm, followed by a forbidden transition at $\lambda = 391$ nm. The latter is due to excitation of a sulphonyl oxygen lone-pair electron into the lowest antibonding π orbital, chiefly located in the O=S=C group. Other medium–strong $\pi \longrightarrow \pi^*$ transitions are predicted at $\lambda = 291$, 253 and 242 nm, and the 4-C=O n $\longrightarrow \pi^*$ transition at $\lambda = 268$ nm.

The CNDO/S program is specifically parametrized for sulphur compounds,[24] but it tends to predict too low transition energies for n $\longrightarrow \pi^*$ transitions in thiocarbonyl compounds, whereas $\pi \longrightarrow \pi^*$ transition energies in general are much better reproduced.[25] The n $\longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions for the *S*-oxide **6** are both predicted to fall near $\lambda = 400$ nm, in good agreement with the results of the analysis of the CD spectrum of **4b**.

Experimental

Syntheses.—The preparation of 6,6-dimethyl-3-thioxo-6,7-dihydro-3*H*-1,2-benzodithiol-4(5*H*)-one **1a** has been described earlier. The preparation of the 6-phenyl analogue **1b** was performed in an analogous way.

2-[*Bis(methylthio)methylene*]-5-*phenylcyclohexane*-1,3-*dione* **2b**. Compound **2b** was prepared by the reaction of 5-phenyl-cyclohexane-1,3-dione[26,27] (0.05 mol), carbon disulphide (0.075

mol) and sodium hydride (0.10 mol) in dry DMF (*N*,*N*-dimethylformamide) (50 cm³), first at 0 °C for 45 min, then at ambient temperature for 4 h, and finally at 50 °C for 15 min. Methyl iodide (0.125 mol) was added to the cooled (0 °C) mixture and after 12 h at ambient temperature the mixture was concentrated under reduced pressure and diluted with water, and the resulting solution was extracted several times with dichloromethane. Evaporation of the dried dichloromethane phase gave *colourless crystals* (80% yield), m.p. 134.5–135 °C after recrystallization from toluene. δ_H(300 MHz; CDCl₃) 2.49 (6 H, s), 2.79, 2.89 (4 H, AB part of A_2B_2X system, J_{AB} 16.7*), 3.37 (1 H, X part of A_2B_2X system, J_{AX} 4.5, J_{BX} 11.6) and 7.21–7.35 (5 H, m); δ_C(75 MHz; CDCl₃) 21.8 (q), 35.9 (d), 46.09 (t), 124.3, 126.5 (d), 126.9 (d), 128.7 (d), 142.2, 190.9 and 192.2; *m/z* (70 eV): 292 (M⁺, 23%), 277 (67), 173 (30), 131 (80), 99 (100), 85 (32) and 45 (41) (Found: M⁺, 292.0590. Calc. for $C_{15}H_{16}O_2S_2$: *M*, 292.0592).

A mixture of **2b** (3.4 mmol), P_4S_{10} (3.4 mmol) and dry sodium hydrogencarbonate (10.2 mmol) in dry THF (50 cm³) was stirred for 16 h at -15 to -20 °C, allowed to warm to room temperature, filtered, and evaporated. Twice repeated flash chromatography[28] on silica (Merck 60) eluting with toluene, gradually diluted with ethyl acetate gave pure 6-*phenyl*-3-*thioxo*-6,7-*dihydro*-3H-1,2-*benzodithiol*-4(5H)-*one* (**1b**) (29%) as red leaflets, m.p. 158–159 °C after recrystallization from toluene. ¹H NMR spectroscopic data are given in Table 3; δ_C(75 MHz; CDCl₃) 38.3 (t), 41.0 (d), 46.1 (t), 126.5 (d), 127.7 (d), 129.1 (d), 135.0, 140.5, 187.3, 188.9 (C=O) and 211.8 (C=S); *m/z* (70 eV) 278 (M⁺, 100%), 174 (60), 109 (28), 103 (42) and 82 (90) (Found: M⁺, 277.9895. Calc. for $C_{13}H_{10}OS_3$: *M*, 277.9894).

Attempted Thionation of **1a** *and* **1b**.—Boron trichloride (1.3 mmol) as a 1.0 mol dm⁻³ dichloromethane solution was added with stirring at ambient temperature to a solution of **1a** (1.0 mmol) and bis(tricyclohexyltin) sulphide[6] (1.1 mmol) in toluene (20 cm³) under an argon atmosphere. After 60 h, **1a** was still present (TLC). Evaporation and flash chromatography as for **1b** gave 73% unchanged **1a** and 10% (37% based on consumed **1a**) of a red, crystalline material, m.p. 152–154 °C (decomp.) after recrystallization from dichloromethane–hexane. Use of bis(trimethylsilyl) sulphide[29] or 2,2,5,5-tetramethyl-2,5-disila-1-thiacyclopentane[30] instead of bis(tricyclohexyltin) sulphide led to somewhat lower yields. The same product was obtained in 82% yield when **1a** (0.75 mmol) was oxidized with MCPBA (0.80 mmol) in dry dichloromethane (25 cm³) at -40 °C.[31] The compound was shown by X-ray crystallography to be 6,6-*dimethyl*-3-*thioxo*-6,7-*dihydro*-3H-1,2-*benzodithiol*-4(5H)-*one S*-*oxide* **4a**; δ_H(300 MHz; CDCl₃) 1.17 (s, 6 H), 2.48 (s, 2 H) and 2.80 (s 2, H); δ_C(75 MHz; CDCl₃) 27.9 (q), 35.7, 42.5 (t), 50.2 (t), 130.0, 174.0, 190.1 and 197.9; *m/z* (16 eV) 246 (M⁺, 100).

6-*Phenyl*-3-*thioxo*-6,7-*dihydro*-3H-1,2-*benzodithiol*-4(5H)-*one S*-*oxide* **4b**. **4b** was obtained in 3–10% yield on attempted thionation of **1b** as above, and in 82% yield by oxidation of **1b** with MCPBA. Red prisms, m.p. 172–174 °C after recrystallization from dichloromethane–hexane; ¹H NMR spectroscopic data are given in Table 3. δ_C(75 MHz; CDCl₃) 36.4 (d), 41.1 (t), 43.3 (t), 126.6 (d), 127.9 (d), 129.2 (d), 131.0, 140.5, 174.1, 189.3 and 197.6; *m/z* (70 eV) 294 (M⁺, 55), 278 (30), 126 (38), 103 (40), 82 (100), 77 (44), 58 (42) and 43 (52) (Found: M⁺, 293.9849. Calc. for $C_{13}H_{10}O_2S_3$: *M*, 293.9843).

X-Ray Crystallography.—Peak profile analysis (ω-scan) on the crystals of both compounds using a Siemens R3m/V diffractometer with Mo-Kα radiation indicated that most of

---

* *J* values are given in Hz throughout the Experimental section.

Table 6 Crystal data and intensity collection for **1a** and **4a**

	1a	4a
Empirical formula	$C_9H_{10}OS_3$	$C_9H_{10}O_2S_3$
Colour, habit	Orange, plate	Orange–red, chunk
Crystal size (mm)	$0.07 \times 0.20 \times 0.22$	$0.14 \times 0.18 \times 0.22$
Space group	$P2_1$; monoclinic	$Pbca$; orthorombic
Unit cell dimensions	$a = 7.040(2)$ Å	$a = 8.684(3)$ Å
	$b = 10.023(4)$ Å, $\beta = 96.96(3)°$	$b = 9.998(3)$ Å
	$c = 7.364(2)$ Å	$c = 24.778(9)$ Å
Volume	$515.8(3)$ Å^3	$2151.5(14)$ Å^3
Z	2	8
Formula weight	230.4	246.4
Density (calc.)	1.483 Mg m^{-3}	1.521 Mg m^{-3}
Absorption coefficient	0.648 mm^{-1}	0.632 mm^{-1}
F(000)	240	1024
Diffractometer used	Siemens R3m/V	
Radiation	Mo-Kα ($\lambda = 0.710\ 73$ Å)	
T/K	297	
Monochromator	Highly oriented graphite crystal	
2θ Range	2.0–$55.0°$	
Scan type	$\theta/2\theta$	
Scan speed	Variable; 2.44 to 14.65° min^{-1} in ω	
Scan range (ω)	$0.98°$ plus Kα-separation	
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
Standard reflections	3 measured every 50 reflections	
Index ranges	$0 \leqslant h \leqslant 8, -12 \leqslant k \leqslant 0, -9 \leqslant l \leqslant 9$	$0 \leqslant h \leqslant 11, -2 \leqslant k \leqslant 12, -6 \leqslant l \leqslant 30$
Reflections collected	$1349\ [889 > 3\sigma(I)]$	$3639\ [1182 > 3\sigma(I)]$
Independent reflections	$1247\ [820 > 3\sigma(I)]$	$1785\ [680 > 3\sigma(I)]$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$	$w^{-1} = \sigma^2(F) + 0.0006F^2$
Number of parameters refined	158	168
Final R indices (obs. data)	$R = 0.0324, R_w = 0.0288$	$R = 0.0439, R_w = 0.0333$
Goodness-of-fit	1.11	1.30
Largest and mean Δ/σ	$0.002, 0.001$	$0.072, 0.007$
Data-to-parameter ratio	$5.2:1$	$4.0:1$
Largest difference peak/hole	$0.23/-0.22$ e Å^{-3}	$0.32/-0.32$ e Å^{-3}

Table 7 Atomic coordinates ($\times 10^4$)

	x	y	z
1a			
S(2)	$-4\ 563(2)$	-443	$-4\ 484(2)$
S(1)	$-6\ 036(2)$	$-415(3)$	$-2\ 183(2)$
S(8)	$-5\ 382(2)$	$-2\ 078(2)$	$-7\ 671(2)$
O(9)	$-9\ 015(6)$	$-3\ 646(6)$	$-6\ 913(4)$
C(3)	$-6\ 070(7)$	$-1\ 665(6)$	$-5\ 673(6)$
C(3a)	$-7\ 623(6)$	$-2\ 097(8)$	$-4\ 713(5)$
C(4)	$-9\ 092(8)$	$-3\ 077(7)$	$-5\ 466(7)$
C(5)	$-10\ 704(9)$	$-3\ 327(9)$	$-4\ 338(8)$
C(6)	$-10\ 138(8)$	$-3\ 264(7)$	$-2\ 263(7)$
C(7)	$-9\ 228(8)$	$-1\ 901(7)$	$-1\ 832(7)$
C(1a)	$-7\ 711(7)$	$-1\ 568(6)$	$-3\ 013(6)$
C(11)	$-8\ 760(12)$	$-4\ 372(8)$	$-1\ 658(9)$
C(10)	$-11\ 939(11)$	$-3\ 406(10)$	$-1\ 307(10)$
4a			
S(8)	$-226(2)$	$5\ 349(2)$	$794(1)$
S(2)	$2\ 251(2)$	$6\ 775(2)$	$284(1)$
S(1)	$4\ 576(2)$	$6\ 511(3)$	$434(1)$
O(12)	$-924(5)$	$6\ 382(6)$	$423(2)$
O(9)	$1\ 260(7)$	$3\ 591(6)$	$1\ 568(2)$
C(3)	$1\ 669(8)$	$5\ 571(8)$	$737(3)$
C(3a)	$2\ 871(9)$	$4\ 905(7)$	$1\ 027(3)$
C(4)	$2\ 573(12)$	$3\ 906(8)$	$1\ 443(3)$
C(5)	$3\ 948(11)$	$3\ 283(11)$	$1\ 702(5)$
C(6)	$5\ 434(9)$	$4\ 128(9)$	$1\ 717(3)$
C(7)	$5\ 721(11)$	$4\ 656(12)$	$1\ 151(4)$
C(1a)	$4\ 328(9)$	$5\ 283(8)$	$898(3)$
C(11)	$5\ 209(15)$	$5\ 289(13)$	$2\ 105(5)$
C(10)	$6\ 772(13)$	$3\ 225(14)$	$1\ 892(5)$

them were not suitable for indexing and intensity data collection. Many had to be selected before a satisfactory crystal was obtained. Finally a piece for each of the compounds was chosen. Some of their reflections also showed broad peak profiles but the diffracted X-rays from the crystal diverged by such a small angle that the intensity were considered to contain enough information to make an elucidation of the structure possible. Experimental details are shown in Table 6. Unit-cell parameters were determined by a least-squares fit of 13–16 peak maxima with 2θ ranging from 10 to 25°. Three standard reflections, no intensity variation, 1349 and 3639 reflections were collected for **1a** and **4a**, respectively. No absorption correction was applied to the data. After Lorentz and polarization correction, 820 and 680 unique reflections having intensities $I > 3.0\sigma(I)$ for **1a** and **4a** were considered observed and were used in the structure analysis.

Based on the systematic absence: $0k0$, $k = 2n + 1$ and E-statistics: $|E^2 - 1| = 0.782$, the space group $P2_1$ was chosen for **1a**. This acentric space group was also confirmed by structure refinement. The space group for **4a** was derived from the following systematic absence: $0kl, k = 2n + 1$; $h0l, l = 2n + 1$; $hk0, h = 2n + 1$. Both structures were solved by direct methods and successive Fourier syntheses. Full-matrix least-squares method based on F was used. The positions for all hydrogen atoms were deduced from difference electron-density maps and were refined with isotropic thermal parameters. The absolute configuration of **1a** was determined with final refinements of the structure with Rogers' η value,[32] which gave $\eta = 1.98(8)$ for the final positions that appear in Table 7. Scattering factors were taken from ref. 33. All calculations were performed on a DEC Micro Vax II computer system using the SHELXTL-Plus

programs.[34] A full list of isotropic and anisotropic thermal parameters and hydrogen-atom coordinates has been deposited at the Cambridge Crystallographic Data Centre.*

Chromatographic Enantiomer Separation.—This was performed with the equipment described by Isaksson and Roschester[35] with methanol as the mobile phase. Neither **1b** nor **4b** gave baseline separation of the UV trace, but by selection of fractions in the first part of the first band and in the last part of the second band and recycling these, complete separation into pure enantiomers was achieved.

CNDO/S Calculations.—These calculations were performed with the program described in ref. 24, employing the Ohno formalism for calculation of two-centre coulomb integrals.[36] The program allows interaction between a maximum of 99 singly excited configurations, but the calculations reported are obtained with only 20 configurations. Increasing the number of configurations to 99 has only moderate effects on transition energies and oscillator strengths, but the mixing in of higher energy transitions complicates the analysis of the various transitions.

Instruments.—NMR spectra were recorded with a Varian Model XL-300 NMR spectrometer, UV spectra with a Cary Model 2290 spectrophotometer, CD spectra with a Jasco Model J-500A spectropolarimeter, and mass spectra with a Jeol Model SX-102 mass spectrometer.

* For details of the CCDC deposition scheme see 'Instructions for Authors (1991),' *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

References
1 Agha Z. Khan and J. Sandström, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2085.
2 S.-O. Lawesson, J. Perregaard, S. Scheibye, H. J. Meyer and I. Thomsen, *Bull. Soc. Chim. Belg.*, 1977, **86**, 679.
3 M. P. Cava and M. I. Levinson, *Tetrahedron*, 1985, **41**, 5061.
4 E. I. G. Brown, D. Leaver and T. J. Rawlings, *J. Chem. Soc., Chem. Commun.*, 1969, 83.
5 G. Calzaferri and R. Gleiter, *J. Chem. Soc., Perkin Trans. 2*, 1975, 559.
6 K. Steliou and M. Mrani, *J. Am. Chem. Soc.*, 1984, **104**, 3104.
7 W. A. Sheppard and J. Dickman, *J. Am. Chem. Soc.*, 1964, **86**, 1891.
8 Y. Tominaga, H. Norisue and C. Kamio, *Heterocycles*, 1990, **31**, 1.
9 G. A. Jeffrey and R. Shiono, *Acta Crystallogr.*, 1959, **12**, 447.
10 E. Block, R. E. Penn, R. J. Olsen and P. F. Sherwin, *J. Am. Chem. Soc.*, 1976, **98**, 1264.
11 R. A. Bates and G. A. Wolfe, *J. Am. Chem. Soc.*, 1968, **90**, 6854.
12 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 260.
13 P. L. Johnson and I. C. Paul, *J. Chem. Soc. B*, 1970, 1296.
14 A. Kucsman and I. Kapovits, in *Studies in Organic Chemistry 19. Organic Sulfur Chemistry. Theoretical and Experimental Advances*, eds. F. Bernardi, I. G. Ccizmadia and A. Mangani, Elsevier, Amsterdam, 1985, p. 191.
15 M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternhell and P. W. Westerman, *J. Am. Chem. Soc.*, 1975, **97**, 1482.
16 G. Hesse and R. Hagel, *Chromatographia*, 1976, **9**, 62.
17 A. Mannschreck, H. Koller and R. Wernicke, *Kontakte (Darmstadt)*, 1985, **1**, 40, and references cited therein.
18 R. Isaksson, P. Erlandsson, L. Hansson, A. Holmberg and S. Berner, *J. Chromatogr.*, 1990, **498**, 257.
19 J. Schellman, *Acc. Chem. Res.*, 1968, **1**, 144.
20 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Chemistry*, Oxford University Press, 1983.
21 E. U. Condon, W. Altar and H. Eyring, *J. Chem. Phys.*, 1937, **5**, 753.
22 J. Roschester, U. Berg, M. Pierrot and J. Sandström, *J. Am. Chem. Soc.*, 1987, **109**, 492.
23 J. Roschester and J. Sandström, *Tetrahedron*, 1989, **45**, 5081.
24 C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, *Tetrahedron*, 1973, **29**, 3399.
25 L. Fälth, U. Håkansson and J. Sandström, *J. Mol. Struct. (Theochem)*, 1989, **186**, 239.
26 R. G. Cooks, D. H. Williams, K. M. Johnson and J. D. Stride, *J. Chem. Soc. C*, 1968, 2199.
27 W. Kirkor and J. Baranowicz, *Lodz. Towarz. Nauk. Wydzial III, Acta Chim.*, 1962, **8**, 69 (*Chem. Abstr.*, 1963, **59**, 7414).
28 W. C. Still, M. Khan and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
29 D. N. Harpp and K. Steliou, *Synthesis*, 1976, **11**, 721.
30 T. L. Guggenheim, *Tetrahedron Lett.*, 1984, **25**, 1253.
31 B. Zwanenburg, A. Wagenaar, L. Thijs and J. Strating, *J. Chem. Soc., Perkin Trans. 1*, 1973, 73.
32 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
33 *International Tables for X-Ray Crystallography*, vol. IV, Kynoch Press, Birmingham, 1974. (Present distributor: Kluwer Academic Publishers, Dordrecht.)
34 G. M. Sheldrick, *SHELXTL-Plus Crystallographic System*, version 4, Siemens Analytical Inc., Madison, WI, 1990.
35 R. Isaksson and J. Roschester, *J. Org. Chem.*, 1985, **50**, 2519.
36 K. Ohno, *Theor. Chim. Acta*, 1964, **2**, 219.