Further Examples of Tandem Dimerization Ring-Opening of Substituted 3-Bromothiophene 1,1-Dioxides. Preparation of Trisubstituted Benzenes. X-Ray Structure Determination of 3,5-Dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-Dioxide

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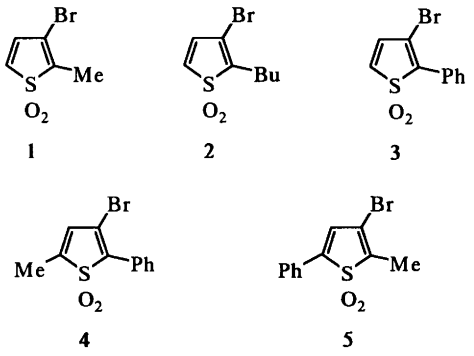
Stirring 3-bromo-2-methylthiophene 1,1-dioxide, 3-bromo-2-butylthiophene 1,1-dioxide and 3-bromo-2-phenylthiophene 1,1-dioxide at room temperature with basic alumina in pentane–dichloromethane solution led to dihydrobenzo[*b*]thiophene 1,1-dioxides. Refluxing of the same reaction mixtures led to the ring-opening products, the trisubstituted benzenes. Refluxing of 3-bromo-5-methyl-2-phenylthiophene 1,1-dioxide in decalin afforded the 3,5-dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide. The structure was established by X-ray crystallography.

We have recently shown that 3-halo-2,5-dialkylthiophene 1,1-dioxides undergo a tandem dimerization ring-opening reaction resulting in a short and convenient method for the synthesis of unsymmetrically pentasubstituted benzenes. From 3-bromo-2,5-dimethylthiophene 1,1-dioxide, 1-(3-bromo-2,5,6-trimethylphenyl)-1-propyne was obtained in 90 % yield.[1] We have now further investigated the scope of this reaction by studying the behaviour of 3-bromo-2-methylthiophene 1,1-dioxide (**1**), 3-bromo-2-butylthiophene 1,1-dioxide (**2**), 3-bromo-2-phenylthiophene 1,1-dioxide (**3**), 3-bromo-5-methyl-2-phenylthiophene 1,1-dioxide (**4**) and 3-bromo-2-methyl-5-phenylthiophene 1,1-dioxide (**5**).



Attempts to prepare compounds **1–3** by the commonly used 3-chloroperbenzoic acid oxidation led to many, partly polymeric products. None of the products was formed in more than 5–10 % yield according to GLC analysis. However, we found that 5-trimethylsilylthiophene 1,1-dioxide derivatives can be used as precursors of **1–3**: conversion of 3-bromo-2-methylthiophene into 3-bromo-2-methyl-5-trimethylsilylthiophene (**6**) by metallation with LDA and reaction with trimethylsilyl chloride, followed by oxidation, gave an 83 % yield of crude 3-bromo-2-methyl-5-trimethylsilylthiophene 1,1-dioxide (**7**), which could be stored for some time in a sealed bottle in a refrigerator. On attempting to purify **7** by chromatography on an Al_2O_3-type 507C neutral column, we made the unexpected observation that desilylation and cyclodimerization occurred on the column at room temperature. Elution with pentane–dichloromethane gave only one isomer, which was shown to be 3,5-dibromo-2,4-dimethyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**8**), formed in 56 % yield, demonstrating the regioselectivity in the cyclodimerization[2] (Scheme 1). Refluxing **7** with basic alumina in pentane–dichloromethane 1:1 solution for 60 h increased the yield to 68 %.

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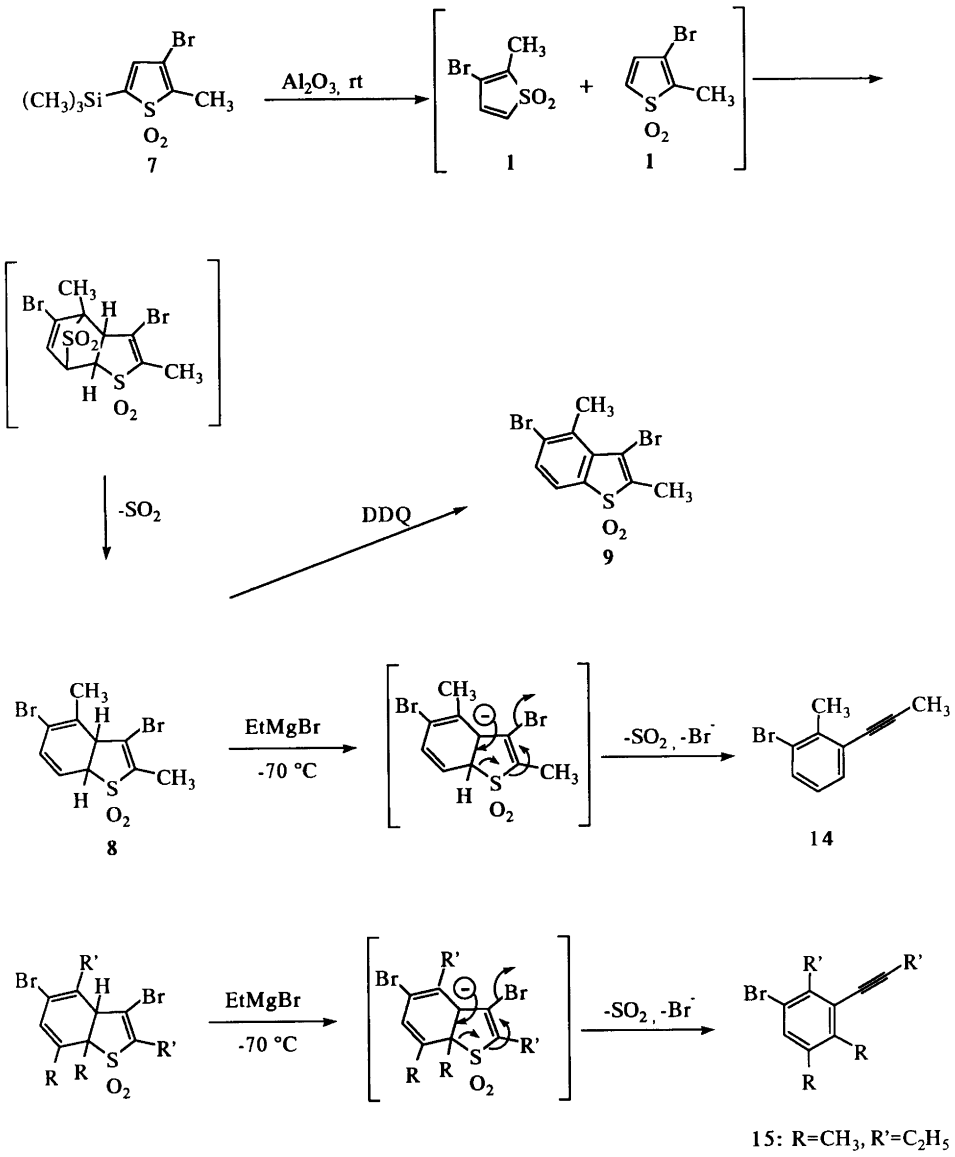


Scheme 1.

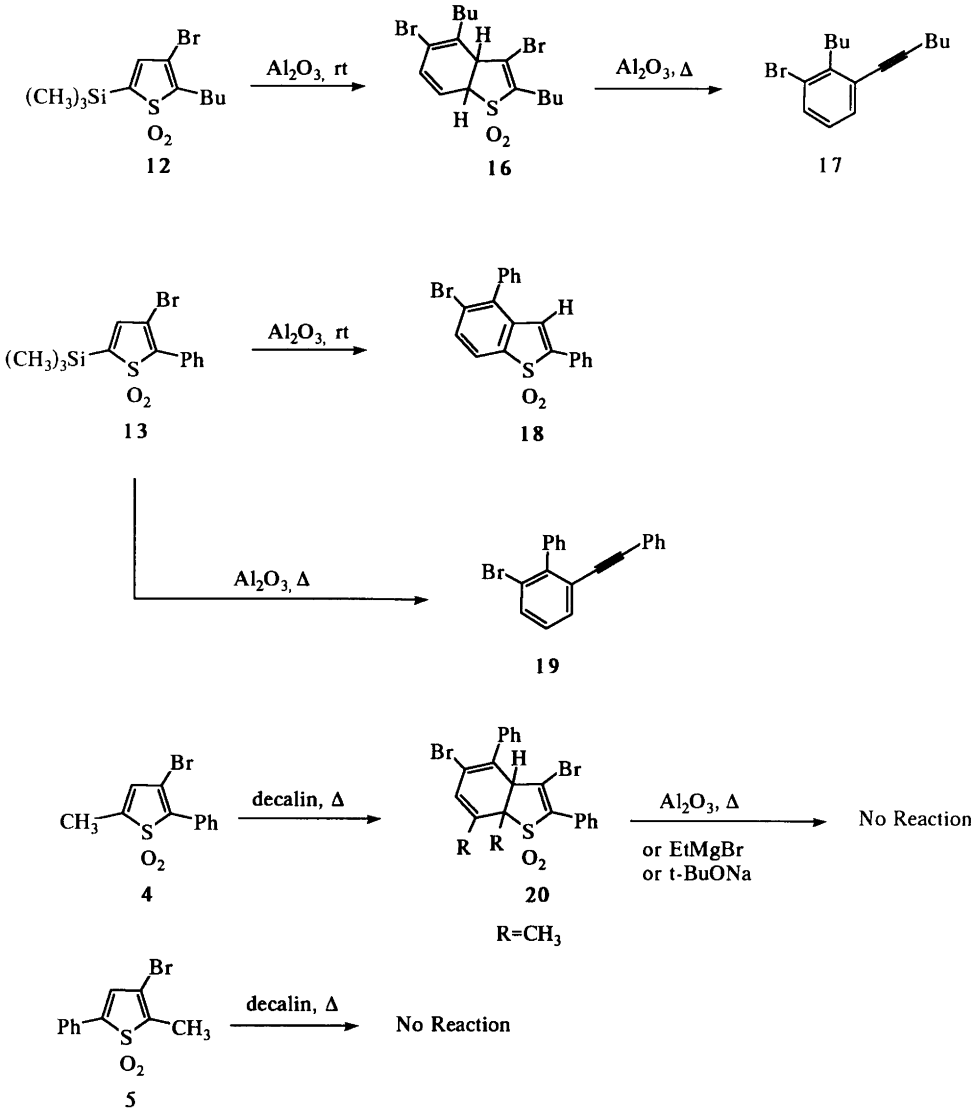
The structure of **8** followed from its NMR spectrum and selective decoupling experiments (see the Experimental part). The H_{3a}–H_{7a} coupling constant was in agreement with the *cis*-coupling previously observed in the parent compound.[3] Treatment of **8** with DDQ in refluxing benzene led to aromatization, giving 3,5-dibromo-2,4-dimethylbenzo[*b*]thiophene 1,1-dioxide (**9**) in 71 % yield.

In order to achieve ring-opening of **8**, the strong base ethylmagnesium bromide was used. Reaction at −70 °C for 4–5 h gave an 89 % yield of 1-(3-bromo-2-methylphenyl)-1-propyne (**14**). Its structure followed from ^{1}H NMR spectra and decoupling experiments (see the Experimental part) (Scheme 1).

Analogously, the reaction of 3,5-dibromo-2,4-diethyl-7,7a-dimethyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide with ethylmagnesium bromide at −70 °C gave a 98 % yield of 1-(3-bromo-5,6-dimethyl-2-ethylphenyl)-1-butyne (**15**) which was previously obtained by refluxing 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide for 160 h in *t-butyl alcohol*.[1]

Metallation followed by silylation was also used for the preparation of 3-bromo-2-butyl-5-trimethylsilylthiophene (**10**) and 3-bromo-2-phenyl-5-trimethylsilylthiophene (**11**). Oxidation of **10** and **11** with 3-chloroperbenzoic acid gave a 77 % yield of 3-bromo-2-butyl-5-trimethylsilylthiophene 1,1-dioxide (**12**) and a 71 % yield of 3-bromo-2-phenyl-5-trimethylsilylthiophene 1,1-dioxide (**13**), respectively.

When **12** was stirred at room temperature with basic alumina in pentane–dichloromethane, desilylation and dimerization was again obtained, giving a 79 % yield of 3,5-dibromo-2,4-dibutyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**16**). The structure followed from the similarity of its NMR spectrum to that of the methyl analogue **8**. Reflux of **16** overnight with basic alumina gave 1-(3-bromo-



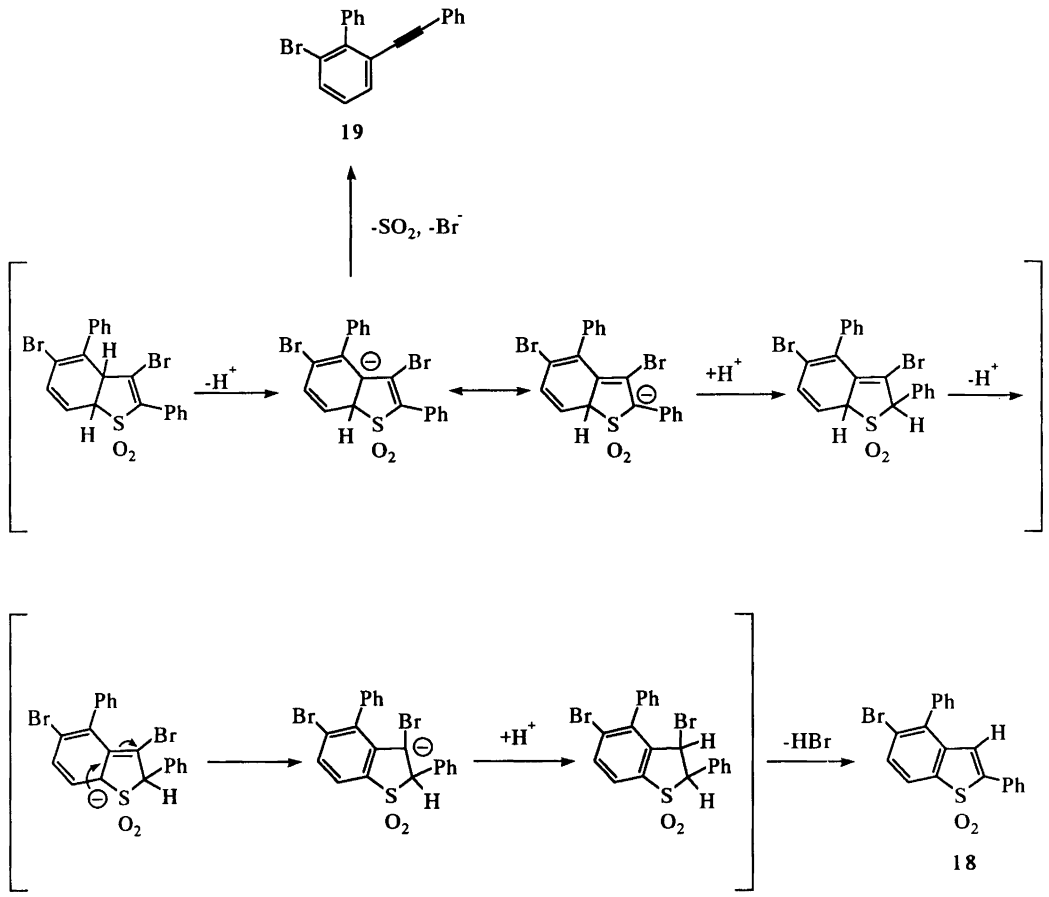
Scheme 2.

2-butylphenyl)-1-hexyne (**17**) (Scheme 2). Thus it seems that ring-opening reactions can be achieved by reflux of the dioxides in t-butyl alcohol,[1] or by treatment of the dimer with a base such as ethylmagnesium bromide, or by reflux of the dimer with basic alumina. Compound **17** could also be obtained in 76 % yield, together with 12 % of **16**, in one step by refluxing **12** with basic alumina.

When **13** was treated with basic alumina in pentane–dichloromethane at room temperature, a new type of reaction was observed. The product obtained (in 52 % yield) was shown to be 5-bromo-2,4-diphenylbenzo[*b*]thiophene 1,1-dioxide (**18**). Its structure followed from its ^{1}H NMR spectrum, which showed a long-range coupling between hydrogens 3 and 7, which has been observed in other benzo[*b*]thiophene 1,1-dioxides.[4]

A possible route to the monobromo compound **18** is a series of allylic rearrangements followed by hydrogen bromide elimination in the cycloaddition adduct, as indicated in Scheme 3. Allylic rearrangements have been observed in the reaction of thiophene 1,1-dioxides with alkoxides and thiolates,[5] and in some other cases.[6] On the other hand when **13** was refluxed with basic alumina, ring-opening occurred and the expected 6-bromobiphenyl-2-yl(phenyl)-acetylene (**19**) was obtained in 69 % yield, together with 27 % of **18** (Scheme 2). In the aryl cases, the primarily formed anion, stabilized by the phenyl group in the 2-position, is apparently not prone to undergo ring-opening, and an allylic rearrangement occurs preferentially. Both reaction paths lead to the formation of benzenoid rings.

Heating of **4**, obtained by oxidation of 3-bromo-5-methyl-2-phenylthiophene with 3-chloroperbenzoic acid, in refluxing decalin gave a compound of composition $C_{22}H_{18}Br_2O_2S$ in 66 % yield. From DEPT (Distortionless Enhancement by Polarization Transfer) experiments, evidence for the presence of two CH_3 carbons at 21.60 and 19.88 ppm, one aliphatic CH carbon at 59.02 ppm, seven



Scheme 3.

CH carbons in the aromatic region and six carbons without hydrogens was obtained. In order to prove the structure an X-ray investigation was carried out, which showed the compound to be 3,5-dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**20**). All attempts to ring-open this compound with various bases failed. Finally, we also prepared **5** by oxidation of 3-bromo-2-methyl-5-phenylthiophene, but all attempts to achieve cyclodimerization failed.

Molecular structure. The molecule **20** with atomic numbering is shown in Fig. 1. Details of the structure determination are given in the Experimental section and coordinates for the non-hydrogen atoms are listed in Table 1. Distances and angles within the molecule are normal (Table 2). In the phenyl groups (C1–C6, C11–C16), the distances vary between 1.35(1) and 1.39(1) Å with C–C–C angles in the range 118.7(8)–121.5(10)°.

Experimental

Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer and were in accordance with the proposed structures. The NMR spectra (^1H, ^{13}C, selective

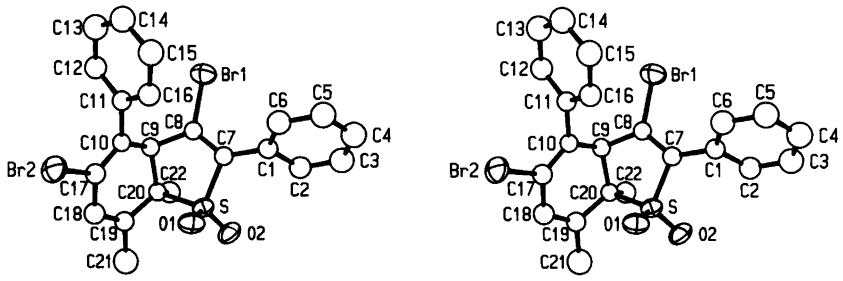


Fig. 1. Stereoscopic view of the molecule with atomic numbering.

Table 1. Fractional atomic coordinates with estimated standard deviations in parentheses and isotropic thermal parameters[a] for 3,5-dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide.

Atom	*x*	*y*	*z*	U/U_{eq}
Br1	0.04311(10)	0.04001(5)	0.67245(9)	0.0601(4)
Br2	0.44532(10)	0.29482(6)	0.68449(9)	0.0649(5)
S	0.24290(22)	0.17697(11)	1.00366(20)	0.0396(9)
O1	0.38382(54)	0.19144(29)	1.03097(52)	0.0491(25)
O2	0.20019(63)	0.17811(31)	1.10900(53)	0.0545(27)
C1	0.2275(8)	0.0239(4)	0.9839(8)	0.038(2)
C2	0.1847(9)	0.0071(5)	0.0807(8)	0.047(2)
C3	0.2188(10)	−0.0584(5)	0.1416(10)	0.062(3)
C4	0.2963(10)	−0.1064(5)	0.1083(10)	0.062(3)
C5	0.3401(10)	−0.0917(5)	1.0149(9)	0.060(3)
C6	0.3076(9)	−0.0259(5)	0.9523(8)	0.052(2)
C7	0.1921(8)	0.0947(4)	0.9168(7)	0.035(2)
C8	0.1315(8)	0.1108(4)	0.7957(7)	0.032(2)
C9	0.1270(10)	0.1897(4)	0.7560(9)	0.038(2)
C10	0.2392(8)	0.2079(4)	0.7089(7)	0.034(2)
C11	0.2692(8)	0.1547(4)	0.6243(7)	0.037(2)
C12	0.2048(9)	0.1583(5)	0.4944(8)	0.048(2)
C13	0.2373(10)	0.1087(5)	0.4194(10)	0.061(3)
C14	0.3305(10)	0.0555(5)	0.4727(9)	0.059(3)
C15	0.3926(10)	0.0502(5)	0.6005(9)	0.059(3)
C16	0.3648(9)	0.1009(5)	0.6768(8)	0.046(2)
C17	0.3043(8)	0.2704(4)	0.7410(8)	0.042(2)
C18	0.2801(9)	0.3229(5)	0.8250(8)	0.048(2)
C19	0.1998(8)	0.3074(4)	0.8876(8)	0.042(2)
C20	0.1316(8)	0.2341(4)	0.8714(7)	0.032(2)
C21	0.1845(15)	0.3590(7)	0.9830(13)	0.071(3)
C22	−0.0088(11)	0.2377(6)	0.8777(11)	0.052(3)

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 2. Selected bond lengths (Å) and angles (°). Standard deviations in parentheses.

S–O1	1.431(6)	O1–S–O2	116.9(4)
S–O2	1.441(6)	C20–S–C7	93.9(4)
S–C20	1.852(8)	S–C7–C8	108.4(6)
S–C7	1.782(8)	S–C7–C1	119.8(6)
C7–C1	1.49(1)	C1–C7–C8	131.7(7)
C7–C8	1.32(1)	C7–C8–C9	118.5(7)
C8–Br1	1.888(7)	C7–C8–Br1	122.1(6)
C8–C9	1.52(1)	Br1–C8–C9	119.3(6)
C9–C20	1.54(1)	C8–C9–C20	105.5(7)
C9–C10	1.52(1)	C8–C9–C10	112.2(7)
C10–C11	1.49(1)	C10–C9–C20	114.5(7)
C10–C17	1.32(1)	C9–C10–C17	119.4(7)
C17–Br2	1.897(8)	C9–C10–C11	118.3(7)
C17–C18	1.46(1)	C11–C10–C17	122.3(7)
C18–C19	1.34(1)	C10–C17–C18	124.0(8)
C19–C21	1.50(2)	C10–C17–Br2	120.6(6)
C19–C20	1.51(1)	Br2–C17–C18	115.3(6)
C20–C22	1.52(1)	C17–C18–C19	121.3(8)
		C18–C19–C20	120.0(7)
		C18–C19–C21	121.4(9)
		C21–C19–C20	118.4(8)
		C19–C20–C9	116.0(7)
		C19–C20–S	106.5(5)
		C19–C20–C22	112.8(7)
		C9–C20–C22	110.7(7)
		S–C20–C9	101.4(5)
		S–C20–C22	108.4(6)

decoupling, COSY, HETCOR and DEPT, $CDCl_3$ as solvent) were recorded on a Varian XL 300 spectrometer. Quantitative gas chromatographic analyses were performed on a Varian 3300 gas chromatograph equipped with a 2 m column of 3 % OV 17 on Gaschrom Q, 100–120 mesh and a flame ionization detector. Mass spectra were obtained on a Finnigan 4021 (Data system Incos 2100) gas chromatograph/mass spectrometer operating at 70 eV. High resolution mass were recorded on a JEOL JMS-SX 102 spectrometer. Elemental microanalyses were performed at *Dornis und Kolbe, Mikroanalytisches Laboratorium,* Mülheim a.d. Ruhr, Germany and *Mikro Kemi AB,* Uppsala, Sweden. Column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM) or aluminium oxide (Al_2O_3) Fluka type-507C neutral (100–125 mesh) and pentane–dichloromethane as the eluent. The Grignard reagent, ethylmagnesium bromide, was a 3 M solution in diethyl ether, purchased from Aldrich Chemical Company Inc. The purity of the 3-chloroperbenzoic acid was 85 %.

3-Bromo-5-methyl-2-phenylthiophene 1,1-dioxide (**4**). This compound was prepared from 3-bromo-5-methyl-2-phenylthiophene[7] (5.06 g, 20.0 mmol) and a solution of 3-chloroperbenzoic acid (10.1 g, 44.0 mmol) in dichloromethane (150 ml). After being stirred for 30 h at room temperature, the reaction afforded 4.2 g (74 %) of the title compound **4**, as described for **7**, as an oil. ^{1}H NMR ($CDCl_3$): δ 7.88–7.47 (m, 5 H, 2-phenyl), 6.49 (q, 1 H, 4-H, J = 1.92 Hz), 2.23 (d, 3 H, 5-CH_3, J = 1.92 Hz). MS: *m/z* 284/286. Anal. $C_{11}H_9BrO_2S$: C, H, Br.

3-Bromo-2-methyl-5-phenylthiophene 1,1-dioxide (**5**). This compound was prepared from 3-bromo-2-methyl-5-phenylthiophene[7] (5.06 g, 20.0 mmol) and a solution of 3-chloroperbenzoic acid (10.1 g, 44.0 mmol) in dichloromethane (150 ml). After being stirred for 36 h at room temperature, the reaction afforded the title compound as described for **7**. Recrystallization from ethanol afforded 4.6 g (81 %) of **5** m.p. 190–192 °C. ^{1}H NMR ($CDCl_3$): δ 7.74–7.44 (m, 5 H, 5-phenyl), 6.85 (s, 1 H, 4-H), 2.17 (s, 3 H, 2-CH_3). MS: *m/z* 284/286. Anal. $C_{11}H_9BrO_2S$: C, H, Br.

3-Bromo-2-methyl-5-trimethylsilylthiophene (**6**). A solution of 1.50 M BuLi (215 ml, 0.330 mol) in hexane was added dropwise to a stirred solution of diisopropylamine (47.0 ml, 0.330 mol) in anhydrous diethyl ether (250 ml) at room temperature under a nitrogen atmosphere. After being stirred for 30 min, the mixture was cooled to −70 °C and 3-bromo-2-methylthiophene[8] (49.6 g, 0.28 mol) was added dropwise. After a further hour of stirring, trimethylsilyl chloride (40.1 ml, 0.32 mol), dissolved in anhydrous ether (30 ml), was added dropwise to the mixture (the reaction

mixture was kept below −50 °C during the addition). After being stirred for 2 h at −70 °C, the reaction mixture was allowed to reach 0 °C, and was hydrolyzed with ice–water. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3×100 ml). The combined ethereal phases were washed with water (3×100 ml) and dried over magnesium sulfate. Removal of the solvent followed by distillation afforded 47.0 g (67 %) of the title product **6** b.p. 112–116 °C/12 mmHg: ^{1}H NMR ($CDCl_3$): δ 7.01 (s, 1 H, 4-H), 2.42 (s, 3 H, 2-CH_3), 0.29 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 248/250. Anal. $C_8H_{13}BrSSi$: C, H, Br.

3-Bromo-2-methyl-5-trimethylsilylthiophene 1,1-dioxide (**7**). To a suspension of 3-chloroperbenzoic acid (10.1 g, 44.0 mmol) and solid sodium hydrogencarbonate (4.2 g, 50.0 mmol) (as acid acceptor), in dichloromethane (150 ml) was added 3-bromo-2-methyl-5-trimethylsilylthiophene (5.0 g, 20.0 mmol) with vigorous stirring, and the mixture was stirred at room temperature for 72 h. (If no sodium hydrogen carbonate was added desilylation occurred for 20–25 % of the starting material, but the oxidation was complete within 2–3 h.) 3-Chlorobenzoic acid was filtered from the cooled solution, and the filtrate was washed twice with saturated sodium carbonate solution, and several times with water. The organic phase was dried over magnesium sulfate, filtered, and evaporated at 0 °C, to give 4.67 g (83 %) of the crude product (**7**), which was stored in a sealed bottle in the refrigerator [stable for up to about a month in the refrigerator when concentrated, but stable in dichloromethane solution for longer periods (>2 years)]. ^{1}H NMR ($CDCl_3$): δ 6.70 (q, 1 H, 4-H, J = 0.54 Hz), 2.09 (d, 3 H, 2-CH_3, J = 0.54 Hz), 0.36 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 280/282. Peak matching on M^+: Calc. for $C_8H_{13}BrO_2SSi$: 279.9589. Found: 279.9593.

*3,5-Dibromo-2,4-dimethyl-*cis*-3a,7a-dihydrobenzo[b]thiophene 1,1-dioxide* (**8**). When 3-bromo-2-methyl-5-trimethylsilylthiophene (5.0 g, 20.0 mmol) was oxidized as described above, the title compound was formed during column chromatography of 3-bromo-2-methyl-5-trimethylsilylthiophene 1,1-dioxide (**6**) through aluminium oxide type 507C neutral, with pentane–dichloromethane (1:1) as the eluent. Recrystallization from ethanol gave 2.0 g (56 %) of **8**, m.p. 146.5–147.5 °C. The yield was improved when **6** (1.41 g, 5.0 mmol) was refluxed together with basic alumina (20 g) in pentane (75 ml) and dichloromethane (75 ml) solution for 60 h. The cooled suspension was filtered off and washed with dichloromethane, and the organic phase was washed a few times with water and dried over magnesium sulfate. Recrystallization from absolute ethanol afforded 0.6 g (68 %) of the title compound. ^{1}H NMR ($CDCl_3$): δ 6.24 (ddq, 1 H, 6-H, J = 9.9, 2.5, 0.6 Hz), 5.71 (ddq, 1 H, 7-H, J = 9.9, 3.0, 0.8 Hz), 4.32 (m, 1 H, 7a-H, J = 8.0, 3.0, 2.5, 0.8 Hz), 4.02 (m, 1 H, 3a-H, J = 8.0, 2.4, 0.7 Hz), 2.19 (br m, 3 H, 4-CH_3, J = 0.8, 0.8, 0.7, 0.6 Hz), 2.07 (d, 3 H, 2-CH_3, J = 2.4 Hz). Irradiation at 6.24 ppm resulted in a double quartet at 5.71 ppm, J = 3.0, 0.8 Hz, a double quartet at 4.32 ppm, J = 8.0, 3.0, 0.8 Hz, a multiplet at 2.19 ppm. Irradiation at 5.71 ppm resulted in a double quartet at 6.24 ppm, J = 2.5, 0.6 Hz, a double double quartet at 4.32 ppm, J = 8.0, 2.5, 0.8 Hz, a multiplet at 2.19 ppm. Irradiation at 4.32 ppm resulted in a double quartet at 6.24 ppm, J = 9.9, 0.6 Hz, a double quartet at 5.71 ppm, J = 9.9, 0.8 Hz, a multiplet at 4.02 ppm, a multiplet at 2.19 ppm. Irradiation at 4.02 ppm resulted in a multiplet at 4.32 ppm, a multiplet at 2.19 ppm, a singlet at 2.07 ppm. Irradiation at 2.19 ppm resulted in a double doublet at 6.24 ppm, J = 9.9, 2.5 Hz, a double doublet at 5.71 ppm, J = 9.9, 3.0 Hz, a double double doublet at 4.32 ppm, J = 8.0, 3.0, 2.5 Hz, a double quartet at 4.02 ppm, J = 8.0, 2.4 Hz. Irradiation at 2.07 ppm resulted in a double quartet at 4.02 ppm, J = 8.0, 0.7 Hz. MS: *m/z* 352/354/356. Anal. $C_{10}H_{10}Br_2O_2S$: C, H, Br.

3,5-Dibromo-2,4-dimethylbenzo[b]thiophene 1,1-dioxide (**9**). A solution of 3,5-dibromo-2,4-dimethyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**8**) (0.177 g, 0.5 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.35 g, 1.5 mmol) in benzene (20 ml) was refluxed for 3 h. The mixture was washed with 2 M sodium hydroxide (3×50 ml), the aqueous phase was extracted with toluene (2×25 ml), and the combined organic phase was washed with water (3×50 ml) and dried over magnesium sulfate. Removal of the solvents followed by recrystallization from absolute ethanol afforded 0.125 g (71 %) of **9** m.p. 228–230 °C. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, 1 H, 6-H, J = 8.1 Hz), 7.45 (d, 1 H, 7-H, J = 8.1 Hz), 2.92 (s, 3 H, 4-CH_3), 2.33 (s, 3 H, 2-CH_3). MS: *m/z* 350/352/354. Anal. $C_{10}H_8Br_2O_2S$: C, H, Br.

3-Bromo-2-butyl-5-trimethylsilylthiophene (**10**). This compound was prepared from 1.50 M BuLi (24.2 ml, 36.3 mmol) in hexane dissolved in dry ether (20 ml), diisopropylamine (4.5 ml, 36.3 mmol) in dry ether (5 ml), 3-bromo-2-butylthiophene[9] (6.8 g, 31.0 mmol) in dry ether (5 ml), and trimethylsilyl chloride (5.0 ml, 50 mmol) in dry ether (5 ml), added as described above for 3-bromo-2-methyl-5-trimethylsilylthiophene (**6**). After being stirred for 3 h at −70 °C with additional stirring overnight at room temperature the reaction yielded a crude product which was treated as described above for **6**. Distillation afforded 6.95 g (77 %) of the title product **10** b.p. 140–146 °C/16–18 mmHg: ^{1}H NMR ($CDCl_3$): δ 7.01 (s, 1 H, 4-H), 2.79 (t, 2 H, 2-CH_2, J = 7.6 Hz), 1.65 (quintet, 2 H, CH_2, J = 7.6 Hz), 1.41 (sextet, 2 H, CH_2, J = 7.6 Hz), 0.95 (t, 3 H, CH_3, J = 7.6 Hz), 0.29 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 290/292. Anal. $C_{11}H_{19}BrSSi$: C, H, Br.

3-Bromo-2-phenyl-5-trimethylsilylthiophene (**11**). This compound was prepared from 2.06 M BuLi (17.7 ml, 36.3 mmol) in hexane dissolved in dry ether (25 ml), diisopropylamine (4.5 ml, 36.3 mmol) in dry ether (10 ml) and 3-bromo-2-phenylthiophene[10] (7.42 g, 31.0 mmol) in dry

ether (10 ml), added as described above for 3-bromo-2-methyl-5-trimethylsilylthiophene (**6**). After being stirred at −70 °C overnight the reaction yielded a crude product which was treated as described above for **6**. Distillation afforded 8.9 g (92 %) of the title product **11**, b.p. 106–112 °C/0.1–0.2 mmHg: ^{1}H NMR ($CDCl_3$): δ 7.7–7.3 (m, 5 H, 2-phenyl), 7.16 (s, 1 H, 4-H), 0.35 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 310/312. Anal. $C_{13}H_{15}BrSSi$: C, H, Br.

3-Bromo-2-butyl-5-trimethylsilylthiophene 1,1-dioxide (**12**). 3-Bromo-2-butyl-5-trimethylsilylthiophene (**10**) (2.92 g, 10.0 mmol), 3-chloroperbenzoic acid (9.6 g, 41.8 mmol) and solid sodium hydrogen carbonate (3.75 g, 45.0 mmol) in dichloromethane (150 ml), was stirred at room temperature for 30 h to give compound **12**. Work-up, as described previously, afforded 2.50 g (77 %) of **12** as an oil. ^{1}H NMR ($CDCl_3$): δ 6.68 (s, 1 H, 4-H), 2.55 (t, 2 H, 2-CH_2, J = 7.7 Hz), 1.70 (quintet, 2 H, CH_2, J = 7.7 Hz), 1.41 (sextet, 2 H, CH_2, J = 7.7 Hz), 0.95 (t, 3 H, CH_3, J = 7.7 Hz), 0.36 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 322/324. Anal. $C_{11}H_{19}BrO_2SSi$: C, H, Br.

3-Bromo-2-phenyl-5-trimethylsilylthiophene 1,1-dioxide (**13**). Compound **13** was prepared from 3-bromo-2-phenyl-5-trimethylsilylthiophene (**11**) (3.1 g, 10 mmol) and 3-chloroperbenzoic acid (9.6 g, 41.8 mmol) in dichloromethane (150 ml), after 2 days of stirring at room temperature and work-up as described above. Recrystallization from ethanol afforded 2.45 g (71 %) of **13** as yellow crystals, m.p. 84.5–85.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.9–7.4 (m, 5 H, 2-phenyl), 6.85 (s, 1 H, 4-H), 0.41 [s, 9 H, 5-Si(CH_3)$_3$]. MS: *m/z* 342/344. Anal. $C_{13}H_{15}BrO_2SSi$: C, H, Br.

1-(3-Bromo-2-methylphenyl)-1-propyne (**14**). A solution of 3.0 M ethylmagnesium bromide (0.22 ml, 0.62 mmol) in anhydrous diethyl ether was added dropwise to a stirred solution of 3,5-dibromo-2,4-dimethyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**8**) (200 mg, 0.57 mmol) in anhydrous diethyl ether (20 ml) at −70 °C under a nitrogen atmosphere. After being stirred for 4–5 h the reaction mixture was hydrolyzed with saturated ammonium chloride. The organic phase was separated and the aqueous phase was extracted with ether (3×10 ml). The combined ethereal phase was washed with water (2×25 ml) and dried over magnesium sulfate. Removal of the solvent followed by column chromatography afforded 105 mg (89 %) of **14** as an oil. IR 2220 cm^{-1} (C≡C stretch); ^{1}H NMR ($CDCl_3$): δ 7.44 (dd, 1 H, 4-H, J = 7.8, 2.7 Hz), 7.31 (dd, 1 H, 6-H, J = 7.8, 2.7 Hz), 6.95 (t, 1 H, 5-H, J = 7.8, 7.8 Hz), 2.52 (s, 3 H, 3-CH_3), 2.10 (s, 3 H, acetylenic CH_3): MS: *m/z* 208/210. Anal. $C_{10}H_9Br$: C, H, Br.

Irradiation at 7.44 ppm resulted in a doublet at 7.31 ppm, J = 7.8 Hz and a doublet at 6.95 ppm, J = 7.8 Hz. Irradiation at 7.31 ppm resulted in a doublet at 7.44 ppm, J = 7.8 Hz and a doublet at 6.95 ppm, J = 7.8 Hz. Irradiation at 6.95 ppm resulted in a doublet at 7.44 ppm, J = 2.7 Hz and a doublet at 7.31 ppm, J = 2.7 Hz.

1-(3-Bromo-5,6-dimethyl-2-ethylphenyl)-1-butyne[1] (**15**). A solution of 3.0 M ethylmagnesium bromide (0.04 ml, 0.12 mmol) in anhydrous diethyl ether was added to a stirred solution of 3,5-dibromo-2,4-diethyl-7,7a-dimethyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide[1] (41 mg, 0.10 mmol) in anhydrous diethyl ether (5 ml) at −70 °C under a nitrogen atmosphere. After being stirred for 2 h, the reaction afforded 26 mg (98 %) of the title compound **15** as an oil, as described above. IR 2230 cm^{-1} (C≡C stretch). ^{1}H NMR ($CDCl_3$): δ 7.25 (s, 1 H, 4-H), 2.97 (q, 2 H, 2-CH_2, J = 7.5 Hz), 2.51 (q, 2 H, acetylenic-CH_2, J = 7.5 Hz), 2.32 (s, 3 H, 5-CH_3), 2.20 (s, 3 H, 6-CH_3), 1.28 (t, 3 H, acetylenic-CH_3, J = 7.5 Hz), 1.17 (t, 3 H, 2-CH_3, J = 7.5 Hz). MS: *m/z* 264/266.

3,5-Dibromo-2,4-dibutyl-cis-3a,7a-dihydrobenzo[b]thiophene 1,1-dioxide (**16**). A suspension of 3-bromo-2-butyl-5-trimethylsilylthiophene 1,1-dioxide (**12**) (1.5 g, 4.6 mmol) and basic aluminium oxide (Fluka type 5016 A Activity Grade I, the Brockmann Scale) (15 g), in pentane (25 ml) and dichloromethane (25 ml) was stirred at room temperature. After vigorous overnight stirring, the aluminium oxide was filtered off and washed with dichloromethane. Removal of the solvents and recrystallization from ethanol afforded 0.80 g (79 %) of **16**, m.p. 102.5–104 °C. ^{1}H NMR ($CDCl_3$): δ 6.21 (dd, 1 H, 6-H, J = 9.9, 2.6 Hz), 5.69 (dd, 1 H, 7-H, J = 9.9, 2.6 Hz), 4.23 (br dt, 1 H, 7a-H, J = 7.5, 2.6, 2.6 Hz), 4.06 (br d, 1 H, 3a-H, J = 7.5 Hz), 2.84–1.34 (m, 12 H, 2,4-di-$CH_2CH_2CH_2$-), 0.95 (dt, 6 H, 2,4-di-CH_3, J = 7.3 Hz). MS: *m/z* 436/438/440. Anal. $C_{16}H_{22}Br_2O_2S$: C, H, Br.

1-(3-Bromo-2-butylphenyl)-1-hexyne (**17**). A suspension of 3-bromo-2-butyl-5-trimethylsilylthiophene 1,1-dioxide (0.32 g, 1.0 mmol) and basic aluminium oxide (Fluka type 5016 A Activity Grade I, the Brockmann Scale) (10 g), in pentane (10 ml) and dichloromethane (10 ml) was refluxed overnight with vigorous stirring. The aluminium oxide was then filtered off and washed with dichloromethane. Removal of the solvents and chromatography on aluminium oxide (neutral: and pentane–dichloromethane 95:5 as the eluent), afforded 110 mg (76 %) of **17** as an oil and 25 mg (12 %) of **16** as a by-product. IR 2210–2215 cm^{-1} (C≡C stretch). ^{1}H NMR ($CDCl_3$): δ 7.43 (dd, 1 H, 4-H, J = 8.1, 1.2 Hz), 7.31 (dd, 1 H, 6-H, J = 7.6, 1.2 Hz), 6.94 (br t, 1 H, 5-H, J = 8.0, 7.6 Hz), 2.94–0.98 (2× butyl groups). MS: *m/z* 292/294. Anal. $C_{16}H_{21}Br$: C, H, Br.

5-Bromo-2,4-diphenylbenzo[b]thiophene 1,1-dioxide (**18**). Compound **18** was prepared from 3-bromo-2-phenyl-5-trimethylsilylthiophene 1,1-dioxide (**13**) (0.4 g, 1.16 mmol), aluminium oxide basic (Fluka Type 5016 A Activity Grade I, the Brockmann Scale) (20 g), pentane (25 ml) and di-

chloromethane (25 ml). After vigorous stirring overnight at room temperature, the aluminium oxide was filtered off and washed with dichloromethane. Removal of the solvents afforded 0.12 g (52 %) of **18** on recrystallization from ethanol, m.p. 204–204.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.83 (d, 1 H, 6-H, J = 8.0 Hz), 7.75–7.30 (m, 10 H, 2,4-diphenyl), 7.63 (dd, 1 H, 7-H, J = 8.0, 0.7 Hz), 6.91 (d, 1 H, 3-H, J = 0.7 Hz). MS: m/z 396/398. Anal. $C_{20}H_{13}BrO_2S$: C, H, Br.

6-Bromobiphenyl-2-yl(phenyl)acetylene (**19**). This compound was prepared from 3-bromo-2-phenyl-5-trimethylsilylthiophene 1,1-dioxide (**13**) (0.51 g, 1.5 mmol) and basic aluminium oxide (15 g), in pentane (25 ml) and dichloromethane (25 ml), as described above. This afforded 0.17 g (69 %) of **19** as an oil and 80 mg (27 %) of **18** as a by-product. IR 2210–2220 cm^{-1} (C≡C stretch). ^{1}H NMR ($CDCl_3$): δ 7.66 (dd, 1 H, 4-H, J = 8.1, 1.2 Hz), 7.58 (dd, 1 H, 6-H, J = 7.7, 1.2 Hz), 7.5–7.1 (m, 10 H, two phenyl groups), 7.20 (t, 1 H, 5-H, J = 8.1, 7.7 Hz). MS: m/z 332/334. Anal. $C_{20}H_{13}Br$: C, H, Br.

*3,5-Dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide* (**20**). A solution of 3-bromo-5-methyl-2-phenylthiophene 1,1-dioxide (**4**) (0.85 g, 3.0 mmol) in decalin (decahydronaphthalene) (20 ml) was refluxed with stirring for 15 h. The solution was chromatographed on silica with pentane–ethyl acetate (7:3) as the eluent, and recrystallized from ethanol. The crystals were brown and contained some impurity. The product was thus purified by HPLC [RI detector (128) column packed with Polygosil C_{18} 500×1/2″, acetonitrile as the eluent, flow 2.5 ml min^{-1}] to give 0.5 g (66 %) of **20**, which crystallized from ethanol as white crystals, m.p. 153–155 °C: ^{1}H NMR ($CDCl_3$): δ 7.25–7.55 (m, 10 H, 2,4-diphenyl), 6.40 (q, 1 H, 6-H, J = 1.7 Hz), 4.14 (s, 1 H, 3a-H), 2.11 (d, 3 H, 7-CH_3, J = 1.7 Hz), 1.77 (s, 3 H, 7a-CH_3). ^{13}C NMR ($CDCl_3$), δ 138.66, 133.49, 132.33, 130.94, 130.23, 129.32, 129.02, 128.80, 128.48, 128.22, 126.91, 118.08, 76.23, 59.02, 21.60 and 19.88 ppm. From the DEPT experiments the following information was obtained: two CH_3 carbons at 21.60 and 19.88 ppm, one CH aliphatic carbon at 59.02 ppm, seven CH at 130.94, 130.23, 129.32, 129.02, 128.80, 128.48 and 128.22 ppm and six carbons without hydrogen at 138.66, 133.49, 132.33, 126.91, 118.08 and 76.23 ppm. MS: m/z 504/506/508. Anal. $C_{22}H_{18}Br_2O_2S$: C, H, Br.

X-Ray structure analysis. A colourless crystal of dimensions 0.28×0.20×0.16 mm was used for the intensity data collection and for determination of cell parameters. The analysis was carried out on a computer-controlled Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71069 Å). The ω–2θ technique was employed with a maximum scan time of 90 s and a scan width of (0.80 + 0.50 tan θ)°. Out of the 2652 measured independent reflections with θ < 22°, 1436 with $I > 3\sigma(I)$ were considered as observed. The intensities of two test reflections remeasured every second hour showed a linear decrease of 17 % during the data collection. All intensities were therefore corrected for this decrease and for Lp and absorption effects.

Crystal data. $C_{22}H_{18}Br_2O_2S$, M_f = 506.24. Space group $P2_1/n$; a = 10.613(3), b = 18.460(4), c = 11.438(2) Å, β = 112.49(2)°, V = 2070.4(6) Å^3, z = 4, D_x = 1.62 g cm^{-3}, μ(Mo K_α) = 39.9 cm^{-1}, t = 22 °C.

The structure was solved by direct methods (MULTAN 80)[11] and refined by full-matrix least-squares, minimizing $\Sigma w(\Delta F)^2$, and allowing the Br, S and O atoms to vibrate anisotropically. In the final refinement, which gave R = 0.037, the phenyl-H atoms were included with fixed positional parameters (C–H = 0.95 Å). The weights were given by $w^{-1} = [\sigma^2(F_o) + (0.015\,F_o)^2 + 1.5]$. The maximum shift/error was 0.01 and final Δρ excursions < 0.42 e Å^{-3}. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[12] A description of the computer programs used has been given by Lundgren.[13] Lists of anisotropic temperature factors, hydrogen atom parameters, distances and angles within the phenyl groups, and structure factors are available from one of the authors (C.S.) on request.

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