The Crystal Structure of 5-Bromo-2,3-dimethylbenzo[*b*]thiophen

BY J. H. C. HOGG AND H. H. SUTHERLAND

Physics Department, The University of Hull, Hull, HU6 7RX, England

Abstract. 5-Bromo-2,3-dimethylbenzo[*b*]thiophen, $C_{10}H_9SBr$, $M = 241 \cdot 2$, is monoclinic, $P2_1/c$; $a = 6 \cdot 44$ (1), $b = 8 \cdot 45$ (1), $c = 17 \cdot 79$ (2) Å, $\beta = 98 \cdot 5$ (1)°, $D_m = 1 \cdot 68$, $D_c = 1 \cdot 67$ g cm^{-3}; $U = 957 \cdot 5$ Å^3, $Z = 4$, $F(000) = 480$. The structure was solved from a sharpened Patterson map and refined by block-diagonal least-squares calculations to $R = 5 \cdot 8\%$ for 1425 structure factors. The five- and six-membered rings are planar and inclined to one another at $0 \cdot 6°$. In the five-membered ring the average C–S bond is $1 \cdot 749$ (10) Å, the C–S–C angle is $91 \cdot 7$ (5)°; there is a long C–C bond of $1 \cdot 446$ (12) Å and a short C–C bond of $1 \cdot 355$ (14) Å.

Introduction. $C_{10}H_9SBr$ forms crystals which discolour on exposure to the atmosphere and which sublime under X-ray irradiation. The density measured by flotation in aqueous cadmium n-dodecatungstaborate at 22°C had a mean value very marginally higher than the calculated density. This could be due to reaction products on the surface of the crystals.

Intensities for 1425 reflexions were collected from Weissenberg photographs with multiple-film packs and Cu $K\alpha$ radiation. Sublimation necessitated the use of four different crystals. However, later analysis showed no significant difference between the R values for the various crystals. The intensities were measured with a Joyce–Loebl flying-spot densitometer and were corrected for Lorentz and polarization factors; overall scale and temperature factors were obtained by Wilson's (1942) method. The structure was solved from minimum functions using a sharpened Patterson synthesis. After block-diagonal least-squares refinement to $R = 0 \cdot 078$ where $R = \sum ||F_o| - |F_c||/\sum|F_o|$, all hydrogen atoms were located by difference synthesis. Refine-

ment of positional, scale and anisotropic thermal parameters for C, S and Br and isotropic thermal parameters for H resulted in a final $R = 0 \cdot 058$. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962).* Table 1 gives the heavy atom coordinates and thermal parameters; the hydrogen atom parameters are quoted in Table 2; intermolecular contacts less than $3 \cdot 75$ Å are shown in Table 3; the numbering of the atoms in the molecule together with the bond lengths and angles are shown in Fig. 1 and the arrangement of the molecules in the unit cell viewed along **a** is shown in Fig. 2. The equations of the mean molecular plane and of the planes of the individual rings with the deviations of the atoms from the planes are given in Table 4.

Table 2. *Fractional coordinates and thermal parameters* (*all* $\times 10^3$) *of the hydrogen atoms*

	X/a	Y/b	Z/c	$U_{iso}(Å^2)$
H(C2)	97	464	418	39
H(C4)	348	448	206	54
H(C5)	656	286	265	18
H(C9)	237	211	572	69
H'(C9)	191	386	537	92
H"(C9)	391	363	603	88
H(C10)	884	151	594	71
H'(C10)	699	−11	580	96
H"(C10)	654	165	630	78

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$ Å^2) *with e.s.d.'s in parentheses*

Thermal parameters are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

|	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Br	−169 (2)	5865 (2)	2624 (1)	50 (1)	49 (1)	53 (1)	7 (1)	−8 (1)	12 (1)
S	7445 (4)	1766 (4)	4291 (1)	41 (1)	40 (2)	39 (1)	8 (2)	15 (2)	−1 (2)
C(1)	3947 (14)	3316 (13)	4192 (5)	40 (4)	27 (6)	29 (3)	−15 (8)	21 (6)	−6 (7)
C(2)	2213 (15)	4236 (12)	3847 (5)	39 (4)	22 (7)	37 (4)	−8 (7)	18 (6)	−13 (7)
C(3)	2124 (16)	4623 (14)	3096 (5)	47 (4)	20 (6)	34 (4)	−5 (9)	11 (7)	0 (8)
C(4)	3635 (18)	4141 (13)	2656 (5)	55 (5)	36 (8)	28 (4)	4 (9)	21 (7)	2 (7)
C(5)	5331 (16)	3259 (13)	2984 (5)	59 (5)	26 (7)	32 (3)	−6 (9)	33 (7)	−11 (7)
C(6)	5466 (14)	2852 (13)	3750 (5)	41 (4)	25 (6)	34 (4)	−7 (8)	21 (6)	−7 (7)
C(7)	6219 (16)	1942 (13)	5104 (5)	48 (5)	35 (7)	28 (4)	−21 (9)	−1 (7)	−7 (7)
C(8)	4409 (15)	2780 (13)	4971 (5)	46 (4)	27 (6)	26 (3)	−17 (8)	9 (6)	−6 (7)
C(9)	3046 (19)	3113 (16)	5562 (6)	59 (5)	55 (9)	35 (4)	−17 (11)	33 (7)	−6 (9)
C(10)	7254 (19)	1197 (17)	5828 (6)	53 (6)	58 (9)	41 (5)	−12 (12)	−16 (9)	10 (10)
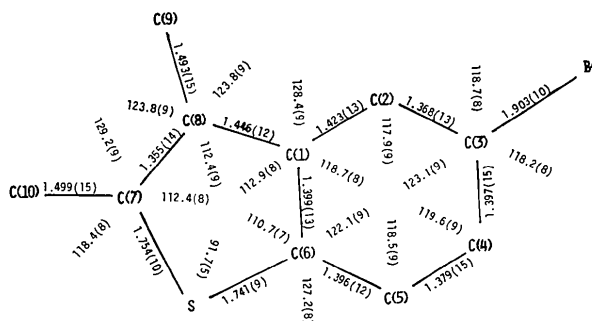
Fig. 1. The molecular structure with bond lengths (Å) and bond angles (°). Estimated standard deviations are in parentheses.
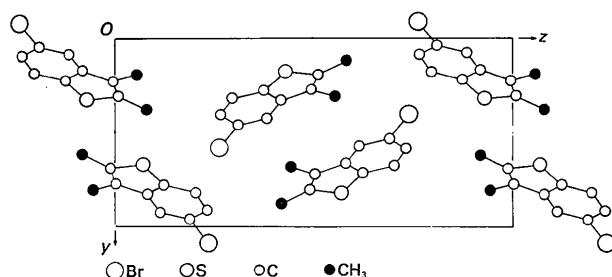

Fig. 2. The crystal packing viewed along the a direction.

Table 3. *Intermolecular distances between atoms less than 3·75 Å apart* (*excluding hydrogen atoms*)

Br·····C(4)	−x, y, −z	3·545
Br·····C(3)	−x, y, −z	3·583
C(1)···C(9)	1−x, 1−y, 1−z	3·578
C(7)···C(7)	1−x, −y, 1−z	3·634
C(7)···C(10)	1−x, −y, 1−z	3·701
C(6)···C(9)	1−x, 1−y, 1−z	3·701
C(1)···C(8)	1−x, 1−y, 1−z	3·709
C(8)···C(10)	1−x, −y, 1−z	3·744

Discussion. The individual five- and six-membered rings are planar but the molecule as a whole shows a small deviation from planarity, the rings being inclined at 0·6° to one another. The outer atoms of the six-membered ring C(2) to C(5), the bromine and the two methyl groups are all displaced in the same direction from the plane of the five-membered ring. The C(3)–Br bond of 1·903 (10) Å is close to the mean bromine to aromatic carbon atom distance of 1·8966 (19) Å (James & Williams, 1973) whilst the C(7)–C(10) and C(8)–C(9) bonds of 1·499 (15) and 1·493 (15) Å respectively are close to the expected value of 1·50 (1) Å.

The mean C–S bond of 1·749 (10) Å is in agreement with the value of 1·740 (8) Å found in dibenzothiophen (Schaffrin & Trotter, 1970) and longer than the value

Table 4. *The equations of the mean planes of* (I) C(1)–C(10), S, Br; (II) C(1)–C(6); (III) C(1), C(6), C(7), C(8), S

(I)	0·4848 X'+0·8378 Y'+0·2510 Z'=4·9156
(II)	0·4836 X'+0·8377 Y'+0·2538 Z'=4·9176
(III)	0·4769 X'+0·8437 Y'+0·2465 Z'=4·8686

Deviations from the mean planes in Å($\times 10^3$)

	I	II	III
Br	8	19	70
S	7	22	0
C(1)	−19	−2	0
C(2)	−17	−1	17
C(3)	−7	5	34
C(4)	−15	−6	19
C(5)	−6	3	12
C(6)	−12	1	0
C(7)	4	24	0
C(8)	−9	11	0
C(9)	−13	11	1
C(10)	28	50	10

of 1·717 Å for thiophen given by Harshbarger & Bauer (1970). The C(1)–C(8) bond of 1·446 (12) Å compares closely with the 1·442 Å of Harshbarger & Bauer and whilst it is longer than the value of 1·419 (7) Å quoted by Bonham & Momany (1963) also for thiophen, it is in good agreement with the 1·441 (1) Å in dibenzothiophen and 1·455 (6) Å in 1:1 trinitrobenzene–3-formylbenzothiophen (Pascard & Pascard-Billy, 1972). The short C(7)–C(8) bond of 1·355 (14) Å is not unexpected although it is shorter than the 1·367 (6) in 1:1 trinitrobenzene–3-formylbenzothiophen; the corresponding bond in thiophen is 1·369 Å. The C–S–C bond angle of 91·7 (5)° is similar to those in related molecules.

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