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Structures of Benzo[*b*]thiophene 1,1-Dioxide (a Redetermination) and of 2,3-Dimethylbenzo[*b*]thiophene 1,1-Dioxide and 2-Bromobenzo[*b*]thiophene 1,1-Dioxide

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Abstract. Benzo[*b*]thiophene 1,1-dioxide, $C_8H_6O_2S$, $M_r = 166{\cdot}19$, monoclinic, $C2/c$, $a = 10{\cdot}331\ (2)$, $b = 9{\cdot}497\ (1)$, $c = 15{\cdot}469\ (2)$ Å, $\beta = 104{\cdot}87\ (2)°$, $V = 1466{\cdot}9\ (4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}50$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 33{\cdot}1$ cm^{-1}, $F(000) = 688$, $T = 291$ K, $R = 0{\cdot}051$ for 1242 observed reflections. 2,3-Dimethylbenzo[*b*]thiophene 1,1-dioxide, $C_{10}H_{10}O_2S$, $M_r = 194{\cdot}25$, triclinic, $P\overline{1}$, $a = 7{\cdot}556\ (4)$, $b = 8{\cdot}107\ (3)$, $c = 8{\cdot}600\ (4)$ Å, $\alpha = 68{\cdot}66\ (4)$, $\beta = 86{\cdot}07\ (5)$, $\gamma = 75{\cdot}95\ (5)°$, $V = 475{\cdot}9\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}356$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 26{\cdot}3$ cm^{-1}, $F(000) = 204$, $T = 291$ K, $R = 0{\cdot}05$ for 1480 observed reflections. 2-Bromobenzo[*b*]thiophene 1,1-dioxide, $C_8H_5BrO_2S$, $M_r = 245{\cdot}09$, monoclinic, $P2_1/n$, $a = 7{\cdot}932\ (3)$, $b = 12{\cdot}112\ (4)$, $c = 8{\cdot}922\ (3)$ Å, $\beta = 91{\cdot}72\ (3)°$, $V = 856{\cdot}7\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}90$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 52{\cdot}6$ cm^{-1}, $F(000) = 480$, $T = 291$ K, $R = 0{\cdot}048$ for 1381 observed reflections. The three molecular structures do not show significant differences in bond lengths and bond angles caused by the bromine atom in the 2-bromo derivative or the methyl groups in the 2,3-dimethyl compound. The five- and six-membered rings are planar for all three molecules.

Introduction. The photo- and thermo-reactivity of benzo[*b*]thiophene 1,1-dioxide (BTO_2) are different from its derivatives, 2,3-dimethylbenzo[*b*]thiophene 1,1-dioxide (Me_2BTO_2) and 2-bromobenzo[*b*]thiophene 1,1-dioxide ($BrBTO_2$). While BTO_2 photodimerizes very easily in benzene solution to give the *anti* head-to-head and the *anti* head-to-tail cyclobutane dimers (Harpp & Heitner, 1970), the photodimerization of $BrBTO_2$ occurs to produce only the *anti* head-to-tail dimer (Schloman & Plummer, 1976) and Me_2BTO_2 dimerizes very slowly to give the single *anti* head-to-head dimer (El Amoudi El Faghi, Geneste & Olivé, 1981). Moreover, BTO_2 shows Diels–Alder (Bordwell, McKillin & Babcock, 1951; Davies & Porter, 1957) as well as 1,3-cycloaddition reactions with mesitonitrile oxide to give the corresponding isoxazolines while Me_2BTO_2 and $BrBTO_2$ are inert towards both types of reactions (Bened *et al.*, 1982). The contrasting reactivity of these three molecules prompted us to study their X-ray structures, following our earlier work on the 2- and 3-methylbenzo[*b*]thiophene 1,1-dioxides (El Amoudi El Faghi, Geneste, Olivé, Rambaud & Declercq, 1988).

Experimental. BTO_2: colourless prismatic crystal, $0{\cdot}15 \times 0{\cdot}22 \times 0{\cdot}37$ mm. Lattice parameters refined using 16 reflections in the range $10 \le 2\theta \le 30°$. No absorption correction. Huber 424 + 511 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, 1330 independent reflections with $(\sin\theta)/\lambda \le 0{\cdot}599$ Å^{-1}. 1242 with $I \ge 2{\cdot}5\sigma(I)$, index range h −12/11, k 0/11, l 0/18, standard reflection $(1\overline{1}2)$ checked every 50 reflections, no significant deviation. Structure solved by direct methods using *SHELX*86 (Sheldrick, 1986). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976), F values, H isotropic with common refined temperature factor ($B = 5$ Å^2), $w = 1/[\sigma^2(F) + 0{\cdot}0417F^2]$, $R = 0{\cdot}051$, $wR = 0{\cdot}059$, $S = 0{\cdot}499$ for 1242 observed reflections. $(\Delta/\sigma)_{\max} < 0{\cdot}6$. Max. and min. heights in final difference Fourier synthesis 0·32 and −0·76 e Å^{-3}.

Me_2BTO_2: colourless thin plates $0{\cdot}37 \times 0{\cdot}34 \times 0{\cdot}07$ mm. Lattice parameters refined using 13 reflections in the range $11 \le 2\theta \le 26°$. Absorption correction: transmission factors between 0·42 and 0·83. Huber 424 + 511 diffractometer, graphite-mono-

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chromatized Cu $K\alpha$ radiation, 1618 independent reflections with $(\sin\theta)/\lambda \leq 0{\cdot}599$ Å^{-1}. 1480 with $I \geq 2{\cdot}5\sigma(I)$, index range h −8/8, k −8/9, l 0/10. Standard reflection ($\bar{1}0\bar{2}$) checked every 50 reflections, no significant deviation. Structure solved by direct methods using *SHELX*86 (Sheldrick, 1986). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976), F values, H isotropic with common refined temperature factor ($B = 8{\cdot}6$ Å^2), $w = 1/[\sigma^2(F) + 0{\cdot}0132F^2]$, $R = 0{\cdot}057$, $wR = 0{\cdot}069$, $S = 0{\cdot}815$ for 1480 observed reflections. $(\Delta/\sigma)_{\max} < 0{\cdot}5$. Max. and min. heights in final difference Fourier synthesis 0·27 and −0·57 e Å^{-3}.

BrBTO$_2$: colourless prismatic crystal, 0·5 × 0·4 × 0·3 mm. Lattice parameters refined using 15 reflections in the range $5 \leq 2\theta \leq 26°$. No absorption correction. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 1968 independent reflections with $(\sin\theta)/\lambda \leq 0{\cdot}649$ Å^{-1}. 1381 with $I \geq 2{\cdot}5\sigma(I)$, index range h −10/10, k 0/15, l 0/11. Standard reflection ($15\bar{4}$) checked every 50 reflections, no significant deviation. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain,

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{\rm eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Benzo[*b*]thiophene 1,1-dioxide				
S1	8409 (0)	359 (1)	6366 (0)	3·28
C2	7835 (2)	−925 (2)	6997 (2)	3·70
C3	6880 (2)	−1698 (2)	6478 (2)	3·67
C3*A*	6548 (2)	−1320 (2)	5527 (1)	3·14
C4	5616 (2)	−1928 (2)	4825 (2)	3·94
C5	5460 (2)	−1388 (3)	3967 (2)	4·36
C6	6228 (2)	−274 (3)	3811 (2)	4·29
C7	7191 (2)	345 (2)	4516 (2)	3·76
C7*A*	7318 (2)	−204 (2)	5356 (1)	2·91
O1	9777 (2)	137 (2)	6358 (1)	4·47
O2	8054 (2)	1743 (2)	6602 (1)	5·08
2,3-Dimethylbenzo[*b*]thiophene 1,1-dioxide				
S1	2674 (1)	3514 (1)	2858 (1)	4·98
C2	2072 (3)	5902 (4)	2318 (3)	5·18
C3	2104 (4)	6325 (4)	3677 (4)	5·33
C3*A*	2597 (3)	4729 (4)	5240 (4)	5·13
C4	2785 (5)	4691 (5)	6844 (4)	6·49
C5	3266 (5)	2999 (6)	8138 (4)	7·40
C6	3527 (5)	1385 (5)	7867 (4)	6·86
C7	3368 (4)	1391 (4)	6263 (4)	5·81
C7*A*	2917 (4)	3063 (4)	5000 (3)	4·84
C8	1681 (5)	7029 (5)	512 (5)	7·03
C9	1701 (5)	8228 (5)	3705 (6)	7·19
O1	1195 (3)	2856 (3)	2520 (3)	6·33
O2	4421 (3)	2967 (3)	2167 (3)	6·37
2-Bromobenzo[*b*]thiophene 1,1-dioxide				
Br	633 (1)	1171 (1)	8743 (1)	5·11
S1	1773 (2)	1884 (1)	5587 (1)	3·26
O1	3022 (5)	2654 (3)	6121 (4)	4·48
O2	157 (5)	2313 (3)	5101 (4)	4·40
C2	1509 (6)	813 (4)	6910 (6)	3·55
C3	2027 (6)	−145 (4)	6387 (6)	3·63
C3*A*	2661 (6)	−86 (4)	4873 (6)	3·37
C4	3345 (7)	−926 (4)	4017 (7)	4·19
C5	3909 (7)	−679 (5)	2604 (7)	4·63
C6	3820 (7)	358 (5)	2021 (6)	4·47
C7	3162 (7)	1219 (5)	2856 (6)	4·00
C7*A*	2605 (6)	963 (4)	4259 (6)	3·25

Table 2. *Bond distances* (Å) *and angles* (°) *of benzo*[*b*]*thiophene* 1,1-*dioxide and its* 2,3-*dimethyl and* 2-*bromo derivatives*

	BTO$_2$	Me$_2$BTO$_2$	BrBTO$_2$
C2—S1	1·757 (2) [1·82]*	1·766 (3)	1·770 (5)
C7*A*—S1	1·579 (2) [1·80]	1·757 (2)	1·770 (5)
O1—S1	1·432 (2) [1·46]	1·437 (2)	1·431 (4)
O2—S1	1·437 (2) [1·45]	1·446 (2)	1·438 (4)
C3—C2	1·323 (3) [1·32]	1·335 (4)	1·320 (8)
C3*A*—C3	1·467 (3) [1·47]	1·480 (4)	1·458 (8)
C4—C3*A*	1·379 (3) [1·36]	1·385 (4)	1·392 (7)
C7*A*—C3*A*	1·391 (3) [1·41]	1·401 (3)	1·383 (7)
C5—C4	1·393 (3) [1·40]	1·397 (5)	1·384 (9)
C6—C5	1·380 (4) [1·39]	1·377 (5)	1·359 (9)
C7—C6	1·402 (3) [1·41]	1·391 (4)	1·393 (8)
C7*A*—C7	1·375 (3) [1·36]	1·374 (4)	1·376 (7)
C8—C2		1·495 (5)	
C9—C3		1·507 (4)	
C2—Br			1·848 (5)
C7*A*—S1—C2	93·0 (1)	94·1 (1)	92·2 (2)
O1—S1—C2	112·2 (1)	111·4 (1)	110·5 (2)
O1—S1—C7*A*	110·9 (1)	111·7 (1)	111·4 (2)
O2—S1—C2	110·4 (1)	110·2 (1)	110·1 (2)
O2—S1—C7*A*	110·9 (1)	110·4 (1)	111·9 (2)
O2—S1—O1	117·0 (1)	116·8 (1)	117·8 (2)
C3—C2—S1	110·7 (2)	110·2 (2)	111·3 (4)
C8—C2—S1		116·9 (2)	
C8—C2—C3		133·0 (3)	
C3*A*—C3—C2	114·8 (2)	114·2 (2)	113·8 (4)
C4—C3*A*—C3	128·6 (2)	128·8 (3)	128·6 (5)
C9—C3—C2		125·5 (3)	
C9—C3—C3*A*		120·4 (3)	
C7*A*—C3*A*—C3	112·3 (2)	113·2 (3)	113·8 (4)
C7*A*—C3*A*—C4	119·2 (2)	118·0 (3)	117·5 (5)
C5—C4—C3*A*	118·9 (2)	118·5 (3)	118·9 (5)
C6—C5—C4	121·1 (2)	122·1 (3)	122·3 (5)
C7—C6—C5	120·7 (2)	120·4 (3)	120·2 (5)
C7*A*—C7—C6	116·9 (2)	116·9 (3)	116·9 (5)
C3*A*—C7*A*—S1	109·3 (1)	108·3 (2)	108·8 (4)
C7—C7*A*—S1	127·5 (2)	127·6 (2)	127·1 (4)
C7—C7*A*—C3*A*	123·2 (2)	124·1 (2)	124·1 (5)
S1—C2—Br			118·2 (3)
C3—C2—Br			130·4 (4)

* Data in square brackets from Towns & Simonsen (1974) (e.s.d.'s 0·01 Å).

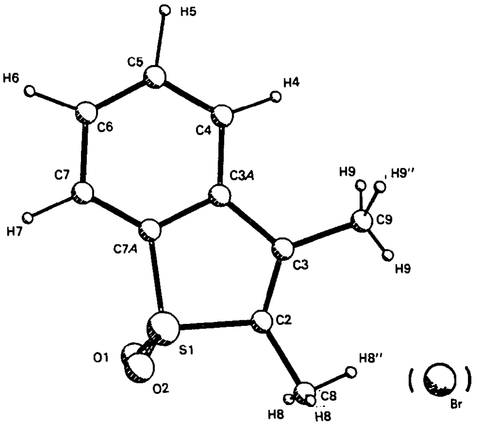

Fig. 1. Numbering of benzo[*b*]thiophene 1,1-dioxide and its 2,3-dimethyl and 2-bromo derivatives.

Declercq & Woolfson, 1980). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976), F values, H isotropic with common refined temperature factor ($B = 4{\cdot}2$ Å^2), $w = 1/[\sigma^2(F) + 0{\cdot}00113F^2]$, $R = 0{\cdot}048$, $wR = 0{\cdot}052$, $S = 1{\cdot}269$ for 1381 observed reflections, $(\Delta/\sigma)_{\max} < 0{\cdot}2$. Max. and min. heights in final difference Fourier synthesis 0·72 and −0·64 e Å^{-3}.

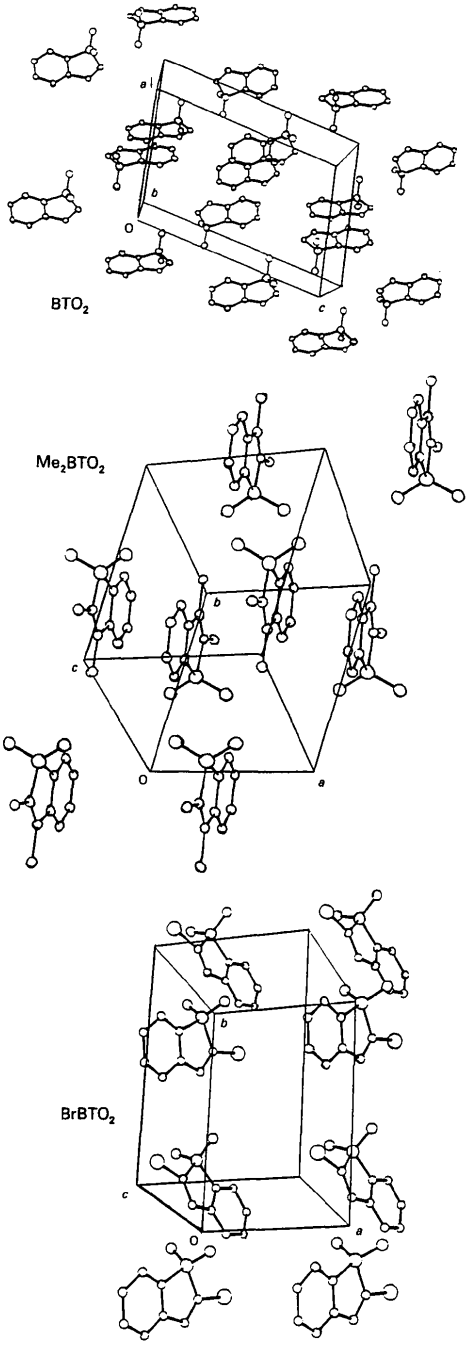

Fig. 2. View of the packing in the unit cells of the benzo[*b*]thiophene 1,1-dioxides (*PLUTO*; Motherwell & Clegg, 1978).

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Mean planes were calculated with *XANADU* (Roberts & Sheldrick, 1975). Figures were drawn with *PLUTO*78 (Motherwell & Clegg, 1978).

Discussion. The atomic coordinates are given in Table 1.* Bond distances and angles are indicated in Table 2. The numbering of the atoms in the three molecules appears in Fig. 1 and the packing in the unit cell for the three dioxides is shown in Fig. 2.

Bond lengths for the three *S*-dioxides are in good agreement with data for 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate (Acheson, Prince, Procter, Wallis & Watkin, 1981), 5-bromo-2,3-dimethylbenzothiophene (Hogg & Sutherland, 1974) and the 2-methyl- and 3-methylbenzothiophene 1,1-dioxides (El Amoudi El Faghi *et al.*, 1988). However, the interatomic C—S distances for BTO$_2$ are noticeably different from data previously reported (Towns & Simonsen, 1974). There is a slight movement towards a quinonoid-type structure in BrBTO$_2$.

The valence angles of BTO$_2$, Me$_2$BTO$_2$ and BrBTO$_2$ are comparable. In BrBTO$_2$ the presence of the bromine atom in the 2-position induces no change in the planarity of the benzothiophene group (*XANADU*; Roberts & Sheldrick, 1975, table deposited).

As in 2-methyl- and 3-methylbenzothiophene 1,1-dioxides (El Amoudi El Faghi *et al.*, 1988) the crystalline cohesion is determined by van der Waals contacts. The crystal packing (Fig. 2) shows that for BTO$_2$ and Me$_2$BTO$_2$ the molecules are parallel to one another but non-coplanar; intermolecular distances between C$_2$—C$_3$ bonds are longer than 4·5 Å. In BrBTO$_2$ molecules inclined to the twofold screw axis and neighbouring molecules are non-parallel.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44278 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 3β-(D-Galactopyranosyl)pregna-5,20-diene–Dimethyl Sulfoxide Solvate

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Abstract. $C_{27}H_{42}O_6.C_2H_6OS$, $M_r = 540·8$, orthorhombic, $P2_12_12_1$, $a = 9·011$ (3), $b = 38·68$ (8), $c = 8·338$ (7) Å, $V = 2906·2$ Å^3, $D_x = 1·236$ g cm^{-3} at 138 K, $Z = 4$, $F(000) = 1176$, $\mu(\mathrm{Cu}\,K\bar{\alpha}) = 12·5$ cm^{-1}, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1·5418$ Å. Structure was determined from 3436 reflections at 138±2K and refined to a final $R = 0·074$ for 2330 observed reflections $[I > 2\sigma(I)]$. The conformation of the steroid nucleus is quite typical for a Δ^5-steroid. Rings *A* and *C* are in a chair conformation, whereas the unsaturated ring *B* assumes an 8β,9α half-chair conformation. The five-membered ring *D* has a half-chair conformation and the orientation of the 17β side chain is consistent with other related pregnene structures. The galactopyranoside ring has the normal $^4C_1$ chair conformation. There is a β-linkage between the galactose and the steroid nucleus.

Introduction. Marine invertebrates have been shown to be rich sources of many natural products including terpenes and steroids. Although a great variety of steroid derivatives have been extracted from various marine organisms (Tursch, Hootele, Kaisin, Losman & Karlsson, 1976; Moldowan, Tan & Djerassi, 1975; Ballantine, Williams & Burke, 1977; Fenical, 1979; Weinheimer, Chang & Matson, 1979), the steroidal glycosides from the marine organisms are relatively rare (Bandurraga & Fenical, 1985). The title compound was isolated from the gorgonian *Pseudoplexaura wagenaari* (collected from Key Biscayne, Florida) and its isolation and identification have been reported in an earlier communication (Wasylyk, Alam, Martin, Weinheimer, Hossain & van der Helm, 1987). The crystal structure determination of the compound was carried out to confirm the chemical structure and to investigate the stereochemical features of a steroidal glycoside, in particular to ascertain the nature of the linkage (α or β) of the galactose to the steroid nucleus.

Experimental. Crystals grown from Me_2SO showed large mosaic spread (~ 1·8°), a rectangular pillar shaped crystal, 0·60 × 0·20 × 0·18 mm, used for X-ray work; all measurements on an Enraf–Nonius CAD-4 diffractometer fitted with a liquid-N_2 low-temperature set up; cell parameters by least-squares fit to $\pm 2\theta$ of 22 reflections, $15 < \theta < 23°$ measured at 138 K using Cu $K\alpha_1$ radiation, space group uniquely determined from systematic extinctions, $h00$, $h = 2n+1$, $0k0$, $k = 2n+1$, $00l$, $l = 2n+1$; intensities of 3436 unique reflections with $2\theta \leq 150°$ at 138±2K using Cu $K\bar{\alpha}$ radiation, $h = 0\rightarrow 11$, $k = 0\rightarrow 48$, $l = 0\rightarrow 10$; θ–2θ scan technique, scan width $(0·90 + 0·20\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(5·0 + 0·86\tan\theta)$ mm, three standard reflections measured every 7200 s of X-ray exposure, maximum variation, 5%; 2330 observed reflections on the basis $I \geq 2\sigma(I)$; Lorentz and polarization corrections, no absorption correction; partial structure obtained from *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1976), and the full structure by difference Fourier syntheses; solvent

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