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Comparison of X-ray Structure of 2- and 3-Methylbenzo[*b*]thiophene 1,1-Dioxides

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Abstract. 2-Methylbenzo[*b*]thiophene 1,1-dioxide: $C_9H_8O_2S$, $M_r = 180{\cdot}23$, monoclinic, $P2_1/c$, $a = 10{\cdot}824\,(4)$, $b = 11{\cdot}473\,(3)$, $c = 7{\cdot}643\,(4)$ Å, $\beta = 117{\cdot}14\,(3)°$, $V = 844{\cdot}7\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}29$ cm^{-1}, $F(000) = 376$, $T = 291$ K, $R = 0{\cdot}038$ for 1450 observed reflections. 3-Methylbenzo[*b*]thiophene 1,1-dioxide: $C_9H_8O_2S$, $M_r = 180{\cdot}23$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}920\,(4)$, $b = 8{\cdot}943\,(3)$, $c = 13{\cdot}852\,(9)$ Å, $V = 857{\cdot}2\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}4$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}25$ cm^{-1}, $F(000) = 376$, $T = 291$ K, $R = 0{\cdot}029$ for 829 observed reflections. The two molecular structures do not show significant differences in bond lengths and bond angles. Only the intermolecular arrangements are very different and can explain the behaviour of these two isomers in their photodimerization. Both molecules are planar.

Introduction. The photochemistry of 2- and 3-substituted benzo[*b*]thiophene 1,1-dioxides in solution leads to cyclobutane compounds (El Amoudi El Faghi, Geneste & Olivé, 1981; Hopkinson, Schloman, Plummer, Wenkert & Raju, 1979). The stereochemistry of the photodimerization is determined by the nature and the position of the substituents. We have studied the molecular structures of the monomers 2- and 3-methylbenzo[*b*]thiophene 1-1-dioxide to determine the effect of the substituent and the conformation of the monomer in the crystalline state.

Experimental. 2-*Methylbenzo*[*b*]*thiophene* 1,1-*dioxide*. Obtained by oxidation of 2-methylbenzo[*b*]thiophene (Geneste, Grimaud, Olivé & Ung, 1977). Colorless crystal, D_m not measured. Prismatic crystal with dimensions 0·27 × 0·32 × 0·35 mm. Lattice parameters refined using 15 reflections in the range $5 \le 2\theta \le 26°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 1931 independent reflections to $(\sin\theta)/\lambda = 0{\cdot}649$ Å^{-1}, 1450 with $I \ge 2{\cdot}5\sigma(I)$. Standard reflection checked every 50 reflections: no significant deviation. No absorption correction. Index range: *h* 0 to 14, *k* 0 to 14, *l* −9 to 8. Structure solved by *SHELX*84 (Sheldrick, 1984). H atoms from difference-Fourier synthesis. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor ($B = 6{\cdot}56$ Å^2). $w = 1/[\sigma^2(F) + 0{\cdot}00025F^2]$, $R = 0{\cdot}038$, $wR = 0{\cdot}042$, $S = 1{\cdot}78$ for 1450 observed reflections. Final maximum shift-to-e.s.d. = 0·05. Maximum and minimum heights in final difference-Fourier synthesis = 0·23 and −0·25 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

3-*Methylbenzo*[*b*]*thiophene* 1,1-*dioxide*. Obtained by oxidation of 3-methylbenzo[*b*]thiophene (Geneste *et al.*, 1977). D_m not measured. Parallelepiped crystal with dimensions 0·15 × 0·40 × 0·4 mm. Lattice parameters refined using 15 reflections in the range $5 \le 2\theta \le 18°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 908 independent reflections to $(\sin\theta)/\lambda = 0{\cdot}595$ Å^{-1}, 829 with $I \ge 2{\cdot}5\sigma(I)$. Standard reflection checked every 50 reflections: no significant deviation. No absorption correction. Index range: *h* 0 to 8, *k* 0 to 10, *l* 0 to 16. Structure solved by *SHELX*84 (Sheldrick, 1984). H atoms from difference-Fourier synthesis. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor ($B = 5{\cdot}4$ Å^2). $w = 1/[\sigma^2(F) + 0{\cdot}0002F^2]$, $R = 0{\cdot}029$, $wR = 0{\cdot}030$, $S = 2{\cdot}51$ for 829 observed reflections. Final maximum shift-to-e.s.d. = 0·15. Maximum and minimum heights in final difference-Fourier synthesis = 0·19 and −0·16 e Å^{-3}. As the dispersion correctionscorrespon-

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ding to Mo radiation are weak, no attempt has been made to determine the absolute configuration. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are given in Tables 1 and 2.* Bond distances and angles are given in Tables 3 and 4. The crystallographic numbering appears in Fig. 1. Bond lengths and angles do not differ significantly, except for the C(2)—S(1) distance and the O(1)—S(1)—C(2) angle. Generally the values are in good agreement with those of 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate (Acheson, Prince, Procter, Wallis & Watkin, 1981) and 5-bromo-2,3-dimethylbenzo[*b*]thiophene (Hogg & Sutherland, 1974). Molecular-planes analysis shows them to be planar. The angle of the aromatic ring with

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2) *of* 2-*methylbenzo*[*b*]*thiophene* 1,1-*dioxide*

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

	x	y	z	B_{eq}
S1	8055 (1)	5765 (<1)	1080 (1)	3·93
C2	9229 (2)	6947 (2)	2001 (3)	3·66
C3	8533 (2)	7936 (2)	1494 (3)	4·02
C3a	7019 (2)	7824 (2)	315 (3)	3·66
C4	6032 (3)	8686 (2)	−450 (4)	5·19
C5	4649 (3)	8375 (3)	−1551 (4)	5·59
C6	4244 (2)	7235 (2)	−1892 (3)	5·04
C7	5221 (2)	6353 (2)	−1141 (3)	4·45
C7a	6591 (2)	5670 (2)	−50 (3)	3·42
C21	10737 (2)	6708 (2)	3175 (4)	5·35
O1	8269 (2)	5121 (1)	−366 (3)	5·92
O2	8033 (2)	5111 (1)	2668 (3)	5·83
H3	8984 (26)	8685 (22)	1892 (34)	6·56
H4	6340 (28)	9473 (23)	−222 (37)	
H5	4044 (27)	8952 (24)	−2008 (37)	
H6	3301 (27)	7079 (21)	−2654 (37)	
H7	4980 (28)	5503 (23)	−1365 (37)	
H21	11312 (25)	7407 (24)	3697 (34)	
H21	11067 (28)	6237 (25)	2543 (37)	
H21″	10897 (25)	6190 (24)	4284 (34)	

Table 2. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2) *of* 3-*methylbenzo*[*b*]*thiophene* 1,1-*dioxide*

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

	x	y	z	B_{eq}
S1	270 (1)	4377 (1)	1342 (<1)	3·31
C2	−893 (5)	4818 (3)	2424 (2)	3·48
C3	128 (4)	4390 (3)	3181 (2)	3·18
C3a	1990 (4)	3676 (3)	2929 (2)	2·93
C4	3407 (5)	3124 (4)	3532 (2)	4·12
C5	5027 (5)	2456 (4)	3141 (3)	4·88
C6	5256 (5)	2340 (4)	2156 (3)	5·02
C7	3871 (5)	2900 (3)	1530 (2)	3·88
C7a	2269 (4)	3566 (3)	1935 (2)	2·97
O1	−799 (4)	3289 (3)	802 (1)	4·81
O2	856 (4)	5716 (2)	839 (1)	4·94
C31	−455 (7)	4571 (4)	4216 (2)	4·93
H2	−2072 (53)	5272 (38)	2417 (21)	5·36
H4	3202 (51)	3208 (37)	4213 (23)	
H5	6016 (53)	2027 (35)	3533 (23)	
H6	6444 (54)	1932 (38)	1872 (22)	
H7	4038 (52)	2876 (36)	818 (23)	
H31	−1534 (55)	5100 (40)	4240 (24)	
H31′	−468 (57)	3683 (36)	4516 (22)	
H31″	495 (51)	4989 (38)	4585 (24)	

Table 3. *Bond distances* (Å) *of* 2- *and* 3-*methylbenzo*[*b*]*thiophene* 1,1-*dioxides*

	2-Methyl	3-Methyl
C2—S1	1·771 (2)	1·746 (3)
C7a—S1	1·751 (2)	1·765 (3)
O1—S1	1·433 (2)	1·434 (2)
O2—S1	1·436 (2)	1·444 (2)
C3—C2	1·319 (3)	1·321 (4)
C21—C2	1·486 (3)	
C3a—C3	1·472 (3)	1·480 (4)
C31—C3		1·498 (4)
C4—C3a	1·376 (3)	1·379 (4)
C7a—C3a	1·388 (3)	1·395 (3)
C5—C4	1·388 (4)	1·381 (5)
C6—C5	1·388 (4)	1·377 (5)
C7—C6	1·384 (3)	1·387 (5)
C7a—C7	1·378 (3)	1·377 (4)

Table 4. *Bond angles* (°) *of* 2- *and* 3-*methylbenzo*[*b*]*thiophene* 1,1-*dioxides*

	2-Methyl	3-Methyl
C7a—S1—C2	92·7 (1)	93·1 (1)
O1—S1—C2	111·2 (1)	113·3 (1)
O2—S1—C7a	110·6 (1)	111·6 (1)
O2—S1—C2	110·5 (1)	110·9 (1)
O2—S1—C7a	111·4 (1)	110·2 (1)
O2—S1—O1	117·0 (1)	117·1 (1)
C3—C2—S1	109·4 (1)	111·7 (2)
C21—C2—S1	119·4 (2)	
C21—C2—C3	131·2 (2)	
C3a—C3—C2	115·6 (2)	113·8 (2)
C31—C3—C2		125·8 (3)
C31—C3—C3a		120·4 (3)
C4—C3a—C3	129·0 (2)	129·1 (2)
C7a—C3a—C3	112·5 (2)	112·6 (2)
C7a—C3a—C4	118·5 (2)	118·3 (3)
C5—C4—C3a	119·2 (2)	119·7 (3)
C6—C5—C4	121·6 (2)	120·9 (3)
C7—C6—C5	120·2 (2)	120·9 (3)
C7a—C7—C6	117·8 (2)	117·2 (3)
C3a—C7a—S1	108·7 (1)	108·8 (2)
C7—C7a—S1	128·4 (2)	128·3 (2)
C7—C7a—C3a	122·8 (2)	123·0 (3)

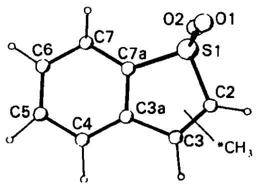

Fig. 1. The crystallographic numbering. The C atom marked with an asterisk is C21 for the 2-methyl isomer, C31 for the 3-methyl isomer.

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* Lists of structure factors, anisotropic thermal parameters and distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44514 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

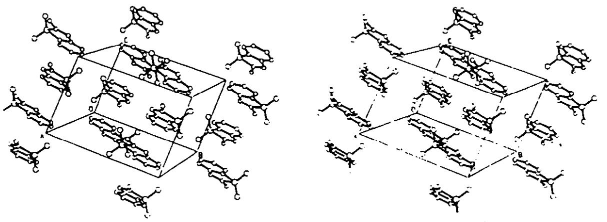

Fig. 2. Stereoview of the packing in the unit cell of 2-methylbenzo[*b*]thiophene 1,1-dioxide (*PLUTO*, Motherwell & Clegg, 1978).

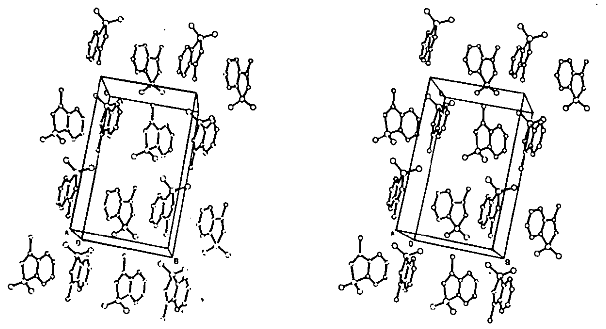

Fig. 3. Stereoview of the packing in the unit cell of 3-methylbenzo[*b*]thiophene 1,1-dioxide (*PLUTO*, Motherwell & Clegg, 1978).

the thiophene is 1·3° for the 2-methyl and 1·6° for the 3-methyl isomer. These values are not significantly different from zero and so the molecules are planar.

The dihedral-angle values (*XANADU*, Roberts & Sheldrick, 1975) show the position of the H for the 2- and 3-methylbenzo[*b*]thiophenes to be the same with respect to the methyl radical: the values of the torsion angles H2—C2—C3—C31, H3—C3—C2—C21 and S1—C2—C3—C3a are 0·0° ($\sigma = 0{\cdot}6°$).

However, the molecular packing is different in the two isomers. The 2-methyl (Fig. 2) molecules are parallel to one another and only van der Waals contacts with radii between 3·5 and 4 Å are present. The 3-methyl (Fig. 3) molecule possesses three twofold screw axes which imply neighbouring molecules are non-parallel to each other and van der Waals contacts are greater than 4·5 Å.

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Complexe 1:2 Hexaoxa-1,4,7,10,13,16 Cyclooctadécane (18-Crown-6)–*N*-*m*-Chlorophényl-urée

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Abstract. $C_{13}H_{19}ClN_2O_4$, $C_7H_7ClN_2O.\frac{1}{2}C_{12}H_{24}O_6$, $M_r = 302{\cdot}45$, monoclinic, $C2/c$, $a = 25{\cdot}590\,(14)$, $b = 7{\cdot}965\,(3)$, $c = 15{\cdot}237\,(9)$ Å, $\beta = 101{\cdot}64\,(4)°$, $V = 3041{\cdot}8\,(28)$ Å^3, $Z = 8$, $D_x = 1{\cdot}32$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}27$ mm^{-1}, $F(000) = 1280$, $T = 293$ K. Final $R = 0{\cdot}046$ for 1093 observed reflections. The centrosymmetrically related guest molecules are almost perpendicular to the 18-crown-6 molecule. The complex adopts the biangular conformation of the macrocycle, and one H atom from each of the amino groups in the guest molecule hydrogen bonds to adjacent O atoms. The present structure is the first evidence of the formation of a discrete 1:2 crown ether–urea molecule complex.

Introduction. Ces dernières années, un grand nombre de complexes des éthers couronne avec des cations et des molécules chargées ont été préparés et étudiés par

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