

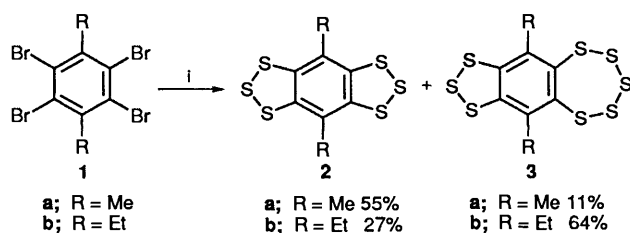
## Oxidation of Benzotrithiole Analogues. Photochemical Rearrangement of Benzotrithiole 2-Oxides to Benzotrithiole 1-Oxides involving Intramolecular Oxygen Migration

Naoki Yomoji, Shouichi Takahashi, Shin-ichi Chida, Satoshi Ogawa and Ryu Sato\*

Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka 020, Japan

4,8-Dialkylbenzo[1,2-*d*;4,5-*d'*]bis[1,2,3]trithioles **2** were readily oxidized by *m*-chloroperbenzoic acid, *N*-bromosuccinimide and *N*-iodosuccinimide to form both benzobistrithiole 1- and 2-oxides (**4** and **5**), and the ratio was dramatically affected by the kind of oxidizing agent used. Irradiation of the oxidized products, benzobistrithiole 2-oxides **5**, in acetonitrile with a high-pressure mercury lamp gave benzobistrithiole 1-oxides **4** quantitatively. Photolysis of benzo- and naphtho-trithiole 2-oxides also yielded benzo- and naphtho-trithiole 1-oxides. These photochemical oxygen migrations were shown to proceed intramolecularly *via* an excited singlet state by  $^{18}\text{O}$ -labelled, cross-over and triplet quencher experiments.

Recently, benzopentathiepine and benzotrithiole derivatives, *i.e.*, varacin and lissoclinotoxin A which exhibit potent antifungal activity and cytotoxicity, have been isolated from the methanolic extracts of marine organisms.<sup>1</sup> Therefore, considerable interest has been focussed on the preparations, structures and reactivity of cyclic polysulfides such as benzopentathiepinines and benzotrithioles. Although there have been many reports on the preparation and reactions of benzopentathiepinines,<sup>2</sup> only a few examples on those of benzotrithioles have been reported.<sup>2a,3</sup> We previously reported the synthesis of novel benzotrithiole analogues, *viz.* 4,8-dialkylbenzobistrithioles **2** (Scheme 1), and the characterization of their structures by X-ray crystallographic analysis.<sup>4</sup>

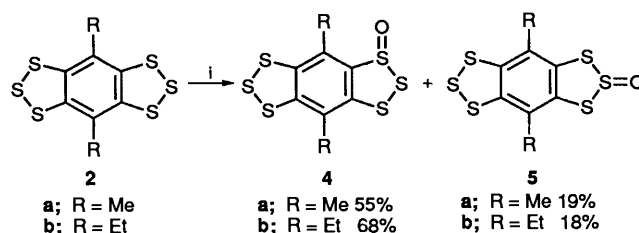


Scheme 1 Reagents and conditions: i,  $\text{S}_8$ ,  $\text{NH}_3$ , 100 °C, 24 h

As a part of our study directed towards the preparation and reactions of trithioles, we have carried out a systematic study on the oxidation of benzobistrithioles **2** by several oxidizing agents and have found that regioselectivity in the oxidation of the sulfur atom in the benzobistrithiole framework was affected by the kind of oxidizing agent used. Furthermore, we have found that the oxidized products, 4,8-dialkylbenzobistrithiole 2-oxides **5**, were slowly converted into 4,8-dialkylbenzobistrithiole 1-oxides **4** on exposure to diffuse light. Here we report on (i) oxidation of benzobistrithioles with several oxidizing agents and (ii) intramolecular photochemical oxygen migration of benzobistrithiole 2-oxides and related sulfoxides.<sup>5</sup>

### Results and Discussion

**Oxidation of Benzobistrithioles 2.**—The oxidation of 4,8-dimethylbenzobistrithiole **2a** with *m*-chloroperbenzoic acid (MCPBA) (1 mol equiv.) at 0 °C for 3 h in the dark gave two oxidized products, 4,8-dimethylbenzobistrithiole 1-oxide **4a** and 4,8-dimethylbenzobistrithiole 2-oxide **5a** in 55 and 19%



Scheme 2 Reagents and conditions: i, MCPBA (1 mol equiv.),  $\text{CH}_2\text{Cl}_2$ , 0 °C, 3 h

yield, respectively (Scheme 2). All oxidations of substrates **2** were carried out in the dark because the oxidized products **5** were slowly converted into their isomers **4** on exposure to diffuse light (as will be related in the latter part of this paper).

The unsymmetrical structure of 1-oxide **4a** was confirmed spectroscopically as follows. The  $^1\text{H}$  NMR spectrum of compound **4a** revealed two singlet peaks, at  $\delta$  2.57 and 2.77, and the  $^{13}\text{C}$  NMR spectrum exhibited eight resonances; six peaks based on six non-equivalent aromatic carbons and two peaks based on two non-equivalent methyl carbons. The IR spectrum of compound **4a** showed a characteristic absorption for an  $-\text{S}-\text{SO}-$  group at  $1083\text{ cm}^{-1}$ . The symmetrical structure of 2-oxide **5a** was also confirmed by a similar procedure to that for compound **4a**. The  $^1\text{H}$  NMR spectrum for 2-oxide **5a** revealed a singlet peak at  $\delta$  2.50 and its  $^{13}\text{C}$  NMR spectrum showed four peaks; three peaks due to aromatic carbons and a peak due to the methyl carbons. Thus, these NMR spectra suggested that compound **5a** has  $\text{C}_s$  symmetry. The IR spectrum of compound **5a** showed a characteristic absorption for the  $-\text{S}-\text{SO}-$  group at  $1124\text{ cm}^{-1}$ .

The oxidation of 4,8-diethylbenzobistrithiole **2b** with 1 mol equiv. of MCPBA under the same conditions also gave two oxidized products, 4,8-diethylbenzobistrithiole 1-oxide **4b** and 4,8-diethylbenzobistrithiole 2-oxide **5b** in 68 and 18% yield, respectively (Scheme 2). The structures of 1-oxide **4b** and 2-oxide **5b** were determined by the same procedures as those used for compounds **4a** and **5a**. These spectral data are given in the Experimental section.

The oxidation of benzobistrithioles **2** with 2 mol equiv. of MCPBA or further oxidation of 1-oxides **4** and 2-oxides **5** with 1 mol equiv. of MCPBA gave a complex mixture.

In summary, we found that the oxidation of benzobistrithioles **2** with MCPBA gave the 1-oxides **4** preferentially,

regardless of the substituents bound to the benzene ring of substrate **2**. These results suggest that the terminal sulfur atoms in the trithiole rings of **2** are more electron-rich compared with the middle sulfur atoms since MCPBA acts as an electrophilic oxidizing agent. In addition, the formation of the 2-oxides **5** in the reaction of compounds **2** with MCPBA can be regarded as unique since the oxidation of Rasheed and Warkentin's trithiole with peracetic acid gave the corresponding 1-oxide as the sole product.<sup>3a</sup>

Some interesting results were obtained by the oxidation of benzobisthioles **2** with *N*-halogenosuccinimides. Thus, the oxidation of compounds **2** with 1 mol equiv. of *N*-bromosuccinimide (NBS) in aqueous dioxane at room temperature for 3 h in the dark gave 1-oxides **4** (**4a**, 60%; **4b**, 65%) together with a trace amount of 2-oxides **5** (**5a** and **5b**,  $\leq 3\%$ ). This predominant oxidation of the terminal sulfur suggested that NBS acted as a more mild and selective oxidizing agent for substrates **2** than MCPBA. Unexpectedly, the oxidation of substrates **2** with 1 mol equiv. of *N*-iodosuccinimide (NIS) for 24 h under the same conditions gave the 2-oxides **5** (**5a**, 42%; **5b**, 41%) as the sole products. Thus, we found that the regioselectivity in the oxidation was dramatically affected by the kind of oxidizing agent used. It is well known that the oxidation of sulfide to sulfoxide with *N*-halogenosuccinimide proceeds *via* an initial nucleophilic attack of the sulfur atom on the halogen atom of the *N*-halogenosuccinimide to form the halogenosulfonium ion as an intermediate, followed by hydrolysis to give the corresponding sulfoxide.<sup>6</sup> However, the mechanism of the NIS oxidation of substrates **2** could be different from that of the general electrophilic oxidation in this case. Although these unusual differences in the regioselectivity between NBS and NIS oxidation cannot be explained at this time, both 1- and 2-oxides were easily obtained after separation by column chromatography.

**Intramolecular Photochemical Oxygen Migrations.**—When the 2-oxides **5** in the solid state or in acetonitrile were exposed to diffuse light for 5 days, oxygen migration took place to give the 1-oxides **4** in  $\sim 20\%$  yield. Irradiation of the 2-oxides **5** in MeCN with a 100 W high-pressure mercury lamp using a Pyrex filter for 1 h gave the 1-oxides **4** quantitatively (Scheme 3).

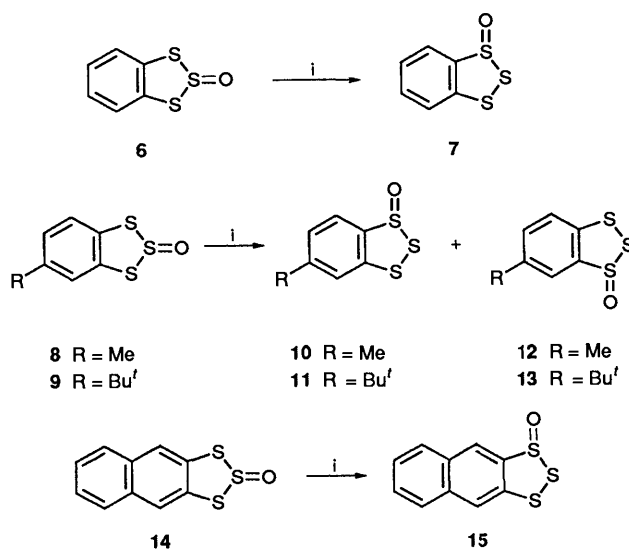


Scheme 3 Conditions: *i*, *h* $\nu$ , MeCN, 1 h (**4** quant.)

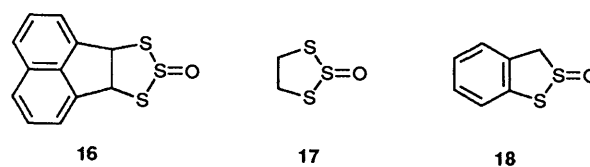
These migrations, however, did not occur thermally and were not initiated by the addition of an acid such as trifluoroacetic acid in the dark. On the other hand, photolysis of 1-oxides **4** under the same conditions left substrates **4** unchanged quantitatively.

To explore the generality of these photochemical oxygen migrations, 1,2,3-benzotrithiole 2-oxides **6**,<sup>7a</sup> **8**,<sup>7b</sup> and **9**, naphtho[2,3-*d*]-1,2,3-trithiole 2-oxide **14**, dihydroacenaphtho[1,2-*d*][1,2,3]trithiolane 8-oxide **16**, 1,2,3-trithiolane 2-oxide **17**, and 3*H*-1,2-benzodithiole 2-oxide **18**, were examined. Photolysis of symmetrical trithiole 2-oxides **6** and **14** in MeCN gave 1,2,3-benzotrithiole 1-oxide **7** and naphtho[2,3-*d*][1,2,3]trithiole 1-oxide **15** in 84 and 88% yield, respectively. Similar irradiation of unsymmetrical trithiole 2-oxides **8** and **9** gave an inseparable mixture ( $\sim 1:1$ ) of the corresponding 1-oxides **10** and **11** and the 3-oxides **12** and **13** (*R* = Me, 85%; *R* = Bu<sup>t</sup>, 83%), respectively. These reactions are summarized in Scheme 4.

On the other hand, dihydroacenaphthotrithiolane 8-oxide **16**, trithiolane 2-oxide **17** and benzodithiole 2-oxide **18** were not converted into the corresponding 1-oxides by irradiation. Accordingly, it is likely that the aromatic ring fused to the



Scheme 4 Conditions: *i*, *h* $\nu$ , MeCN, 1 h

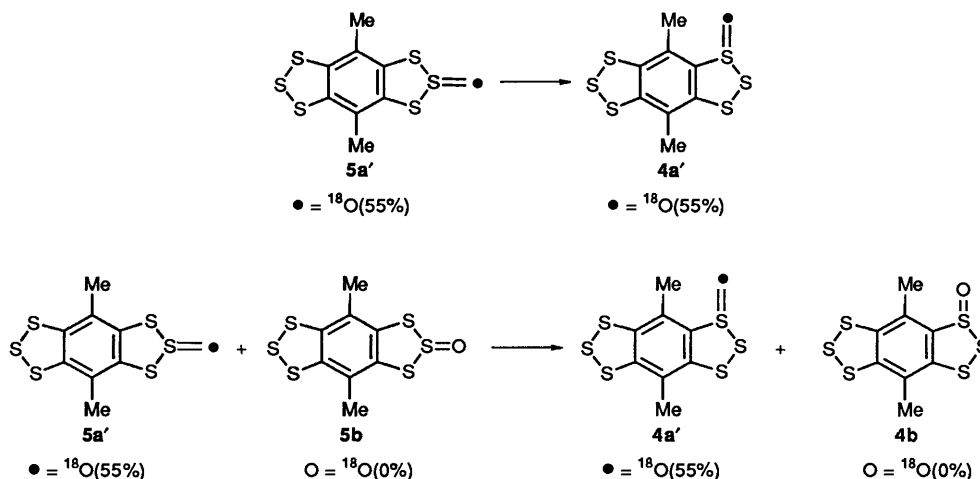
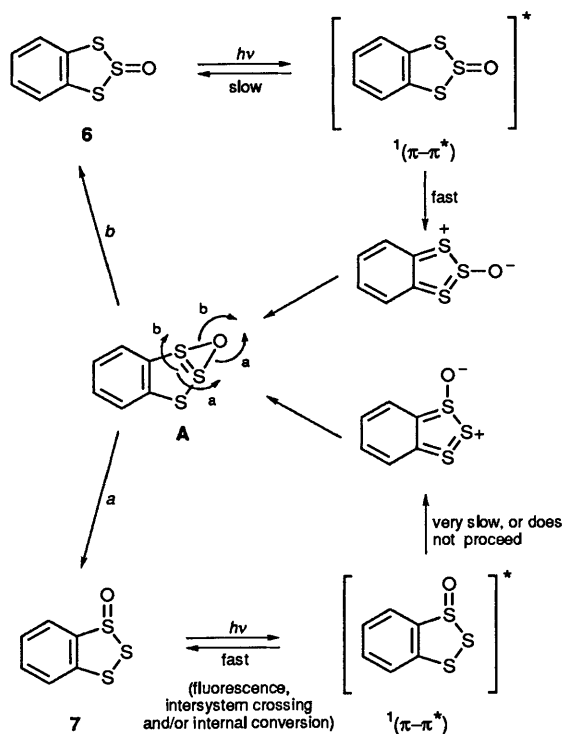


trithiole 2-oxide ring plays an important role in these oxygen migrations.

In order to determine whether the oxygen migration proceeds intra- or inter-molecularly, we carried out <sup>18</sup>O-labelled and cross-over experiments. <sup>18</sup>O-labelled 2-oxide **5a'** (<sup>18</sup>O content 55%) was prepared by the treatment of compound **2a** with NIS (1 mol equiv.) followed by hydrolysis with H<sub>2</sub><sup>18</sup>O. Photolysis of the <sup>18</sup>O-labelled 2-oxide **5a'** in MeCN containing dissolving oxygen gave <sup>18</sup>O-containing 1-oxide **4a'** (<sup>18</sup>O content 55%). The possibility for a trioxide intermediate which was reported on the O<sub>2</sub>-catalysed isomerization of trinorbornanetrithiolane 2-oxide is ruled out.<sup>8</sup> The cross-over photolysis experiment using a 1:1 mixture of <sup>18</sup>O-labelled 2-oxide **5a'** and non-labelled 2-oxide **5b** in MeCN under argon gave <sup>18</sup>O-containing 1-oxide **4a'** (<sup>18</sup>O content 55%) and none-<sup>18</sup>O-incorporating 1-oxide **4b**. These results clearly indicate that the photochemical oxygen migration proceeded intramolecularly, and are summarized in Scheme 5.

Furthermore, it seems that these oxygen migrations proceeded *via* an excited singlet state because the reactions were not quenched under irradiation in the presence of some triplet quenchers such as oxygen, cyclohexa-1,3-diene and penta-1,3-diene. Trithiole 2-oxides **5**, **6**, **8**, **9** and **14** in MeCN showed a strong UV absorption band in the range 245–285 nm ( $\epsilon \sim 8000$ ) which could be assigned as a  $\pi$ - $\pi^*$  transition of the aromatic ring fused to the trithiole 2-oxide ring. It appears attractive to assume that the reaction started from the  $\pi$ - $\pi^*$  transition since photolysis of trithiole 2-oxides in a quartz tube increased the yields of the corresponding 1- and 3-oxides.

**Proposed Mechanism.**—On the basis of the results described above, although a possible mechanism which may involve ring opening cannot be ruled out, we propose a mechanism for these photochemical rearrangements without ring opening<sup>9</sup> as shown in Scheme 6, where \* indicates benzotrithiole monoxide singlet. Benzotrithiole 2-oxide **6** is first photolysed to form singlet excited **6**, which is rapidly transformed into the strained intermediate **A**. According to path *a* and path *b*, intermediate **A** is converted into

Scheme 5 Conditions: i,  $h\nu$ , MeCN,  $\text{O}_2$ , 1 h; ii,  $h\nu$ , MeCN, 1 hScheme 6 Plausible mechanism for the rearrangement 6  $\rightarrow$  7

benzotrithiole 1-oxide 7 and back to the 2-oxide 6, respectively. Although benzotrithiole 1-oxide 7 is also converted into its excited singlet state by irradiation, the rate of quenching (involving fluorescence, intersystem crossing and/or internal conversion) of singlet excited 7 may be much faster than that of conversion of singlet excited 7 into intermediate A. Consequently, the reaction is characteristic of a one-way photochemical rearrangement involving intramolecular oxygen migration.

**Conclusions.**—The regioselective oxidation of benzotrithiole analogues has shown that the terminal sulfur atoms in the trithiole rings are more electron rich than are the middle sulfur atoms. We have demonstrated, to the best of our knowledge,<sup>10</sup> the first photochemical oxygen migration which proceeded intramolecularly *via* an excited singlet state of benzotrithiole 2-oxides and their analogues.

## Experimental

**General Details.**—M.p.s were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Hitachi 295 or on a JASCO FT-7300 spectrometer. UV spectra were recorded on a JASCO Ubest-30 UV/VIS spectrophotometer. NMR spectra were recorded on a Hitachi R-22, a Varian XL-GEM200, a JEOL EX270 or a Bruker AC400P instrument. All NMR spectra were recorded in deuteriochloroform as solvent and the chemical shifts were recorded relative to internal tetramethylsilane as standard. Coupling constants ( $J$ ) are given in Hz. Mass spectra were obtained on a Hitachi M-2000 mass spectrometer. Elemental analyses were performed on a Yanagimoto MT-3 instrument.

**Preparation of 4,8-Dimethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2a.**—Liquid ammonia (30 cm<sup>3</sup>) was charged into an evacuated titanium autoclave containing 1,2,4,5-tetrabromo-3,6-dimethylbenzene 1a (422 mg, 1 mmol) and elemental sulfur (800 mg, 25 mmol). The reaction mixture was heated at 100 °C for 24 h and was then cooled to room temperature. The reaction mixture was added to hexane (400 cm<sup>3</sup>) containing *m*-dinitrobenzene (400 mg) through a needle valve. The solution was stirred at room temperature until the liquid ammonia had evaporated off completely and then the solvent was removed under reduced pressure. The resulting reaction mixture was chromatographed on silica gel with carbon tetrachloride-hexane (1 : 3) as eluent to give a mixture of the title compound 2a and 6,10-dimethyl[1,2,3]trithio[4,5-h]benzopentathiepine 3a. Fractional crystallization of the mixture from methylene dichloride yielded the title compound 2a (162 mg, 55%) as dark red needles. Evaporation of the filtrate followed by recrystallization from methylene dichloride yielded tricycle 3a (39 mg, 11%) as reddish crystals. When the reaction mixture was added to methylene dichloride instead of hexane, the product yields were changed to 2a (11%) and 3a (70%); see ref. 4.

**Data for compound 2a;** m.p. 214–215 °C (Found: C, 32.5; H, 2.1. C<sub>8</sub>H<sub>6</sub>S<sub>6</sub> requires C, 32.6; H, 2.05%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 2905, 1410, 1370, 1325, 1295, 1130 and 1000;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm 239 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  9400), 294 (13 900) and 351 (2200);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.40 (s, Me);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 24.57 (Me), 141.33; another *ipso* carbon could not be detected because compound 2a was only slightly soluble in general deuteriosolvents;  $m/z$  294 (M<sup>+</sup>, 100%), 262 (33) and 230 (11).

**Data for compound 3a;** m.p. 129–131 °C (Found: C, 26.7; H, 1.7. C<sub>8</sub>H<sub>6</sub>S<sub>8</sub> requires C, 26.8; H, 1.7%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 2910, 1400, 1370, 1320, 1295, 1115 and 995;  $\lambda_{\text{max}}$ (hexane)/nm 292 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  15 500) and 365sh;  $\delta_{\text{H}}$  (400 MHz;

$\text{CDCl}_3$ ) 2.62 (s, Me);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 24.89 (Me), 136.03, 143.99 and 144.82;  $m/z$  358 ( $\text{M}^+$ , 18%), 294 (100) and 262 (28).

**Preparation of 4,8-Diethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2b.**—In a similar manner to that described for compound **2a**, 1,2,4,5-tetrabromo-3,6-diethylbenzene **1b** (450 mg, 1 mmol) was converted into the *title compound 2b* (87 mg, 27%) as dark red needles (from  $\text{CH}_2\text{Cl}_2$ ) and 6,10-diethyl[1,2,3]trithiolo[4,5-h]benzopentathiepine **3b** (247 mg, 64%) as reddish brown crystals (from  $\text{CH}_2\text{Cl}_2$ ).

Data for compound **2b**; m.p. 142–143 °C (Found: C, 36.95; H, 3.0.  $\text{C}_{10}\text{H}_{10}\text{S}_6$  requires C, 37.2; H, 3.1%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2950, 2910, 1440, 1375, 1345, 1330, 1305, 1120 and 1050;  $\nu_{\text{max}}(\text{hexane})/\text{nm}$  239 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  8300), 298 (11 800) and 348 (1800);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.17 (6 H, t, *J* 7.6,  $\text{MeCH}_2$ ) and 2.74 (4 H, q, *J* 7.6,  $\text{MeCH}_2$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 13.43 ( $\text{MeCH}_2$ ), 33.22 ( $\text{MeCH}_2$ ), 133.59 and 141.20;  $m/z$  322 ( $\text{M}^+$ , 100%), 307 (3), 290 (5) and 258 (12).

Data for compound **3b**; m.p. 115–116 °C (Found: C, 30.9; H, 2.6.  $\text{C}_{10}\text{H}_{10}\text{S}_8$  requires C, 31.1; H, 2.6%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2950, 2910, 2850, 1440, 1360, 1335, 1305, 1200, 1120 and 1055;  $\nu_{\text{max}}(\text{hexane})/\text{nm}$  268 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  9500), 294 (15 100) and 362 (2800);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.20 (6 H, t, *J* 7.5,  $\text{MeCH}_2$ ), 2.98 (2 H, dq, *J* 13.6 and 7.5,  $\text{MeCHH}$ ) and 3.07 (2 H, dq, *J* 13.6 and 7.5,  $\text{MeCHH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.59 ( $\text{MeCH}_2$ ), 32.60 ( $\text{MeCH}_2$ ), 142.31, 143.86 and 144.86;  $m/z$  386 ( $\text{M}^+$ , 8%), 322 (100) and 258 (28).

**Oxidation of 4,8-Dimethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2a with MCPBA.**—To a solution of dimethylbenzobistrithiole **2a** (60 mg, 0.2 mmol) in methylene dichloride (90  $\text{cm}^3$ ) at 0 °C was added slowly a solution of MCPBA (Kanto; 87% purity; 40 mg, 0.2 mmol, 1 mol equiv.) in methylene dichloride (10  $\text{cm}^3$ ). After completion of the addition, the mixture was stirred for 3 h at 0 °C, then was washed successively with 10% aq. sodium hydrogen sulfite (2  $\times$  10  $\text{cm}^3$ ), 10% aq. sodium hydrogen carbonate (2  $\times$  10  $\text{cm}^3$ ), and brine (2  $\times$  10  $\text{cm}^3$ ). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Chromatography of the residue on silica gel with chloroform–carbon tetrachloride (1:1) as eluent yielded 4,8-dimethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 1-oxide **4a** (34 mg, 55%) as yellow crystals (from chloroform–hexane) and 4,8-dimethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2-oxide **5a** (12 mg, 19%) as yellow needles (from chloroform–hexane).

Data for compound **4a**; m.p. 226 °C (decomp.) (Found: C, 31.0; H, 1.9.  $\text{C}_8\text{H}_6\text{OS}_6$  requires C, 30.9; H, 1.95%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2908, 1395, 1304 and 1083 (–SO–S–);  $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$  252 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  8500), 286 (9600) and 362 (2500);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.57 (3 H, s, Me) and 2.77 (3 H, s, Me);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 23.27 (Me), 24.58 (Me), 126.78, 129.24, 141.93, 146.00, 146.66 and 149.74;  $m/z$  310 ( $\text{M}^+$ , 39%), 294 (51) and 262 (100).

Data for compound **5a**; m.p. 223 °C (decomp.) (Found: C, 31.0; H, 2.0%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2923, 1399, 1323 and 1124 (–SO–S–);  $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$  219 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  18 700), 282 (8500) and 342 (1500);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.50 (s, Me);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 24.63 (Me), 127.25, 135.63 and 142.62;  $m/z$  310 ( $\text{M}^+$ , 76%), 294 (40) and 262 (100).

**Oxidation of 4,8-Diethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2b with MCPBA.**—In a similar manner to that described for compound **2a**, diethylbenzobistrithiole **2b** (72 mg, 0.2 mmol) was oxidized with MCPBA (40 mg, 0.2 mmol, 1 mol equiv.) to give 4,8-diethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 1-oxide **4b** (46 mg, 68%) as yellow crystals (from chloroform–hexane) and 4,8-diethylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2-

oxide **5b** (12 mg, 18%) as yellow needles (from chloroform–hexane).

Data for compound **4b**; m.p. 158 °C (decomp.) (Found: C, 35.3; H, 3.0.  $\text{C}_{10}\text{H}_{10}\text{OS}_6$  requires C, 35.5; H, 3.0%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2950, 1500, 1445, 1385, 1330, 1130 and 1090 (–SO–S–);  $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$  254 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  7200), 290 (8100) and 365 (2200);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.29 (3 H, t, *J* 7.6,  $\text{MeCH}_2$ ), 1.33 (3 H, t, *J* 7.6,  $\text{MeCH}_2$ ), 2.92 (1 H, dq, *J* 14.1 and 7.6,  $\text{MeCHH}$ ), 2.93 (1 H, dq, *J* 14.1 and 7.6,  $\text{MeCHH}$ ), 3.10 (1 H, dq, *J* 14.8 and 7.6,  $\text{MeCHH}$ ) and 3.13 (1 H, dq, *J* 14.8 and 7.6,  $\text{MeCHH}$ );  $\delta_{\text{C}}$  (67 MHz;  $\text{CDCl}_3$ ) 12.76 ( $\text{MeCH}_2$ ), 14.72 ( $\text{MeCH}_2$ ), 31.81 ( $\text{MeCH}_2$ ), 33.44 ( $\text{MeCH}_2$ ), 133.35, 135.85, 141.56, 145.46, 146.79 and 149.90;  $m/z$  338 ( $\text{M}^+$ , 59%), 322 (36) and 290 (100).

Data for compound **5b**; m.p. 118 °C (decomp.) (Found: C, 35.2; H, 3.0%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2900, 1440, 1385, 1340 and 1110 (–SO–S–);  $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$  221 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  21 200), 284 (10 800) and 339 (1900);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.22 (6 H, t, *J* 7.6,  $\text{MeCH}_2$ ), 2.83 (2 H, dq, *J* 14.2 and 7.6,  $\text{MeCHH}$ ) and 2.87 (2 H, dq, *J* 14.2 and 7.6,  $\text{MeCHH}$ );  $\delta_{\text{C}}$  (67 MHz;  $\text{CDCl}_3$ ) 13.08 ( $\text{MeCH}_2$ ), 33.19 ( $\text{MeCH}_2$ ), 133.82, 135.43 and 142.42;  $m/z$  338 ( $\text{M}^+$ , 64%), 322 (35) and 290 (100).

**Oxidation of compound 2a with NBS.**—To a solution of dimethylbenzobistrithiole **2a** (30 mg, 0.1 mmol) in 10% aq. 1,4-dioxane (90  $\text{cm}^3$ ) was added a solution of NBS (Tokyo Kasei; 80% purity; 23 mg, 0.1 mmol, 1 mol equiv.) in 1,4-dioxane (5  $\text{cm}^3$ ). The mixture was stirred for 3 h at room temperature before being poured into water and extracted with methylene dichloride (3  $\times$  20  $\text{cm}^3$ ). The organic layer was washed successively with saturated aq. sodium thiosulfate (1  $\times$  10  $\text{cm}^3$ ) and brine (3  $\times$  20  $\text{cm}^3$ ), dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Chromatography of the residue on silica gel with chloroform–carbon tetrachloride (1:1) as eluent yielded dimethylbenzobistrithiole 1-oxide **4a** (19 mg, 60%) and a trace amount of dimethylbenzobistrithiole 2-oxide **5a** ( $\leq$  1 mg,  $\leq$  3%).

**Oxidation of compound 2b with NBS.**—In a similar manner to that described for the oxidation of compound **2a** with NBS, diethylbenzobistrithiole **2b** (32 mg, 0.1 mmol) was oxidized with NBS (23 mg, 0.1 mmol, 1 mol equiv.) to give diethylbenzobistrithiole 1-oxide **4b** (22 mg, 65%) and a trace amount of diethylbenzobistrithiole 2-oxide **5b** ( $\leq$  1 mg,  $\leq$  3%).

**Oxidation of compound 2a with NIS.**—In a similar manner to that described for the oxidation of compound **2a** with NBS except for the reaction time (24 h), dimethylbenzobistrithiole **2a** (30 mg, 0.1 mmol) was oxidized with NIS (Tokyo Kasei; 76% purity; 30 mg, 0.1 mmol, 1 mol equiv.) to give dimethylbenzobistrithiole 2-oxide **5a** (13 mg, 42%).

**Oxidation of compound 2b with NIS.**—In a similar manner to that described for the oxidation of compound **2a** with NIS, diethylbenzobistrithiole **2b** (32 mg, 0.1 mmol) was oxidized with NIS (30 mg, 0.1 mmol, 1 mol equiv.) to give diethylbenzobistrithiole 2-oxide **5b** (14 mg, 41%).

**Photolysis of Benzobistrithiole 2-Oxides 5.**—A solution of the benzobistrithiole 2-oxide **5a** (8 mg, 0.026 mmol) or **5b** (9 mg, 0.026 mmol) in acetonitrile (20  $\text{cm}^3$ ) under argon was irradiated through a Pyrex filter with a 100 W high-pressure mercury lamp for 1 h. After evaporation of the solvent, TLC analysis on silica gel with chloroform–carbon tetrachloride (1:1) revealed that substrate **5a** or **5b** ( $R_f$  0.6) was converted into the corresponding benzobistrithiole 1-oxides **4a** or **4b** ( $R_f$  0.3) quantitatively.

**1,2,3-Benzotrithiole 2-Oxide 6.**—To a solution of benzene-1,2-dithiol (1.42 g, 10 mmol) in benzene (90 cm<sup>3</sup>) was added dropwise a solution of thionyl dichloride (0.8 cm<sup>3</sup>, 11 mmol) in benzene (10 cm<sup>3</sup>). After completion of the addition, the reaction mixture was stirred for 1 h. The resulting yellow mixture was washed successively with 10% aq. sodium hydrogen carbonate (2 × 20 cm<sup>3</sup>) and brine (3 × 20 cm<sup>3</sup>), dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Chromatography of the residue on silica gel with chloroform-carbon tetrachloride (1 : 1) as eluent yielded the title compound **6** (1.43 g, 76%) as yellow needles (from chloroform-hexane), m.p. 76–77 °C (lit.,<sup>7a</sup> 77 °C) (Found: C, 38.5; H, 2.4. Calc. for C<sub>6</sub>H<sub>4</sub>OS<sub>3</sub>: C, 38.3; H, 2.1%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1556, 1442, 1425, 1250, 1108 (–SO–S–), 748 and 667;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  250 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  5300);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.35 (2 H, dd, *J* 5.9 and 2.7, ArH) and 7.59 (2 H, dd, *J* 5.9 and 2.7, ArH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 124.58, 127.31 and 135.70; *m/z* 188 (M<sup>+</sup>, 100%), 172 (14) and 140 (100).

**5-Methyl-1,2,3-benzotrithiole 2-Oxide 8.**—In a similar manner to that described for compound **6**, the treatment of 4-methylbenzene-1,2-dithiol (1.56 g, 10 mmol) with thionyl dichloride (0.8 cm<sup>3</sup>, 11 mmol) gave the title compound **8** (1.58 g, 78%) as yellow needles (from chloroform-hexane), m.p. 95–96 °C (lit.,<sup>7b</sup> 97.3–97.8 °C) (Found: C, 41.8; H, 2.9. Calc. for C<sub>7</sub>H<sub>6</sub>OS<sub>3</sub>: C, 41.6; H, 3.0%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2915, 1581, 1455, 1256, 1110 (–SO–S–), 872 and 823;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  255 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  5000) and 310sh;  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 2.39 (3 H, s, Me), 7.16 (1 H, d, *J* 8.2, ArH), 7.40 (1 H, s, ArH) and 7.46 (1 H, d, *J* 8.2, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 20.98 (Me), 124.58, 125.20, 128.77, 132.67, 136.09 and 138.16; *m/z* 202 (M<sup>+</sup>, 98%), 186 (11) and 154 (100).

**5-tert-Butyl-1,2,3-benzotrithiole 2-Oxide 9.**—In a similar manner to that described for compound **6**, the treatment of 4-tert-butylbenzene-1,2-dithiol<sup>11</sup> (1.98 g, 10 mmol) with thionyl dichloride (0.8 cm<sup>3</sup>, 11 mmol) gave the title compound **9** (2.07 g, 85%) as a yellow oil (Found: C, 49.4; H, 5.0. C<sub>10</sub>H<sub>12</sub>OS<sub>3</sub> requires C, 49.1; H, 4.95%;  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  2963, 1455, 1379, 1255, 1128 (–SO–S–) and 818;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  254 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  7100);  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 1.33 (9 H, s, Bu<sup>t</sup>), 7.39 (1 H, dd, *J* 8.4 and 1.6, ArH), 7.52 (1 H, d, *J* 8.4, ArH) and 7.60 (1 H, d, *J* 1.6, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 31.31 (Me), 34.96 (CMe<sub>3</sub>), 121.80, 124.51, 125.42, 132.56, 136.09 and 151.72; *m/z* 244 (M<sup>+</sup>, 100%), 228 (91) and 196 (100).

**Naphtho[2,3-d][1,2,3]trithiole 2-Oxide 14.**—In a similar manner to that described for compound **6**, the treatment of naphthalene-2,3-dithiol<sup>11,12</sup> (1.92 g, 10 mmol) with thionyl dichloride (0.8 cm<sup>3</sup>, 11 mmol) gave the title compound **14** (1.98 g, 83%) as yellow plates (from chloroform-hexane), m.p. 192 °C (decomp.) (Found: C, 50.2; H, 2.4. C<sub>10</sub>H<sub>6</sub>OS<sub>3</sub> requires C, 50.4; H, 2.5%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3052, 1567, 1485, 1426, 1312, 1103 (–SO–S–), 877 and 739;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  246 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  27 800), 283 (6900) and 355sh;  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 7.54 (2 H, dd, *J* 6.3 and 3.3, ArH), 7.84 (2 H, dd, *J* 6.3 and 3.3, ArH) and 8.10 (2 H, s, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 124.12, 127.59, 127.78, 132.50 and 135.46; *m/z* 238 (M<sup>+</sup>, 22%), 222 (11) and 190 (100).

**6b,9a-Dihydroacenaphtho[1,2-d][1,2,3]trithiolane 8-Oxide 16.**—In a similar manner to that described for compound **6**, treatment of acenaphthene-1,2-dithiol (218 mg, 1.0 mmol), which was prepared by the reduction of 6b,9a-dihydroacenaphtho[1,2-d][1,2,3]trithiolane<sup>13</sup> with lithium aluminium hydride, with thionyl dichloride (0.08 cm<sup>3</sup>, 1.1 mmol) to give an inseparable mixture (~2.5 : 1) of endo- and exo-isomer **16** as yellow needles (from chloroform-hexane), m.p. 145–152 °C

(Found: C, 54.6; H, 3.0. C<sub>12</sub>H<sub>8</sub>OS<sub>3</sub> requires C, 54.5; H, 3.05%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2920, 1590, 1490, 1360, 1075 (–SO–S–), 820 and 780;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  227 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  29 800), 283sh and 295 (6600);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 6.84 (2 H, s, CH), 6.86 (2 H, s, CH), 7.44 (2 H, d, *J* 6.9, ArH), 7.51 (2 H, d, *J* 6.9, ArH), 7.57 (2 H, dd, *J* 8.0 and 6.9, ArH), 7.59 (2 H, dd, *J* 8.3 and 6.9, ArH), 7.74 (2 H, d, *J* 8.0, ArH) and 7.83 (2 H, d, *J* 8.3, ArH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 71.58, 73.65, 120.73, 121.31, 125.18, 125.93, 128.64, 128.79, 131.23, 131.46, 133.05, 134.33, 138.06 and 142.68; *m/z* 364 (2M<sup>+</sup> – 2SO – 2S – 4H, 100%).

**1,2,3-Trithiolane 2-Oxide 17.**—In a similar manner to that described for compound **6**, treatment of ethane-1,2-dithiol (0.47 g, 5 mmol) with thionyl dichloride (0.4 cm<sup>3</sup>, 5.5 mmol) gave the title compound **17** (0.60 g, 86%) as a pale yellow oil (Found: C, 17.1; H, 2.9. C<sub>2</sub>H<sub>4</sub>OS<sub>3</sub> requires C, 17.1; H, 2.9%;  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  2964, 2922, 1413, 1279, 1233, 1096 (–SO–S–), 940 and 829;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  248 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  1500);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 3.99 (2 H, ddd, *J* 16.4, 8.9 and 5.4, CHH) and 4.23 (2 H, ddd, *J* 16.4, 8.9 and 5.4, CHH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 46.66; *m/z* 140 (M<sup>+</sup>, 92%), 124 (28) and 92 (100).

**3H-1,2-Benzodithiole 2-Oxide 18.**—To a solution of 3H-1,2-benzodithiole (0.77 g, 5 mmol) in methylene dichloride (100 cm<sup>3</sup>) at 0 °C was slowly added a solution of MCPBA (1.00 g, 5 mmol, 1 mol equiv.) in methylene dichloride (20 cm<sup>3</sup>). After completion of the addition, the mixture was stirred for 1 h at 0 °C. Then the mixture was washed successively with 10% aq. sodium hydrogen sulfite (2 × 10 cm<sup>3</sup>), 10% aq. sodium hydrogen carbonate (2 × 10 cm<sup>3</sup>), and brine (2 × 10 cm<sup>3</sup>). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Chromatography of the residue on silica gel with ethyl acetate-hexane (1 : 3) as eluent yielded the title compound **18** (0.57 g, 67%) as a pale yellow oil (Found: C, 49.1; H, 3.5. C<sub>7</sub>H<sub>6</sub>OS<sub>2</sub> requires C, 49.4; H, 3.55%;  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  1458, 1440, 1379, 1081 (–SO–S–) and 739;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  236 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  8400), 279sh and 294sh;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 4.58 (2 H, s, CH<sub>2</sub>), 7.24 (1 H, dd, *J* 7.9 and 7.4, ArH), 7.33 (1 H, dd, *J* 7.6 and 7.4, ArH), 7.41 (1 H, d, *J* 7.9, ArH) and 7.44 (1 H, d, *J* 7.6, ArH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 68.21, 124.47, 126.44, 127.34, 129.15, 133.94 and 136.29; *m/z* 170 (M<sup>+</sup>, 53%), 154 (16) and 122 (100).

**Photolysis of 1,2,3-Benzotrithiole 2-Oxide 6.**—A solution of the trithiole 2-oxide **6** (19 mg, 0.1 mmol) in acetonitrile (20 cm<sup>3</sup>) under argon was irradiated through a Pyrex filter with a 100 W high-pressure mercury lamp for 1 h. After evaporation of the solvent, chromatography of the residue on silica gel with chloroform-carbon tetrachloride (1 : 1) as eluent yielded 1,2,3-benzotrithiole 1-oxide **7** (16 mg, 84%) as yellow crystals (from chloroform-hexane), m.p. 73–74 °C (Found: C, 38.4; H, 2.4. C<sub>6</sub>H<sub>4</sub>OS<sub>3</sub> requires C, 38.3; H, 2.1%;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1556, 1440, 1420, 1247, 1064 (–SO–S–), 752 and 529;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  243 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  5800), 281 (1600) and 350sh;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.39 (1 H, ddd, *J* 7.8, 7.4 and 0.9, ArH), 7.49 (1 H, ddd, *J* 7.8, 7.4 and 0.8, ArH), 7.72 (1 H, dd, *J* 7.8 and 0.8, ArH) and 7.98 (1 H, dd, *J* 7.8 and 0.9, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 123.74, 126.51, 126.61, 131.34, 145.10 and 150.19; *m/z* 188 (M<sup>+</sup>, 100%), 172 (13) and 140 (100).

**Photolysis of 5-Methyl-1,2,3-benzotrithiole 2-Oxide 8.**—In a similar manner to that described for compound **6**, photolysis of the trithiole 2-oxide **8** (20 mg, 0.1 mmol) yielded an inseparable mixture (~1 : 1) of 5-methyl-1,2,3-benzotrithiole 1-oxide **10** and 6-methyl-1,2,3-benzotrithiole 1-oxide **12** (17 mg, 85%) as a yellow viscous oil (Found: C, 41.6; H, 3.2. C<sub>7</sub>H<sub>6</sub>OS<sub>3</sub> requires C, 41.6; H, 3.0%;  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  2954, 2920, 1581, 1457, 1259, 1090 (–SO–S–) and 814;  $\lambda_{\max}(\text{MeCN})/\text{nm}$  220 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1}$

cm<sup>-1</sup> 12 300), 250sh, 287sh and 364sh;  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 2.44 (6 H, s, Me), 7.21 (1 H, d, *J* 8.1, ArH), 7.32 (1 H, d, *J* 8.1, ArH), 7.53 (1 H, s, ArH), 7.61 (1 H, d, *J* 8.1, ArH), 7.79 (1 H, s, ArH) and 7.86 (1 H, d, *J* 8.1, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 20.90 (Me), 21.36 (Me), 123.71, 124.19, 126.64, 127.14, 127.92, 132.80, 137.56, 142.08, 143.00, 145.96, 147.99 and 150.79; *m/z* 202 (M<sup>+</sup>, 33%), 186 (15) and 154 (55).

**Photolysis of 5-tert-Butyl-1,2,3-benzotrithiole 2-Oxide 9.**—In a similar manner to that described for compound **6**, photolysis of the trithiole 2-oxide **9** (24 mg, 0.1 mmol) yielded an inseparable mixture (~1:1) of 5-tert-butyl-1,2,3-benzotrithiole 1-oxide **11** and 6-tert-butyl-1,2,3-benzotrithiole 1-oxide **13** (20 mg, 83%) as a yellow oil (Found: C, 49.3; H, 5.0. C<sub>10</sub>H<sub>12</sub>OS<sub>3</sub> requires C, 49.1; H, 4.95%);  $\nu_{\text{max}}$ (neat)/cm<sup>-1</sup> 2963, 1578, 1457, 1380, 1094 (–SO–S–) and 824;  $\lambda_{\text{max}}$ (MeCN)/nm 220 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 14 000), 252sh, 292sh and 360sh;  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 1.34 (18 H, s, Bu<sup>t</sup>), 7.43 (1 H, dd, *J* 8.4 and 1.7, ArH), 7.54 (1 H, dd, *J* 8.4 and 1.8, ArH), 7.65 (1 H, d, *J* 8.4, ArH), 7.72 (1 H, d, *J* 1.7, ArH), 7.90 (1 H, d, *J* 8.4, ArH) and 7.98 (1 H, d, *J* 1.8, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 31.13, 31.22, 35.05, 35.35, 120.66, 123.49, 123.65, 124.65, 126.47, 129.51, 141.93, 145.90, 147.63, 150.81, 151.05 and 156.13; *m/z* 244 (M<sup>+</sup>, 100%), 228 (31) and 196 (100).

**Photolysis of Naphtho[2,3-d][1,2,3]trithiole 2-Oxide 14.**—In a similar manner to that described for compound **6**, photolysis of the trithiole 2-oxide **14** (24 mg, 0.1 mmol) yielded naphtho[2,3-d][1,2,3]trithiole 1-oxide **15** (21 mg, 88%) as yellow crystals (from chloroform–hexane), m.p. 132 °C (decomp.) (Found: C, 50.6; H, 2.8. C<sub>10</sub>H<sub>6</sub>OS<sub>3</sub> requires C, 50.4; H, 2.5%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 3053, 2924, 1615, 1572, 1485, 1308, 1267, 1072 (–SO–S–), 881 and 752;  $\lambda_{\text{max}}$ (MeCN)/nm 223 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 17 500), 248 (24 900), 319 (1700) and 366sh;  $\delta_{\text{H}}$  (200 MHz; CDCl<sub>3</sub>) 7.59 (1 H, t, *J* 8.0, ArH), 7.68 (1 H, t, *J* 8.0, ArH), 7.85 (1 H, d, *J* 8.0, ArH), 7.97 (1 H, d, *J* 8.0, ArH), 8.16 (1 H, s, ArH) and 8.49 (1 H, s, ArH);  $\delta_{\text{C}}$  (50 MHz; CDCl<sub>3</sub>) 122.92, 127.30, 127.70, 127.89, 129.83, 130.12, 131.19, 133.96, 140.11 and 150.10; *m/z* 238 (M<sup>+</sup>, 29%), 222 (32) and 190 (100).

**Preparation of <sup>18</sup>O-Labelled 2-Oxide 5a'.**—In a similar manner to that described for the oxidation of compound **2a** with NIS, the treatment of compound **2a** (30 mg, 0.1 mmol) with NIS (30 mg, 0.1 mmol, 1 mol equiv.) in 1,4-dioxane (90 cm<sup>3</sup>) containing H<sub>2</sub><sup>18</sup>O (Aldrich; 95% atom <sup>18</sup>O; 0.5 cm<sup>3</sup>) gave the title compound **5a'** (12 mg, 38%; <sup>18</sup>O content, 55%) as yellow needles.

**Photolysis of <sup>18</sup>O-Labelled 2-Oxide 5a'.**—A solution of the <sup>18</sup>O-labelled 2-oxide **5a'** (8 mg, 0.026 mmol; <sup>18</sup>O content 55%) in acetonitrile (20 cm<sup>3</sup>) under oxygen was irradiated through a Pyrex filter with a 100 W high-pressure mercury lamp for 1 h. After evaporation of the solvent, chromatography of the residue on silica gel with chloroform–carbon tetrachloride (1:1) as eluent yielded the <sup>18</sup>O-incorporated 1-oxide **4a'** (<sup>18</sup>O content, 55%) quantitatively.

**Cross-over Photolysis of a Mixture of <sup>18</sup>O-Labelled 2-Oxide 5a' and Non-labelled 2-Oxide 5b.**—A solution of a 1:1 mixture of <sup>18</sup>O-labelled 2-oxide **5a'** (8 mg, 0.026 mmol; <sup>18</sup>O content 55%) and non-labelled 2-oxide **5b** (9 mg, 0.026 mmol) in acetonitrile (20 cm<sup>3</sup>) under argon was irradiated through a Pyrex filter with a 100 W high-pressure mercury lamp for 1 h. After evaporation of the solvent, chromatography of the residue on silica gel with chloroform–carbon tetrachloride (1:1) as eluent yielded the <sup>18</sup>O-containing 1-oxide **4a'** (<sup>18</sup>O content, 55%) and none-<sup>18</sup>O-incorporated 1-oxide **4b** quantitatively.

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