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The Crystal and Molecular Structure of *anti*-8-Tricyclo[3,2,1,$0^{2,4}$]octyl *p*-bromobenzenesulphonate

By A. C. Macdonald and J. Trotter

Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada

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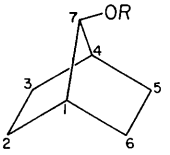
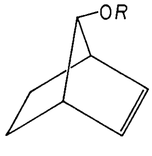
The crystal structure of *anti*-8-tricyclo[3,2,1,$0^{2,4}$]octyl *p*-bromobenzenesulphonate, $C_{14}H_{15}O_3SBr$, has been determined to provide quantitative molecular data to assist in the interpretation of the variation of solvolytic reactivity in norbornane derivatives. The crystals are monoclinic, with 8 molecules in a unit cell of dimensions $a = 23{\cdot}76$, $b = 7{\cdot}06$, $c = 19{\cdot}49$ Å, $\beta = 120{\cdot}3°$, space group $C2/c$. The intensities of 1045 reflexions were measured with a scintillation counter, using Cu $K\alpha$ radiation. The structure was determined by Patterson and Fourier methods, and the parameters were refined by differential syntheses and least squares. The final R value is 0·093. The configuration of the cyclopropyl methylene group is *exo*. The bond distances are all normal, but the valency angles in the norbornane nucleus differ from the tetrahedral value; the angles in the cyclopropyl ring are all 60°, and the angle at the bridgehead is 96·7°. The intermolecular distances all correspond to normal van der Waals interactions.

Introduction

Saturated norbornane derivatives, with substituents on the methylene bridge or 7-position (I), show a lack of solvolytic reactivity when compared with other secondary compounds, such as 2-adamantyl or cyclohexyl derivatives (Schleyer & Nicholas, 1961, where an extensive list of references is given). The effects on the solvolysis rate of the introduction of elements of unsaturation into the bicycloheptane nucleus are remarkable; the rate of hydrolysis of II (R = *p*-bromobenzenesulphonyl) is 10^4 greater than that of I; of III, 10^{11} greater; and of IV, 10^{14} greater. These large increases have generally been interpreted in terms of anchimeric assistance due to homoallylic or other non-classical electron delocalization, or of a variation in the C(1)–C(7)–C(4) angle. A quantitative assessment of this latter factor has been prevented by the lack of any molecular structure data, and the angle has generally been estimated from models, or derived from empirical relations involving infrared stretching frequencies.



(I)



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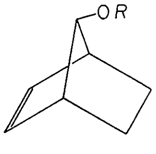

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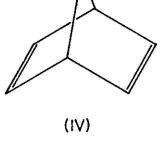

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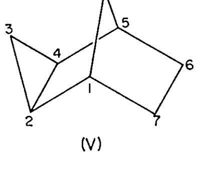

(V)

Reaction of *anti*-7-norbornenol (III, R = H) with diazomethane (Pincock & Wells, 1964*a*) yields *anti*-8-tricyclo[3,2,1,$0^{2,4}$]octanol (V, R = H, or the isomer with the cyclopropyl methylene group *endo*). We have undertaken an X-ray analysis of the crystal structure of the *p*-bromobenzenesulphonyl derivative of V, to establish the configuration of the cyclopropyl methylene group, and to measure the molecular dimensions, in particular the C(1)–C(8)–C(5) angle, to assist in the interpretation of the solvolytic reactivity in norbornane derivatives. The analysis shows that the compound is the *exo* isomer.

Experimental

Crystals of *anti*-8-tricyclo[3,2,1,$0^{2,4}$]octyl *p*-bromobenzenesulphonate are colourless needles elongated along *b*. The density was measured by flotation in aqueous potassium iodide, and the unit-cell dimensions and space group were determined from rotation and Weissenberg photographs, and on the G.E. Spectrogoniometer.

Crystal data (λ(Cu $K\alpha$) = 1·5418 Å).
anti-8-Tricyclo[3,2,1,$0^{2,4}$]octyl *p*-bromobenzenesulphonate (*exo* isomer), $C_{14}H_{15}O_3SBr$; M.W. 343·2; m.p. 86 °C.
Monoclinic,

$$a = 23{\cdot}76 \pm 0{\cdot}02,\ b = 7{\cdot}06 \pm 0{\cdot}01\ ,$$
$$c = 19{\cdot}49 \pm 0{\cdot}02\ \text{Å};\ \beta = 120{\cdot}26° \pm 0{\cdot}04°.$$

$U = 2825$ Å^3.
$D_m = 1{\cdot}62$ g.cm^{-3}, $Z = 8$, $D_x = 1{\cdot}614$ g.cm^{-3}.
$F(000) = 1392$.
Absorption coefficient for X-rays,

$$\lambda = 1{\cdot}5418\ \text{Å},\ \mu = 57\ \text{cm}^{-1}.$$

Table 1. *Measured and calculated structure factors*

The values listed are *h*, *k*, *l*, $\frac{1}{4}|F_o|$ and $\frac{1}{4}F_c$; unobserved reflexions, which are listed as 0·0, have $\frac{1}{4}|F_o| < 2$

2	0	0	42.0	-48.8
4	0	0	31.7	-31.9
6	0	0	39.9	-41.2
8	0	0	19.9	20.0
10	0	0	7.5	-1.2
12	0	0	9.0	-9.0
14	0	0	23.0	-24.3
16	0	0	7.8	9.2
18	0	0	15.4	15.9
-18	0	2	4.2	3.3
-16	0	2	9.1	11.6
-14	0	2	3.5	3.6
-12	0	2	29.3	-27.1
-10	0	2	24.6	-25.3
-8	0	2	5.0	7.5
-6	0	2	106.4	139.5
-4	0	2	19.8	-24.4
-2	0	2	6.7	-12.2
0	0	2	4.9	6.8
2	0	2	12.2	-6.5
4	0	2	14.8	-12.8
6	0	2	37.6	-35.9
8	0	2	35.2	-33.1
10	0	2	28.8	30.1
12	0	2	21.0	20.7
14	0	2	9.3	-11.3
16	0	2	8.7	-9.8
-18	0	4	20.6	-19.6
-16	0	4	0.0	-0.1
-14	0	4	25.2	24.6
-12	0	4	17.5	19.3
-10	0	4	20.2	-18.8
-8	0	4	57.7	-56.4
-6	0	4	79.0	84.1
-4	0	4	8.0	10.5
-2	0	4	31.0	-27.6
0	0	4	85.5	-98.9
2	0	4	44.7	41.3
4	0	4	26.5	29.4
6	0	4	4.5	5.1
8	0	4	29.3	-31.3
10	0	4	0.0	-2.6
12	0	4	3.1	1.9
14	0	4	20.2	20.9
16	0	4	12.4	-14.5
-20	0	6	14.3	14.7
-18	0	6	11.5	-10.3
-16	0	6	14.4	-14.6
-14	0	6	36.6	-34.8
-12	0	6	52.7	53.0
-10	0	6	3.4	5.5
-8	0	6	24.2	-22.3
-6	0	6	44.2	-42.7
-4	0	6	63.1	56.2
-2	0	6	25.9	23.6
0	0	6	10.7	-8.5
2	0	6	47.7	-43.0
4	0	6	19.1	-18.8
6	0	6	33.8	34.3
8	0	6	18.7	20.9
10	0	6	19.2	-22.6
12	0	6	7.0	0.0
14	0	6	9.8	10.1
-20	0	8	19.0	-17.2
-18	0	8	30.5	31.5
-16	0	8	18.3	-17.0
-14	0	8	12.7	-11.9
-12	0	8	8.5	-6.3
-10	0	8	56.3	55.4
-8	0	8	26.1	22.8
-6	0	8	45.0	-42.8
-4	0	8	28.4	-27.0
-2	0	8	0.0	0.0
0	0	8	47.1	45.0
2	0	8	24.1	-23.0
4	0	8	0.0	-0.4
6	0	8	9.2	-9.4
8	0	8	22.0	23.9
10	0	8	6.8	-6.8
14	0	8	13.5	-16.3
16	0	8	12.2	14.3
-22	0	10	15.2	-15.3
-20	0	10	0.0	-0.1
-18	0	10	8.6	6.4
-16	0	10	26.4	25.8
-14	0	10	8.6	8.9
-12	0	10	34.2	-34.5
-10	0	10	3.9	-6.0
-8	0	10	29.5	29.6
-6	0	10	9.2	8.2
-4	0	10	21.7	-22.9
-2	0	10	7.0	-7.6
0	0	10	1.4	-1.4
2	0	10	37.7	37.9
4	0	10	17.9	-18.4
6	0	10	14.4	-15.5
8	0	10	15.3	-16.3
10	0	10	26.2	28.2
-24	0	12	15.4	11.9
-18	0	12	40.4	-36.5
-16	0	12	22.2	21.9
-14	0	12	22.1	22.5
-12	0	12	8.9	-5.7
-10	0	12	18.1	-17.1
-8	0	12	10.4	-9.6
-6	0	12	19.0	17.8
-4	0	12	18.1	17.0
-2	0	12	25.4	-25.5
0	0	12	24.3	-25.0
2	0	12	8.1	8.3
4	0	12	14.8	14.5
6	0	12	3.4	0.5
-18	0	14	0.0	1.1
-16	0	14	8.0	-7.2
-14	0	14	0.0	0.9
-12	0	14	13.5	14.1
-10	0	14	2.6	0.5
-8	0	14	27.0	-27.4
-6	0	14	20.0	-19.3
-4	0	14	24.3	23.4
-2	0	14	4.1	2.7
0	0	14	6.4	6.0
2	0	14	20.9	-19.2
4	0	14	15.6	16.4
-18	0	16	15.8	14.5
-16	0	16	20.1	-19.0
-14	0	16	12.6	-12.2
-12	0	16	6.8	-6.8
-10	0	16	24.7	23.9
-8	0	16	7.7	-9.6
-6	0	16	0.0	1.0
-4	0	16	12.9	-10.4
-2	0	16	21.6	22.0
-16	0	18	18.0	17.8
-8	0	18	19.2	18.9
-4	0	18	8.6	-8.4
-16	0	20	14.0	13.2
1	1	0	11.6	13.9
3	1	0	22.2	-22.6
5	1	0	63.7	-63.7
7	1	0	27.1	26.2
9	1	0	40.5	41.2
11	1	0	8.4	6.7
13	1	0	23.0	-23.5
15	1	0	8.2	-8.6
17	1	0	9.5	10.4
-17	1	1	7.6	-6.6
-15	1	1	2.3	0.5
-13	1	1	0.0	2.1
-11	1	1	4.5	-3.9
-9	1	1	20.9	18.6
-7	1	1	26.0	-23.0
-5	1	1	56.6	55.9
-3	1	1	7.1	6.6
-1	1	1	21.6	-18.9
1	1	1	46.7	-44.2
3	1	1	14.1	14.9
5	1	1	29.7	-26.0
7	1	1	5.1	8.2
9	1	1	4.9	-5.3
11	1	1	7.0	8.7
13	1	1	4.1	-4.6
15	1	1	12.6	12.1
17	1	1	8.7	-8.8
-17	1	2	9.5	8.7
-15	1	2	18.4	19.1
-13	1	2	2.0	-1.7
-11	1	2	40.3	-41.6
-9	1	2	21.2	-20.3
-7	1	2	62.0	63.4
-5	1	2	29.9	-28.2
-3	1	2	29.0	-30.1
-1	1	2	55.1	-57.6
1	1	2	72.4	77.6
3	1	2	50.0	53.0
5	1	2	21.1	-20.7
7	1	2	30.4	-32.3
9	1	2	4.1	5.4
11	1	2	23.9	26.4
13	1	2	0.0	-0.7
15	1	2	13.8	-15.2
17	1	2	4.3	-0.3
-17	1	3	2.9	-0.5
-15	1	3	10.1	9.7
-13	1	3	21.9	-20.3
-11	1	3	30.9	28.4
-9	1	3	5.4	-3.7
-7	1	3	6.1	6.0
-5	1	3	2.6	-0.4
-3	1	3	12.1	14.2
-1	1	3	74.1	-78.8
1	1	3	42.4	44.5
3	1	3	17.9	-15.6
5	1	3	4.2	5.7
7	1	3	12.9	-12.4
9	1	3	22.1	19.9
11	1	3	9.4	-9.7
13	1	3	0.0	0.5
15	1	3	3.4	1.6
-17	1	4	13.9	-14.2
-15	1	4	6.6	-4.8
-13	1	4	44.5	43.0
-11	1	4	45.9	-41.6
-9	1	4	3.2	-6.4
-7	1	4	0.0	-5.5
-5	1	4	72.5	76.2
-3	1	4	10.9	11.2
-1	1	4	25.8	-26.1
1	1	4	46.0	-42.7
3	1	4	29.7	29.2
5	1	4	42.9	40.3
7	1	4	16.8	-17.3
9	1	4	23.0	-23.2
11	1	4	3.4	-1.6
13	1	4	18.6	20.3
15	1	4	5.5	-4.0
-17	1	5	14.2	13.2
-15	1	5	9.6	-9.1
-13	1	5	0.0	0.6
-11	1	5	24.0	22.2
-9	1	5	2.6	0.5
-7	1	5	15.5	-16.0
-5	1	5	0.0	1.1
-3	1	5	16.9	-15.5
-1	1	5	7.9	7.4
1	1	5	1.7	1.3
3	1	5	20.3	-20.0
5	1	5	11.8	12.5
7	1	5	4.0	-4.2
9	1	5	9.5	9.3
11	1	5	9.0	-10.0
13	1	5	7.2	7.2
-17	1	6	25.1	-22.6
-15	1	6	12.5	-12.9
-13	1	6	29.1	28.7
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-9	1	6	11.1	-11.4
-7	1	6	41.9	-42.8
-5	1	6	29.1	-26.1
-3	1	6	50.3	49.5
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1	1	6	32.2	-35.2
3	1	6	13.0	-16.4
5	1	6	20.6	22.5
7	1	6	14.9	16.9
9	1	6	19.3	-20.7
11	1	6	9.5	-11.2
13	1	6	5.4	-5.6
-17	1	7	8.9	8.0
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-13	1	7	8.0	6.7
-11	1	7	5.0	-4.2
-9	1	7	5.7	-5.6
-7	1	7	3.5	2.2
-5	1	7	8.5	-8.6
-3	1	7	20.4	-17.5
-1	1	7	22.6	23.1
1	1	7	37.3	-34.5
3	1	7	28.1	28.4
5	1	7	5.4	-5.2
7	1	7	4.3	3.2
9	1	7	8.6	-8.8
11	1	7	14.9	15.5
-17	1	8	8.5	8.7
-15	1	8	4.4	-5.4
-13	1	8	26.8	-28.3
-11	1	8	10.0	11.0
-9	1	8	8.2	11.3
-7	1	8	1.4	1.5
-5	1	8	41.2	-39.1
-3	1	8	3.5	0.8
-1	1	8	44.5	43.5
1	1	8	6.9	9.0
3	1	8	31.4	-32.0
5	1	8	23.6	-24.8
7	1	8	3.5	5.2
9	1	8	20.3	22.4
11	1	8	5.8	-5.9
-17	1	9	10.7	-10.2
-15	1	9	8.1	7.8
-13	1	9	2.8	-2.7
-11	1	9	7.7	-8.1
-9	1	9	1.7	-1.2
-7	1	9	3.0	3.8
-5	1	9	19.4	-18.2
-3	1	9	11.4	11.5
-1	1	9	1.8	0.5
1	1	9	4.3	-3.7
3	1	9	10.0	10.1
5	1	9	3.4	-3.6
7	1	9	0.0	-1.8
9	1	9	3.9	1.7
-17	1	10	24.1	24.3
-15	1	10	2.5	-0.4
-13	1	10	6.3	-15.5
-11	1	10	33.0	-32.5
-9	1	10	21.3	19.7
-7	1	10	40.5	40.7
-5	1	10	12.6	-9.7
-3	1	10	24.3	-32.0
-1	1	10	10.3	-11.0
1	1	10	21.2	19.8
3	1	10	8.9	8.7
5	1	10	10.2	-10.9
7	1	10	7.8	-7.1
9	1	10	14.0	16.1
-17	1	11	5.4	6.3
-15	1	11	3.0	-2.2
-13	1	11	6.7	5.7
-11	1	11	9.3	-9.7
-9	1	11	1.6	0.3
-7	1	11	3.1	-1.4
-5	1	11	5.1	-4.4
-3	1	11	12.4	11.0
-1	1	11	11.0	-11.7
1	1	11	8.1	12.1
3	1	11	15.9	-14.8
5	1	11	14.5	15.4
7	1	11	6.2	-5.2
-17	1	12	6.8	-7.2
-15	1	12	11.3	11.7
-13	1	12	18.1	17.1
-11	1	12	16.0	-16.2
-9	1	12	18.2	-17.7
-7	1	12	4.1	4.3
-5	1	12	30.4	30.2
-3	1	12	3.9	-4.5
-1	1	12	13.5	-15.1
1	1	12	14.9	-14.5
3	1	12	29.3	32.0
5	1	12	3.9	-2.4
-17	1	13	6.4	4.7
-15	1	13	7.3	-7.9
-13	1	13	1.9	-1.0
-11	1	13	3.7	-4.1
-9	1	13	4.9	2.7
-7	1	13	3.5	-4.0
-5	1	13	6.4	5.3
-3	1	13	11.7	-11.4
-1	1	13	16.0	17.1
1	1	13	7.2	-5.9
3	1	13	2.6	1.7
-17	1	14	16.9	-17.7
-15	1	14	6.9	-6.5
-13	1	14	15.5	17.1
-11	1	14	19.0	20.0
-9	1	14	12.7	-12.7
-7	1	14	9.1	-9.7
-5	1	14	3.1	-3.6
-3	1	14	24.1	26.4
-1	1	14	12.3	-13.4
1	1	14	8.6	-7.7
-17	1	15	15.0	-14.7
-15	1	15	4.8	4.0
-13	1	15	2.7	-2.7
-11	1	15	2.7	1.9
-9	1	15	6.0	-5.4
-7	1	15	9.8	9.6
-5	1	15	3.9	-3.0
-3	1	15	2.5	2.0
-1	1	15	5.7	5.8
-17	1	16	8.9	6.9
-15	1	16	7.6	-7.3
-13	1	16	6.6	-6.0
-11	1	16	9.6	10.1
-9	1	16	11.5	10.2
-7	1	16	11.9	-12.6
-5	1	16	19.0	-20.5
-3	1	16	8.8	9.5
-15	1	17	7.7	6.4
-13	1	17	4.9	-2.4
-11	1	17	3.6	-1.5
-9	1	17	4.4	1.3
-7	1	17	8.7	7.6
0	2	0	38.4	33.6
2	2	0	29.9	28.2
4	2	0	41.2	-38.9
6	2	0	26.1	-24.4
8	2	0	17.1	18.8
10	2	0	29.7	30.1
12	2	0	23.0	-25.2
14	2	0	4.1	-5.9
16	2	0	4.5	5.7
-16	2	1	7.7	8.0
-14	2	1	7.7	-6.9
-12	2	1	12.6	11.5
-10	2	1	23.1	-22.5
-8	2	1	16.2	15.9
-6	2	1	1.8	-2.4
-4	2	1	23.0	21.6
-2	2	1	35.3	-34.6
0	2	1	23.9	23.4
2	2	1	12.3	-9.7
4	2	1	6.9	9.4
6	2	1	8.0	-8.6
8	2	1	7.8	6.7
10	2	1	5.6	-5.7
12	2	1	3.1	-3.1
14	2	1	5.3	5.2
16	2	1	6.3	-6.3
-16	2	2	29.0	29.8
-14	2	2	4.3	3.5
-12	2	2	32.5	-31.0
-10	2	2	4.1	-3.7
-8	2	2	20.7	22.0
-6	2	2	40.3	42.1
-4	2	2	8.2	-7.8
-2	2	2	62.1	-64.0
0	2	2	6.1	3.9
2	2	2	49.9	51.4
4	2	2	14.9	-12.4
6	2	2	39.7	-39.5
8	2	2	13.1	-14.5
10	2	2	25.9	25.8
12	2	2	19.1	19.7
14	2	2	10.4	-11.6
16	2	2	14.1	-14.4
-16	2	3	11.0	-9.1
-14	2	3	6.3	4.1
-12	2	3	2.7	2.5
-10	2	3	15.9	15.1
-8	2	3	9.2	-10.5
-6	2	3	1.1	7.8
-4	2	3	15.5	-12.7
-2	2	3	8.6	10.0
0	2	3	2.3	-5.5
2	2	3	1.4	-2.0
4	2	3	7.7	-4.2
6	2	3	6.1	5.0
8	2	3	3.4	3.1
10	2	3	20.4	-19.7
12	2	3	17.3	17.7
14	2	3	5.3	-6.7
-16	2	4	3.6	0.7
-14	2	4	22.3	23.2
-12	2	4	17.8	16.4
-10	2	4	24.3	-24.0
-8	2	4	42.1	-41.2
-6	2	4	20.3	19.7
-4	2	4	44.0	45.3
-2	2	4	51.4	-45.5
0	2	4	28.0	-23.2
2	2	4	44.7	-39.9
4	2	4	58.5	58.8
6	2	4	8.1	8.8
8	2	4	16.2	-18.3
10	2	4	13.9	-14.6
12	2	4	21.1	21.4
14	2	4	4.1	2.4
-16	2	5	8.1	-7.6
-14	2	5	9.1	8.2
-12	2	5	2.6	-1.6
-10	2	5	15.9	15.4
-8	2	5	34.8	-32.2
-6	2	5	8.5	7.8
-4	2	5	2.0	-4.3
-2	2	5	6.2	7.6
0	2	5	4.6	-3.8
2	2	5	10.0	9.3
4	2	5	16.7	-15.0
6	2	5	6.2	7.6
8	2	5	4.0	-4.0
10	2	5	2.7	2.1
12	2	5	2.2	2.2
14	2	5	4.1	-2.5
-16	2	6	13.1	-13.9
-14	2	6	11.0	-10.6
-12	2	6	19.5	21.4
-10	2	6	2.6	4.8
-8	2	6	19.6	-29.7
-6	2	6	25.3	-26.8
-4	2	6	2.3	5.8
-2	2	6	48.0	46.3
0	2	6	24.8	-21.9
2	2	6	27.3	-27.0
4	2	6	12.6	10.9
6	2	6	36.6	36.0
8	2	6	3.9	-2.0
10	2	6	4.6	-6.0
12	2	6	9.5	-8.7
-16	2	7	16.7	17.1
-14	2	7	22.6	-21.2
-12	2	7	11.6	12.0
-10	2	7	28.0	-24.6
-8	2	7	20.5	19.3
-6	2	7	3.6	-6.1
-4	2	7	20.0	18.2
-2	2	7	25.1	-22.3
0	2	7	13.0	14.0
2	2	7	2.7	1.7
4	2	7	17.3	-16.8
6	2	7	7.1	5.7
8	2	7	4.8	-5.0
10	2	7	11.1	11.2
12	2	7	6.4	-5.6
-16	2	8	1.6	1.0
-14	2	8	28.0	-28.3
-12	2	8	10.8	-12.3
-10	2	8	42.2	39.3
-8	2	8	13.8	12.7
-6	2	8	31.2	-31.3
-4	2	8	29.5	-30.9
-2	2	8	36.7	34.7
0	2	8	31.8	30.7

Table 1 (*cont.*)

2	2	8	6.2	5.4
4	2	8	27.2	- 28.1
6	2	8	4.4	4.4
8	2	8	13.4	14.5
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-16	2	9	3.3	- 0.9
-14	2	9	2.9	- 1.2
-12	2	9	5.8	- 6.6
-10	2	9	9.1	7.3
- 8	2	9	2.3	2.3
- 6	2	9	2.5	0.7
- 4	2	9	5.7	4.5
- 2	2	9	16.8	- 15.4
0	2	9	6.3	6.1
2	2	9	15.3	- 15.8
4	2	9	15.5	15.4
6	2	9	4.4	- 4.2
8	2	9	8.2	9.2
-16	2	10	23.0	22.4
-14	2	10	2.3	- 2.5
-12	2	10	19.1	- 21.1
-10	2	10	13.0	- 12.6
- 8	2	10	27.0	27.5
- 6	2	10	21.2	19.7
- 4	2	10	7.3	- 7.9
- 2	2	10	29.5	- 29.3
0	2	10	25.8	23.6
2	2	10	13.5	14.9
4	2	10	8.0	- 9.2
6	2	10	12.3	- 11.6
8	2	10	5.9	- 5.6
-16	2	11	12.5	- 11.5
-14	2	11	9.5	8.9
-12	2	11	3.8	- 4.1
-10	2	11	15.2	13.8
- 8	2	11	18.1	- 16.2
- 6	2	11	5.9	6.6
- 4	2	11	9.9	- 10.3
- 2	2	11	11.7	11.8
0	2	11	14.0	- 13.8
2	2	11	8.1	9.5
4	2	11	4.0	5.0
6	2	11	4.1	3.5
-16	2	12	6.1	- 5.2
-14	2	12	23.5	25.8
-12	2	12	4.6	- 3.8
-10	2	12	18.5	- 19.3
- 8	2	12	6.7	- 7.8
- 6	2	12	26.8	27.4
- 4	2	12	5.4	5.9
- 2	2	12	17.3	- 19.8
0	2	12	7.7	- 5.6
2	2	12	2.7	0.4
4	2	12	11.8	12.3
-16	2	13	6.9	5.4
-14	2	13	2.0	2.1
-12	2	13	2.0	1.2
-10	2	13	2.3	- 2.5
- 8	2	13	4.2	2.0
- 6	2	13	4.9	- 4.1
- 4	2	13	6.2	- 6.3
- 2	2	13	9.4	11.0
0	2	13	2.5	- 1.8
2	2	13	4.8	4.3
-16	2	14	13.4	- 13.9
-14	2	14	5.0	7.0
-12	2	14	16.0	16.4
-10	2	14	2.4	- 2.0
- 8	2	14	19.4	- 18.9
- 6	2	14	7.7	- 7.0
- 4	2	14	16.6	18.1
- 2	2	14	8.4	10.0
0	2	14	8.4	- 7.3
-16	2	15	9.3	7.2
-14	2	15	4.3	- 4.3
-12	2	15	1.7	0.2
-10	2	15	11.1	- 12.2
- 8	2	15	18.4	17.6
- 6	2	15	15.6	- 15.9
- 4	2	15	7.7	9.1
- 2	2	15	5.0	- 3.1
-14	2	16	17.1	- 17.2
-12	2	16	3.8	1.7
-10	2	16	18.7	19.0
- 8	2	16	3.6	- 0.7
- 6	2	16	7.2	- 5.5
- 4	2	16	5.4	- 3.6
1	3	0	26.3	25.3
3	3	0	27.3	- 26.7
5	3	0	34.7	- 33.6
7	3	0	0.0	- 0.9
9	3	0	43.3	43.0
11	3	0	14.0	- 14.6
13	3	0	3.4	- 2.9
15	3	0	12.2	- 12.4
-15	3	1	2.2	- 1.2
-13	3	1	8.4	- 6.5
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- 9	3	1	4.7	- 3.4
- 7	3	1	2.3	- 2.4
- 5	3	1	15.7	15.7
- 3	3	1	4.3	- 5.1
- 1	3	1	7.5	- 7.1
1	3	1	2.3	2.8
3	3	1	5.1	- 5.6
5	3	1	2.0	0.5
7	3	1	2.9	0.7
9	3	1	3.5	1.6
11	3	1	6.9	7.0
13	3	1	3.7	5.3
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-15	3	2	13.5	13.2
-13	3	2	7.4	- 8.0
-11	3	2	25.6	- 27.9
- 9	3	2	8.6	8.1
- 7	3	2	24.4	25.3
- 5	3	2	2.9	1.2
- 3	3	2	35.8	- 34.4
- 1	3	2	29.7	- 25.9
1	3	2	9.5	10.7
3	3	2	48.6	49.7
5	3	2	27.2	- 26.8
7	3	2	10.4	- 11.1
9	3	2	0.0	0.6
11	3	2	27.6	29.4
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-15	3	3	6.3	- 3.8
-13	3	3	3.0	1.7
-11	3	3	9.5	7.9
- 9	3	3	16.5	- 17.6
- 7	3	3	13.6	14.9
- 5	3	3	8.3	- 6.3
- 3	3	3	10.3	9.4
- 1	3	3	9.9	- 8.4
1	3	3	13.8	- 14.6
3	3	3	3.4	1.3
5	3	3	16.7	16.9
7	3	3	10.8	9.3
9	3	3	6.2	- 5.3
11	3	3	2.1	0.1
13	3	3	9.2	- 8.7
-15	3	4	21.1	20.8
-13	3	4	8.2	9.3
-11	3	4	4.4	5.5
- 9	3	4	42.5	- 44.9
- 7	3	4	5.3	4.3
- 5	3	4	17.7	17.3
- 3	3	4	41.2	39.7
- 1	3	4	54.4	- 52.3
1	3	4	8.4	- 7.5
3	3	4	37.5	35.7
5	3	4	20.1	20.0
7	3	4	8.2	- 7.4
9	3	4	19.0	- 20.5
11	3	4	4.0	3.6
13	3	4	6.4	6.8
-15	3	5	0.0	- 1.8
-13	3	5	5.7	5.4
-11	3	5	16.1	- 13.6
- 9	3	5	26.7	25.0
- 7	3	5	11.9	- 11.9
- 5	3	5	8.5	- 7.7
- 3	3	5	13.4	- 12.1
- 1	3	5	21.4	19.2
1	3	5	3.1	- 0.6
3	3	5	11.0	10.5
5	3	5	2.8	1.1
7	3	5	4.9	- 4.9
9	3	5	5.6	4.4
11	3	5	11.2	- 10.4
-15	3	6	16.1	- 16.1
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-11	3	6	12.5	12.5
- 9	3	6	8.7	4.7
- 7	3	6	33.8	- 34.1
- 5	3	6	1.5	- 0.9
- 3	3	6	44.9	43.6
- 1	3	6	2.2	4.1
1	3	6	17.5	- 15.7
3	3	6	26.3	- 26.3
5	3	6	17.4	15.8
7	3	6	9.8	10.1
9	3	6	3.0	- 0.4
11	3	6	21.4	- 22.0
-15	3	7	4.7	2.5
-13	3	7	6.2	- 6.7
-11	3	7	3.0	1.9
- 9	3	7	2.5	1.8
- 7	3	7	3.4	- 3.8
- 5	3	7	2.1	- 3.0
- 3	3	7	7.0	7.5
- 1	3	7	6.3	6.2
1	3	7	12.6	10.9
3	3	7	5.2	- 5.7
5	3	7	6.4	- 6.0
7	3	7	0.0	- 0.5
9	3	7	3.6	- 1.2
-15	3	8	19.5	- 19.1
-13	3	8	8.5	- 9.1
-11	3	8	2.2	- 1.9
- 9	3	8	48.6	48.4
- 7	3	8	30.5	- 28.3
- 5	3	8	20.6	- 17.8
- 3	3	8	19.6	- 19.5
- 1	3	8	36.9	38.7
1	3	8	4.1	- 5.1
3	3	8	10.0	- 11.5
5	3	8	14.5	- 15.1
7	3	8	15.0	15.8
9	3	8	7.8	7.7
-15	3	9	5.2	3.9
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-11	3	9	5.8	4.8
- 9	3	9	21.4	- 18.9
- 7	3	9	18.0	17.6
- 5	3	9	14.2	13.9
- 3	3	9	10.4	- 10.4
- 1	3	9	2.1	0.9
1	3	9	4.1	- 2.2
3	3	9	0.0	- 0.0
5	3	9	0.0	0.6
7	3	9	5.6	- 4.2
-15	3	10	22.6	19.7
-13	3	10	23.5	- 24.2
-11	3	10	10.1	- 11.7
- 9	3	10	6.8	- 6.3
- 7	3	10	29.2	31.8
- 5	3	10	11.2	- 10.0
- 3	3	10	15.7	- 17.7
- 1	3	10	1.5	- 2.5
1	3	10	20.5	20.0
3	3	10	10.9	11.8
5	3	10	11.7	- 11.9
-15	3	11	8.6	- 7.1
-13	3	11	11.0	11.2
-11	3	11	2.3	- 0.3
- 9	3	11	6.8	- 5.8
- 7	3	11	10.6	11.9
- 5	3	11	8.1	- 9.0
- 3	3	11	5.1	2.5
- 1	3	11	2.8	1.5
1	3	11	3.5	- 2.5
3	3	11	3.4	- 5.9
5	3	11	4.7	3.3
-15	3	12	14.5	15.8
-13	3	12	6.1	6.8
-11	3	12	8.1	- 6.4
- 9	3	12	26.1	- 26.6
- 7	3	12	28.3	28.6
- 5	3	12	9.0	8.6
- 3	3	12	5.1	5.3
- 1	3	12	18.3	- 18.5
1	3	12	4.8	3.7
3	3	12	2.2	4.2
-15	3	13	6.6	- 4.8
-13	3	13	3.9	3.6
-11	3	13	2.7	- 0.7
- 9	3	13	6.8	5.6
- 7	3	13	6.1	- 8.1
- 5	3	13	2.9	2.1
- 3	3	13	2.1	1.3
- 1	3	13	4.3	3.1
1	3	13	9.1	- 7.7
-15	3	14	18.9	- 18.9
-13	3	14	27.5	28.5
-11	3	14	3.2	1.7
- 9	3	14	2.5	- 2.0
- 7	3	14	15.2	- 15.8
- 5	3	14	6.4	8.2
- 3	3	14	7.3	7.2
- 1	3	14	7.5	6.4
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-11	3	15	3.3	0.9
- 9	3	15	5.3	2.8
- 7	3	15	4.7	- 0.0
- 5	3	15	4.0	2.6
0	4	0	32.6	28.0
2	4	0	7.7	8.0
4	4	0	28.4	- 30.6
6	4	0	4.1	2.7
8	4	0	10.2	9.5
10	4	0	25.3	27.0
12	4	0	16.3	- 16.9
14	4	0	18.0	- 16.1
-14	4	1	12.2	12.2
-12	4	1	11.0	- 12.1
-10	4	1	4.3	3.6
- 8	4	1	4.2	- 3.0
- 6	4	1	5.4	6.7
- 4	4	1	6.2	- 5.3
- 2	4	1	3.7	- 2.8
0	4	1	2.6	- 3.0
2	4	1	4.5	- 2.7
4	4	1	15.5	15.6
6	4	1	0.0	- 1.5
8	4	1	3.7	- 1.8
10	4	1	2.1	- 0.5
12	4	1	7.4	8.0
14	4	1	5.8	- 5.3
-14	4	2	5.3	5.0
-12	4	2	5.4	- 5.1
-10	4	2	20.4	- 22.1
- 8	4	2	23.7	23.7
- 6	4	2	19.1	20.2
- 4	4	2	11.5	- 9.7
- 2	4	2	28.3	- 30.6
0	4	2	13.6	11.7
2	4	2	25.5	23.2
4	4	2	19.1	17.7
6	4	2	27.9	- 28.4
8	4	2	19.3	- 18.5
10	4	2	18.2	18.1
12	4	2	4.4	- 5.0
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-10	4	3	10.7	- 11.7
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- 6	4	3	11.1	- 11.4
- 4	4	3	3.0	3.3
- 2	4	3	10.0	9.8
0	4	3	0.0	- 2.7
2	4	3	4.4	6.3
4	4	3	2.4	- 0.5
6	4	3	13.0	14.4
8	4	3	10.7	- 12.2
10	4	3	0.0	0.5
12	4	3	8.8	- 7.1
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-12	4	4	0.0	1.0
-10	4	4	16.0	- 15.6
- 8	4	4	10.7	- 8.9
- 6	4	4	12.7	12.1
- 4	4	4	25.1	25.5
- 2	4	4	10.2	- 11.0
0	4	4	28.9	- 25.3
2	4	4	6.5	- 5.7
4	4	4	27.1	26.7
6	4	4	10.0	- 10.3
8	4	4	7.0	- 7.5
10	4	4	13.5	- 13.7
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-10	4	5	6.9	- 6.7
- 8	4	5	9.1	7.8
- 6	4	5	6.7	- 8.5
- 4	4	5	4.0	6.7
- 2	4	5	5.3	4.2
0	4	5	17.1	16.5
2	4	5	11.7	- 12.2
4	4	5	1.6	- 2.1
6	4	5	6.8	- 6.2
8	4	5	6.8	6.6
10	4	5	8.3	- 6.0
-14	4	6	4.5	- 1.7
-12	4	6	13.9	15.2
-10	4	6	24.5	24.2
- 8	4	6	39.5	- 40.6
- 6	4	6	8.4	- 9.7
- 4	4	6	10.1	10.0
- 2	4	6	27.0	27.4
0	4	6	14.9	- 13.7
2	4	6	16.5	- 15.1
4	4	6	5.7	- 6.9
6	4	6	22.8	24.5
8	4	6	5.0	4.3
-14	4	7	6.4	5.3
-12	4	7	11.5	- 11.0
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- 8	4	7	3.5	3.1
- 6	4	7	9.2	8.6
- 4	4	7	11.6	- 9.9
- 2	4	7	5.8	6.3
0	4	7	4.5	- 4.6
2	4	7	9.3	7.2
4	4	7	11.5	- 11.0
6	4	7	2.6	0.6
8	4	7	4.1	2.9
-14	4	8	22.2	- 22.7
-12	4	8	6.5	5.0
-10	4	8	7.6	6.5
- 8	4	8	10.7	12.1
- 6	4	8	7.2	- 5.4
- 4	4	8	13.5	- 13.1
- 2	4	8	8.1	6.3
0	4	8	22.4	22.1
2	4	8	2.5	- 1.8
4	4	8	25.1	- 24.9
6	4	8	8.2	8.5
-14	4	9	9.7	8.1
-12	4	9	7.9	- 9.2
-10	4	9	4.2	1.1
- 8	4	9	3.0	- 1.6
- 6	4	9	9.9	11.1
- 4	4	9	5.4	3.0
- 2	4	9	5.9	- 5.8
0	4	9	6.8	- 6.9
2	4	9	7.4	7.6
4	4	9	3.9	- 2.8
-14	4	10	5.5	- 2.9
-12	4	10	10.2	- 10.3
-10	4	10	3.4	- 3.0
- 8	4	10	26.7	28.3
- 6	4	10	3.6	0.8
- 4	4	10	9.6	- 9.9
- 2	4	10	23.5	- 25.4
0	4	10	18.9	18.6
2	4	10	4.6	3.1
4	4	10	3.7	- 0.8
-14	4	11	8.0	- 6.0
-12	4	11	13.2	14.2
-10	4	11	2.9	- 3.4
- 8	4	11	5.8	8.0
- 6	4	11	10.4	- 11.4
- 4	4	11	15.6	14.6
- 2	4	11	14.9	- 14.9
0	4	11	6.8	4.9
2	4	11	5.4	- 2.8
-14	4	12	16.2	17.2
-12	4	12	6.1	- 5.9
-10	4	12	5.4	- 4.7
- 8	4	12	20.0	- 21.3
- 6	4	12	15.4	14.9
- 4	4	12	11.4	11.4
- 2	4	12	14.5	- 12.7
0	4	12	11.6	- 10.8
-12	4	13	4.7	0.7
-10	4	13	12.4	9.9
- 8	4	13	12.8	- 11.9
- 6	4	13	4.4	- 0.6
- 4	4	13	4.9	- 2.0
- 8	4	14	20.8	- 20.0
1	5	0	18.9	19.1
3	5	0	9.3	- 8.5
5	5	0	27.4	- 29.2
7	5	0	13.3	13.8
9	5	0	7.9	7.3
11	5	0	4.1	1.3
-11	5	1	13.7	- 15.3
- 9	5	1	4.3	- 0.5
- 7	5	1	6.0	5.8
- 5	5	1	4.1	1.9
- 3	5	1	5.8	5.0
- 1	5	1	7.3	- 7.6
1	5	1	0.0	1.4
3	5	1	5.3	- 4.3
5	5	1	12.9	14.7
7	5	1	18.9	- 20.7
9	5	1	8.4	10.1
11	5	1	7.9	- 7.3
-11	5	2	18.4	- 19.4
- 9	5	2	3.3	0.9
- 7	5	2	15.1	14.7
- 5	5	2	10.7	10.8
- 3	5	2	19.0	- 19.3
- 1	5	2	12.6	- 12.4
1	5	2	20.3	17.8
3	5	2	15.5	15.5
5	5	2	12.5	- 12.3
7	5	2	6.8	- 6.7
9	5	2	3.4	- 0.3
-11	5	3	5.4	- 4.0
- 9	5	3	12.2	12.1
- 7	5	3	10.8	- 10.1
- 5	5	3	9.0	10.8
- 3	5	3	5.4	- 4.8
- 1	5	3	6.1	5.6
1	5	3	17.4	- 18.5
3	5	3	3.4	4.9
5	5	3	3.3	- 2.5
7	5	3	7.1	6.9
9	5	3	5.7	- 4.3
-11	5	4	8.1	- 7.3
- 9	5	4	16.2	- 16.3
- 7	5	4	4.1	- 2.8
- 5	5	4	27.6	27.3
- 3	5	4	8.7	8.1
- 1	5	4	19.5	- 19.6
1	5	4	3.1	- 1.1
3	5	4	11.6	10.7
5	5	4	9.5	9.5
7	5	4	8.6	- 7.9
-11	5	5	14.7	17.2
- 9	5	5	5.4	- 5.2
- 7	5	5	4.5	- 5.0
- 5	5	5	6.4	- 4.3
- 3	5	5	5.6	- 5.1
- 1	5	5	7.3	8.4
1	5	5	4.1	- 4.2
3	5	5	1.3	0.4
5	5	5	3.1	0.0
7	5	5	6.0	7.2
-11	5	6	14.2	15.3
- 9	5	6	2.5	- 1.1
- 7	5	6	12.5	- 13.8
- 5	5	6	4.7	6.0
- 3	5	6	19.5	19.6
- 1	5	6	3.6	3.3
1	5	6	17.6	- 17.2
3	5	6	14.9	- 15.2
5	5	6	6.5	5.7
-11	5	7	3.9	- 0.3
- 9	5	7	8.7	- 9.0
- 7	5	7	17.0	18.7

Table 1 (*cont.*)

-5	5	7	12.0	-13.5
-3	5	7	3.4	4.1
-1	5	7	5.8	-5.5
1	5	7	13.9	13.3
3	5	7	4.8	-5.4
5	5	7	3.7	2.9
-11	5	8	16.4	16.6
-9	5	8	14.0	13.7
-7	5	8	2.7	0.2
-5	5	8	23.3	-23.4
-3	5	8	3.0	-1.7
-1	5	8	6.6	5.6
1	5	8	2.6	2.1
3	5	8	7.0	-5.4
-11	5	9	10.9	-10.1
-9	5	9	9.0	10.8
-7	5	9	7.6	-8.0
-5	5	9	6.1	5.5
-3	5	9	4.0	-4.9
-1	5	9	3.5	2.2
1	5	9	9.0	-6.7
-11	5	10	10.8	-10.4
-9	5	10	7.0	5.1
-7	5	10	7.6	6.9
-5	5	10	5.5	-3.7
-3	5	10	13.7	-14.2
-1	5	10	4.5	1.1
-9	5	11	6.2	-5.7
-7	5	11	10.0	-9.0
-5	5	11	6.3	7.7
0	6	0	22.4	19.1
2	6	0	6.7	-6.8
4	6	0	7.0	-4.6
6	6	0	8.1	-7.3
-6	6	1	9.3	9.7
-4	6	1	4.2	0.3
-2	6	1	4.8	0.6
0	6	1	12.0	-12.4
2	6	1	8.5	8.2
4	6	1	3.1	1.5
6	6	1	5.1	-2.2
-6	6	2	16.2	16.7
-4	6	2	12.0	-11.3
-2	6	2	17.6	-18.4
0	6	2	7.0	5.7
2	6	2	14.7	13.6
4	6	2	2.9	3.6
-6	6	3	5.4	-1.3
-4	6	3	5.9	3.5
-2	6	3	7.5	6.6
0	6	3	13.6	-12.6
2	6	3	7.6	8.3
4	6	3	5.7	-3.8
-6	6	4	14.9	14.7
-4	6	4	4.1	1.1
-2	6	4	4.5	1.7
0	6	4	17.7	-17.4
2	6	4	4.7	5.7
-6	6	5	12.7	-14.1
-4	6	5	6.7	7.6
-2	6	5	5.4	-0.2
0	6	5	4.8	2.5
-6	6	6	12.8	-13.9
-4	6	6	10.3	10.5
-2	6	6	9.2	7.4

Absent reflexions: *hkl* when $(h+k)$ is odd, *h*0*l* when *l* is odd. Space group *Cc* (C_s^4) or *C*2/*c* (C_{2h}^6). Analysis has proceeded satisfactorily in *C*2/*c*.

The intensities of the reflexions were measured on a General Electric XRD5 Spectrogoniometer with Single Crystal Orienter, with a scintillation counter and Cu $K\alpha$ radiation (nickel filter and pulse height analyser), and the moving crystal—moving counter technique (Furnas, 1957). All the 1062 reflexions in the range $0 < 2\theta(\text{Cu } K\alpha) \leq 90°$ (corresponding to a minimum interplanar spacing $d = 1{\cdot}09$ Å) were examined, and 1034 (97%) had an intensity above background. In addition the intensities of eleven higher-order *h*0*l* reflexions were measured. All the intensities were corrected for background, Lorentz and polarization factors were applied, and the structure amplitudes were derived. The crystal used was mounted with *b* parallel to the φ axis of the goniostat, and was approximately cylindrical with diameter 0·1 mm, so that absorption corrections were not considered necessary.

Structure analysis

The *x* and *z* coordinates of the bromine and sulphur atoms were determined from the *b*-axis Patterson projection, and a two-dimensional Fourier series was summed using signs based on the Br and S contributions. On the resulting electron-density map all of the atoms were fairly well resolved, except two of the atoms in the cyclopropyl ring which overlapped in projection. Even at this stage it was clear that the cyclopropyl methylene group had the *exo* configuration. Structure factors were calculated for *h*0*l* reflexions, using the scattering factors of *International Tables for X-ray Crystallography* (1962) for bromine, sulphur, oxygen, and carbon, with $B = 4{\cdot}5$ Å^2 for all the atoms; *R*, the usual discrepancy index, was 0·19.

The *x* and *z* parameters of the Br and S atoms were confirmed, and the *y* parameters determined, from the three-dimensional Patterson function. y_{Br} was close to zero, and to assist in sign determination, parameters were obtained for the two carbon atoms in the benzene ring to which the Br and S were bonded, by assuming normal bond distances. A three-dimensional Fourier series was then summed, with signs based on these four atoms (Br, S and 2 C), and all the atoms in the molecule were clearly resolved on the resulting electron-density distribution. Structure factors were calculated, with $B = 4{\cdot}5$ Å^2, and *R* was 0·28 for the observed *hkl* reflexions.

Refinement of the positional and isotropic thermal parameters was carried out by computing differential syntheses, with calculated syntheses for applying 'backshift' corrections to the atomic coordinates and for adjusting the thermal parameters, and five cycles reduced *R* to 0·125. Further refinement proceeded by (block-diagonal) least squares. The function minimized was $\Sigma w(F_o - F_c)^2$, with $\sqrt{w} = |F_o|/44$ when $|F_o| < 44$, and $\sqrt{w} = 44/|F_o|$ when $|F_o| \geq 44$. Refinement was complete in three cycles, anisotropic thermal parameters being used in the final cycle for those atoms whose thermal motion was greatest. The positional parameter shifts in the final cycle were zero for Br and S, and small for the C and O atoms, the mean shifts in the *x*, *y*, and *z* direction being 0·004, 0·005 and 0·004 Å respectively. The final measured and calculated structure factors are listed in Table 1; *R* is 0·093 for the 1045 observed reflexions.

A final three-dimensional Fourier series was summed

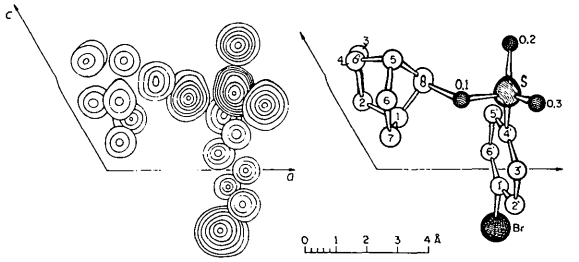

Fig. 1. Sections of the final three-dimensional electron-density distribution through the atomic centres parallel to (010). Contours start at 2 e.Å^{-3}, and are at intervals of 1 e.Å^{-3} for C and O, 2 e.Å^{-3} for S, and 5 e.Å^{-3} for Br. A perspective drawing of the molecule is also shown.

and superimposed sections of the resulting electron-density distribution are shown in Fig. 1, together with a perspective drawing of the molecule.

Atomic parameters and molecular dimensions

The positional and thermal parameters from the final least-squares cycle are given in Table 2, x, y, and z being fractional coordinates referred to the monoclinic crystal axes, B isotropic temperature factors (Å²), and B_{ij} the anisotropic thermal parameters in the expression:

$$\exp -\{B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk\} .$$

The bond distances and valency angles in the molecule are given in Table 3, together with their standard deviations computed from the least-squares residuals.

Table 2. *Final positional (fractional) and thermal parameters*

Atom	x	y	z	B (Å²)
Br	0·1131	0·0085	0·3837	(5·50)
S	0·2367	0·6539	0·6484	3·15
O(1)	0·1731	0·7434	0·6382	(3·29)
O(2)	0·2736	0·5709	0·7260	(4·20)
O(3)	0·2651	0·8014	0·6243	(4·88)
C(1′)	0·1520	0·2010	0·4625	4·01
C(2′)	0·1620	0·3794	0·4408	4·65
C(3′)	0·1890	0·5176	0·4974	4·05
C(4′)	0·2066	0·4703	0·5772	3·14
C(5′)	0·1983	0·2911	0·5969	4·16
C(6′)	0·1717	0·1543	0·5421	4·43
C(1)	0·0687	0·5776	0·5930	4·69
C(2)	0·0309	0·5082	0·6319	(5·95)
C(3)	0·0673	0·4213	0·7138	(7·29)
C(4)	0·0568	0·6318	0·7071	(6·36)
C(5)	0·1069	0·7625	0·7023	4·86
C(6)	0·0688	0·9054	0·6361	6·05
C(7)	0·0407	0·7838	0·5599	5·82
C(8)	0·1337	0·6328	0·6637	(3·75)

Anisotropic thermal parameters (×10⁴)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Br	35	264	50	−15	44	2
O(1)	18	190	31	6	29	22
O(2)	24	227	32	9	24	4
O(3)	27	210	51	21	42	−3
C(2)	30	303	54	−58	36	−23
C(3)	39	448	64	−1	62	−57
C(4)	32	383	58	−104	48	−39
C(8)	21	204	30	2	26	3

There are several regions in the molecule where it is of interest to examine planarity, particularly in the tricyclo-octane nucleus, and the equations of, displacements of atoms from, and angles between various planes are given in Table 4. In these equations X', Y and Z' are coordinates in Å referred to orthogonal axes a, b and c^*.

All the intermolecular separations ≤ 4·0 Å were calculated, and the most significant contacts are listed in Table 5. The packing of the molecules in the unit cell is illustrated in Fig. 2.

Table 3. *Bond distances and standard deviations, and valency angles*

The standard deviations of the angles vary from 0·6 to 1·9°

Bond	l	σ
Br–C(1′)	1·90 Å	$0·01_6$ Å
S–O(1)	1·55	$0·01_0$
S–O(2)	1·44	$0·01_1$
S–O(3)	1·44	$0·01_2$
Mean S=O	1·44	
S–C(4′)	1·77	$0·01_6$
C(1′)–C(2′)	1·39	$0·02_3$
C(2′)–C(3′)	1·37	$0·02_3$
C(3′)–C(4′)	1·43	$0·02_2$
C(4′)–C(5′)	1·37	$0·02_1$
C(5′)–C(6′)	1·34	$0·02_4$
C(6′)–C(1′)	1·42	$0·02_4$
Mean C_{ar}–C_{ar}	1·39	
O(1)–C(8)	1·48	$0·02_1$
C(1)–C(2)	1·52	$0·02_8$
C(2)–C(3)	1·51	$0·03_1$
C(3)–C(4)	1·50	$0·03_1$
C(2)–C(4)	1·54	$0·03_1$
C(4)–C(5)	1·55	$0·02_8$
C(5)–C(6)	1·52	$0·02_8$
C(6)–C(7)	1·54	$0·03_1$
C(7)–C(1)	1·59	$0·03_0$
C(1)–C(8)	1·51	$0·02_8$
C(5)–C(8)	1·51	$0·02_8$
Mean C–C	1·53	

Angle	θ
Br–C(1′)–C(2′)	119·5°
Br–C(1′)–C(6′)	118·4
S–C(4′)–C(3′)	117·6
S–C(4′)–C(5′)	121·2
C(1′)–C(2′)–C(3′)	119·2
C(2′)–C(3′)–C(4′)	118·1
C(3′)–C(4′)–C(5′)	121·2
C(4′)–C(5′)–C(6′)	121·4
C(5′)–C(6′)–C(1′)	118·0
C(6′)–C(1′)–C(2′)	122·2
Mean	119·7
O(1)–S–O(2)	109·8
O(1)–S–O(3)	104·4
O(1)–S–C(4′)	102·5
O(2)–S–O(3)	120·0
O(2)–S–C(4′)	108·6
O(3)–S–C(4′)	110·1
Mean at S	109·2
S–O(1)–C(8)	118·6
O(1)–C(8)–C(1)	110·9
O(1)–C(8)–C(5)	110·0
C(1)–C(8)–C(5)	96·7
C(1)–C(2)–C(4)	103·8
C(5)–C(4)–C(2)	103·4
C(1)–C(7)–C(6)	103·3
C(5)–C(6)–C(7)	103·3
C(2)–C(1)–C(7)	105·3
C(2)–C(1)–C(8)	102·5
C(7)–C(1)–C(8)	99·2
C(4)–C(5)–C(6)	107·5
C(4)–C(5)–C(8)	101·4
C(6)–C(5)–C(8)	101·5
C(1)–C(2)–C(3)	119·4
C(5)–C(4)–C(3)	119·9
C(2)–C(3)–C(4)	61·5
C(3)–C(4)–C(2)	59·5
C(3)–C(2)–C(4)	59·0

Table 4. *Equations of various planes, deviations of the atoms from the planes* (Å), *and angles between the normals*

Equations

A: C(1), C(5), C(6), C(7)
$0{\cdot}979X'+0{\cdot}197Y-0{\cdot}058Z'+3{\cdot}889=0$

B: C(1), C(2), C(4), C(5)
$0{\cdot}528X'-0{\cdot}670Y+0{\cdot}522Z'-0{\cdot}271=0$

C: C(2), C(3), C(4)
$0{\cdot}992X'+0{\cdot}124Y+0{\cdot}011Z'+4{\cdot}870=0$

D: C(1), C(5), C(8)
$0{\cdot}367X'+0{\cdot}774Y-0{\cdot}515Z'+3{\cdot}530=0$

Deviations

Atom	Δ_A	Δ_B	Δ_C	Δ_D
C(1)	0·006	0		0
C(2)		−0·007	0	
C(3)			0	
C(4)		+0·006	0	
C(5)	−0·006	0		0
C(6)	0·007			
C(7)	−0·009			
C(8)				0

Angles

$A\wedge B$	111°
$A\wedge D$	123°
$B\wedge D$	126°
$B\wedge C$	117°

Table 5. *Shorter intermolecular distances*

All intermolecular distances ≤ 4 Å between a standard (1) and neighbouring molecules were calculated; only the more significant crystallographically independent separations are listed

Atom (molecule 1)	to Atom	in Molecule	*d*
Br	O(3)	6	3·69 Å
Br	C(4′)	6	3·96
S	O(2)	5	3·92
O(1)	O(2)	5	3·25
O(2)	C(5′)	5	3·53
O(3)	C(2′)	10	3·45
O(3)	C(3′)	10	3·33
C(1)	C(1)	2	3·62
C(6)	O(2)	5	3·53
C(5)	O(2)	5	3·28

Molecule			
1	x	y	z
2	$-x$	$1-y$	$1-z$
5	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
6	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
10	$\frac{1}{2}-x$	$\frac{3}{2}-y$	$1-z$

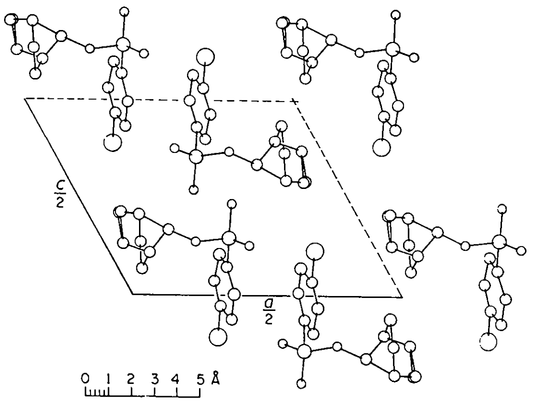

Fig. 2. Projection along *b*, showing the packing of the molecules in the unit cell.

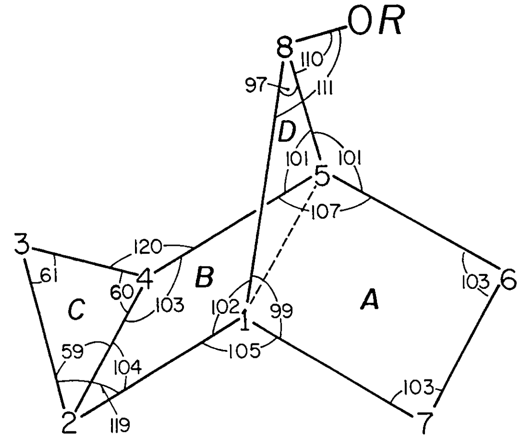

Fig. 3. Bond angles in the tricyclo-octane nucleus.

Discussion

The analysis has shown that the compound examined is the *exo* isomer of *anti*-8-tricyclo[3,2,1,0^{2,4}]octyl *p*-bromobenzenesulphonate. The interesting part of the structure is of course the tricyclo-octane nucleus. The mean C–C single bond distance is 1·53 Å, and none of the bonds differs significantly from the mean value. The valency angles are given in Table 3 and are illustrated in Fig. 3; the tricyclo-octane nucleus has symmetry *m* within experimental error. All the angles in the bicycloheptane part of the structure are less than the tetrahedral angle, and the skeleton is considerably strained. The angle at the bridgehead (C(1)–C(8)–C(5)) is 96·7 ± 1·3°. The angles in the cyclopropyl ring do not differ significantly from 60°. The angles between the various planes illustrated in Fig. 3 are given in Table 4.

The rate of solvolysis of *anti*-8-tricyclo[3,2,1,0^{2,4}]-octyl *p*-bromobenzenesulphonate (*exo* isomer, V, R = *p*-Br.C_6H_4.SO_2–) is of the same order of magnitude as that of I (R = *p*-Br.C_6H_4.SO_2–) (Pincock & Wells, 1964*b*), so that if the bridgehead angle is of significance in determining the rate of solvolysis, then the value of 97° observed in the present case must be typical of a lack of solvolytic reactivity. It has been postulated as one possible reason for the changes in solvolytic reactivity in this type of compound that, since the transition state involves sp^2 hybridization at the bridgehead atom, an increase in the bridgehead angle would facilitate formation of the transition state and hence increase the rate of solvolysis. No conclusion about this postulate can be drawn from the data on the one molecule described in the present paper, but we hope to carry out a detailed analysis of III (R = *p*-bromobenzoyl), and a comparison of the two structures should then allow some definite conclusions to be drawn.

The bond distances and valency angles in the *p*-bromobenzenesulphonyl group (Table 3) are all normal. The intermolecular separations (Table 5) all correspond to van der Waals interactions.

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The Crystal Structure of Alunite*

By Rong Wang, W. F. Bradley and H. Steinfink

Department of Chemical Engineering, University of Texas, Austin, Texas, U.S.A.

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A single-crystal diffraction analysis of alunite, $KAl_3(SO_4)_2(OH)_6$, yields an internally consistent set of bond lengths and angles which include significant revisions of previously determined values. The sulfate group includes one unique oxygen more strongly bonded to sulfur than are the other three.

Introduction

An analysis of the alunite structure, $KAl_3(SO_4)_2(OH)_6$, has been reported previously by Hendricks (1937). The structure is rhombohedral, but with α quite close to 60°, which provides aspects related to a face centered cube. In his analysis, Hendricks assigned alunite to the space group $R3m$ on the basis of a pyroelectric test, although the reported structural coordinates display a center of symmetry. Pabst (1947) carried out the computations for assumed models for alunite and two other isostructural compositions which were necessary for the correct assignment of rhombohedral or hexagonal indices which properly accounted for the observed intensities of the several powder patterns.

The dimensions of the alunite hexagonal cell found by Pabst agreed closely with those reported by Hendricks, and the structural model which best accounted for the observed intensities was in space group $R\bar{3}m$. The Hendricks bond lengths deviated somewhat from comparable subsequently determined values in other hydrous aluminum-bearing compositions (Kamb, 1960; Radoslovich, 1960; Newnham, 1961), although not to such degree but that the Hendricks parameters afforded adequate basis for Pabst's index assignments. This refinement of parameters based on single-crystal data was undertaken to examine these deviations.

Experimental

Least-square refinements of measurements from a powder photograph yield hexagonal unit-cell dimensions $a=6\cdot970\pm0\cdot001$, $c=17\cdot27\pm0\cdot01$ Å. These agree essentially with the previous determinations. Two single-crystal flakes were used for the collection of intensity data. A triangular shaped fragment whose edges measured 0·3 mm and which was 0·025 mm thick was used for the precession camera, and a hexagonal fragment with sides of 0·1 mm and 0·025 mm thick was used for the Weissenberg camera. The *hk*0, *hk*2, *hk*3, *hk*10, and *hk*11 reflections were collected with the Weissenberg camera with the multiple film technique and Cu $K\alpha$ radiation. The *hhl* and *h*0*l* reflections were obtained from precession photographs taken with molybdenum $K\alpha$ radiation; a total of 123

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