

Acta Cryst. (1987). **C43**, 561–562

X-ray Structure of a Head-to-Tail Photodimer of 2-Methylbenzo[*b*]thiophene 1,1-Dioxide

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(Received 17 June 1986; accepted 7 October 1986)

Abstract. *r*-1,*c*-2,*c*-3,*c*-4-Di(2',3'-benzothiophene 1,1-dioxide)-1,3-dimethylcyclobutane (alternative name: 5a,10a-dimethyldibenzo[*d*:*d'*]cyclobuta[1,2-*b*:4,3-*b'*]-dithiophene 5,5,10,10-tetraoxide), C₁₈H₁₆O₄S₂, *M_r* = 360.4, monoclinic, *P*2₁/*c*, *a* = 8.423 (1), *b* = 22.698 (3), *c* = 8.819 (1) Å, β = 102.94 (1)°, *V* = 1643.2 (3) Å³, *Z* = 4, *D_x* = 1.45 g cm⁻³, λ(Cu *K*α) = 1.54178 Å, μ = 30.1 cm⁻¹, *F*(000) = 752, *T* = 291 K, *R* = 0.044 for 2616 observed reflections. The molecular structure shows no significant differences in bond lengths and angles between the two benzo[*b*]thiophene groups and the molecule is essentially symmetrical with respect to the cyclobutane ring. Bond lengths and angles are normal.

Introduction. The assignment of structure to the dimers obtained by irradiation of substituted benzo[*b*]thiophene 1,1-dioxides was based on ¹³C and ¹H NMR (El Amoudi, Geneste & Olivé, 1981; Hopkinson, Schloman, Plummer, Wenkert & Raju, 1979); for benzo[*b*]thiophene 1,1-dioxide itself, the structures of the two dimers obtained were based on chemical methods (Harpp & Heitner, 1970).

In this article we report the X-ray structure of the head-to-tail dimer obtained from irradiation of 2-methylbenzo[*b*]thiophene 1,1-dioxide whose stereochemistry contrasts with that reported previously (El Amoudi *et al.*, 1981; Hopkinson *et al.*, 1979).

Experimental. Colourless prismatic crystal, 0.17 × 0.20 × 0.25 mm. Lattice parameters refined using 23 reflections in the range 10 < 2θ < 24°. No absorption correction. Huber 424 + 511 diffractometer, graphite-monochromatized Cu *K*α radiation, 2959 independent reflections with (sinθ)/λ ≤ 0.599 Å⁻¹. 2616 with *I* ≥ 2.5σ(*I*), index range *h* -10/9, *k* 0/27, *l* 0/10.

Standard reflection ($\bar{1}51$) checked every 50 reflections, no significant deviation. Structure solved by direct methods using *SHELX84* (Sheldrick, 1984). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX76* (Sheldrick, 1976), *F* values. H isotropic with common refined temperature factor (*B* = 4.87 Å²). *w* = 1/[σ²(*F*) + 0.01510*F*²]. *R* = 0.044, *wR* = 0.053, *S* = 0.625 for 2616 observed reflections. Final max. shift-to-e.s.d. ratio 0.8. Max. and min. heights in final difference Fourier synthesis 0.25 and -0.50 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Mean planes were calculated with *XANADU* (Roberts & Sheldrick, 1975); figures were drawn with *PLUTO78* (Motherwell & Clegg, 1978).

Discussion. The atomic coordinates are given in Table 1* and Fig. 1 is a view of the dimer. Fig. 2 shows the packing in the unit cell. Bond distances are given in Table 2.

The bond distances and bond angles for the two benzo[*b*]thiophene groups on the cyclobutane ring are indistinguishable and comparable to those of the 2-methyl and 3-methylbenzo[*b*]thiophene 1,1-dioxides (El Amoudi, Geneste, Olivé, Rambaud & Declercq, 1987). The cyclobutane bonds are simple C–C bonds (*International Tables for X-ray Crystallography*, 1962) but the values of the angles are significantly different from 90° [range: 87.3 (2)–88.7 (2)°] which causes a

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles, mean-plane calculations and intermolecular contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43502 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

slight ($\pm 0.14 \text{ \AA}$) out-of-plane deformation. These values are in good agreement with those in the literature (Moriarty, 1974).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2)

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i a_j a_i^* \cdot a_j^*$$

	x	y	z	B_{eq}
S(1)	92 (1)	3547 (<1)	8803 (1)	2.97
C(2)	-353 (3)	3547 (1)	6718 (3)	3.03
C(3)	1039 (3)	3193 (1)	6228 (2)	2.84
C(4)	4035 (3)	2981 (1)	7650 (3)	3.60
C(5)	5220 (3)	3028 (1)	9004 (4)	4.27
C(6)	4905 (3)	3268 (1)	10353 (3)	4.11
C(7)	3353 (3)	3457 (1)	10360 (3)	3.58
C(7A)	2169 (3)	3409 (1)	8992 (3)	2.62
C(3A)	2474 (3)	3191 (1)	7612 (2)	2.67
C(21)	-2114 (4)	3352 (2)	6108 (4)	4.78
O(1)	-273 (3)	4093 (1)	9463 (2)	4.39
O(2)	-629 (2)	3024 (1)	9295 (2)	4.07
O(1')	4134 (3)	3612 (1)	4753 (3)	4.28
O(2')	2401 (3)	4364 (1)	3256 (2)	4.26
S(1')	2792 (1)	4009 (<1)	4639 (1)	3.06
C(2')	968 (3)	3653 (1)	4890 (3)	2.98
C(3')	127 (3)	4096 (1)	5825 (3)	3.06
C(4')	1292 (4)	4935 (1)	7775 (3)	3.77
C(5')	2648 (5)	5265 (1)	8462 (4)	4.77
C(6')	4119 (4)	5199 (1)	8044 (4)	4.79
C(7')	4284 (3)	4804 (1)	6909 (3)	3.81
C(7A')	2925 (3)	4471 (1)	6244 (3)	2.89
C(3A')	1430 (3)	4515 (1)	6667 (3)	2.88
C(21')	48 (4)	3427 (2)	3300 (3)	4.30

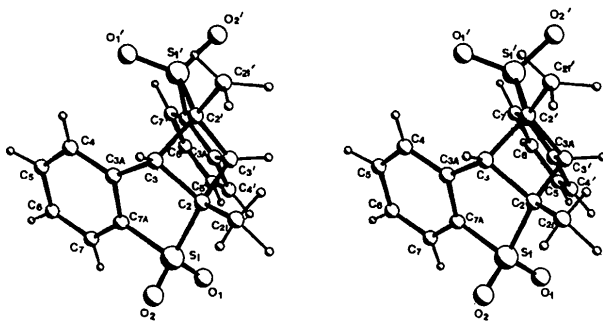


Fig. 1. Stereoview of the molecule with the atom numbering.

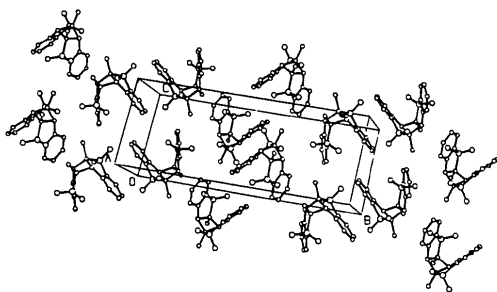


Fig. 2. View of the packing in the unit cell.

Table 2. Bond distances (\AA)

C(2)—S(1)	1.793 (2)	C(3A)—C(7A)	1.390 (3)
C(7A)—S(1)	1.748 (2)	S(1')—O(1')	1.432 (2)
O(1)—S(1)	1.431 (2)	S(1')—O(2')	1.438 (2)
O(2)—S(1)	1.443 (2)	C(2')—S(1')	1.793 (2)
C(3)—C(2)	1.561 (3)	C(7A')—S(1')	1.745 (2)
C(21)—C(2)	1.525 (3)	C(3')—C(2')	1.565 (3)
C(3')—C(2)	1.575 (3)	C(21')—C(2')	1.531 (3)
C(3A)—C(3)	1.513 (3)	C(3A')—C(3')	1.515 (3)
C(2')—C(3)	1.567 (3)	C(5')—C(4')	1.386 (4)
C(5)—C(4)	1.379 (4)	C(3A')—C(4')	1.389 (3)
C(3A)—C(4)	1.392 (3)	C(6')—C(5')	1.379 (4)
C(6)—C(5)	1.387 (4)	C(7')—C(6')	1.374 (4)
C(7)—C(6)	1.378 (4)	C(7A')—C(7')	1.386 (3)
C(7A)—C(7)	1.387 (3)	C(3A')—C(7A')	1.394 (3)

The dimer is made up of five principal planes (the two benzothiophene residues, the two SO_2 units and the cyclobutane ring), and is symmetrical with respect to the cyclobutane ring to within the limits of experimental errors. When the dimer is viewed along the C(2)—C(3) and C(3')—C(2') benzothiophene bonds, it appears as a U-shaped structure.

This 'U-structure', the *r-ccc* htt dimer according to the Rules for the Nomenclature of Organic Chemistry, Section E (IUPAC, 1976) (*i.e.* head-to-tail *cis syn cis* dimer) involves relatively short O(1)—C(4') and O(1')—C(4) distances [2.916 (3) and 2.943 (3) \AA , respectively]. However, there is no hydrogen bond, the C—H...O angles being 72 (2) and 73 (2) $^\circ$.

Many van der Waals contacts at distances less than 3.5 \AA assure the cohesion of the crystal.

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