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The Crystal and Molecular Structure of Siccanin p-Bromobenzenesulphonate

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The crystal structure of siccanin p-bromobenzenesulphonate, $C_{28}H_{33}O_5SBr$, has been determined in order to elucidate the molecular structure and absolute configuration of siccanin, $C_{22}H_{30}O_3$, an antibiotic isolated from the cultured broth of Helminthosporium siccans Drechsler. The unit cell is orthorhombic with dimensions, $a = 11 \cdot 06$, $b = 22 \cdot 87$, $c = 10 \cdot 34$ Å, containing four molecules. The space group is $P2_12_12_1$. The structure was solved by the heavy atom method and refined by the method of block-matrix least-squares for 1537 observed reflexions including anisotropic thermal parameters. The final R value was $0 \cdot 12$. It was revealed that siccanin is a triprenylphenol compound involving a bicyclic sesquiterpene moiety and a phenolic ring. The former consists of a cis-fused decalin system, which is the first example found in natural products having a drimane carbon skeleton.

Introduction

Ishibashi (1962) isolated a phenolic antibiotic, siccanin, from cultured broth of Helminthosporium siccans Drechsler. It was reported that this substance exhibits inhibitory activities against various fungi, especially strongly against Trichophyton interdigitale and T. asteroids (Ishibashi, 1962). In the present study, the molecular structure of siccanin is determined by an X-ray crystal structure analysis of siccanin p-bromobenzenesulphonate, a heavy atom derivative of siccanin. A preliminary short note on this work has already been published (Hirai, Nozoe, Tsuda & Iitaka, 1967).

Experimental

Direct bromination of siccanin was first attempted but it failed in obtaining a crystalline derivative suitable for X-ray work. The p-bromobenzenesulphonyl ester of siccanin was then prepared by the treatment of siccanin with p-bromobenzenesulphonyl chloride in pyridine. The crystals were grown from a mixture of methanol and n-hexane. These crystals are orthorhombic colourless prisms elongated along the c axis. The lattice constants were determined from a and b axis equatorial precession photographs taken with Cu Kα radiation. The density was measured by flotation in aqueous solutions of potassium iodide.

Crystal data

Siccanin p-bromobenzenesulphonate, $C_{28}H_{33}O_5SBr$, M.W. 561·5, m.p. 156°C.

Orthorhombic,

$a = 11 \cdot 06 \pm 0 \cdot 04$, $b = 22 \cdot 87 \pm 0 \cdot 03$, $c = 10 \cdot 34 \pm 0 \cdot 03$ Å;

$U = 2615 \cdot 4$ Å^3.

$D_m = 1 \cdot 42$ g.cm^{-3}, $D_x = 1 \cdot 42$ g.cm^{-3}.

$F(000) = 1168$, $Z = 4$.

$\mu(\text{Cu } K\alpha) = 35 \cdot 4$ cm^{-1}.

Absent spectra, $(h00)$ when h is odd, $(0k0)$ when k is odd, $(00l)$ when l is odd.

Space group $P2_12_12_1$.

Three-dimensional intensity data were recorded on multiple-film equi-inclination Weissenberg photographs

Table 1. *The final atomic parameters and their standard deviations*

x, *y* and *z* are the fractional coordinates. To represent the correct absolute configuration these coordinates should refer to the left-handed coordinate system. The temperature factors are expressed in the form:

$$T = -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) .$$

Mean standard deviations in bond lengths (Å):

σ(Br–C)	=	0·025	σ(S–O)	=	0·017
σ(C–C)	=	0·031			

σ(S–C) = 0·020 σ(O–C) = 0·021

Mean standard deviations in bond angles (°):

σ(Br–C–C)	=	1·8	σ(O–S–O)	=	0·9
σ(S—C–C)	=	1·5	σ(C–O–C)		1·3
σ(C–C–C, tetrahedral)	=	1·5			

σ(O–S–C) = 0·9 σ(S–O–C) = 1·0
σ(O–C–C) = 1·5
σ(C–C–C, aromatic) = 1·8

taken with Cu *Kα* radiation. Layer lines of zero to seven around the *a* axis and zero to three around the *b* axis were collected. Measurement of the intensities was


(*a*) R = H   Siccanin

(*b*) R = Br —— F —— SO₂
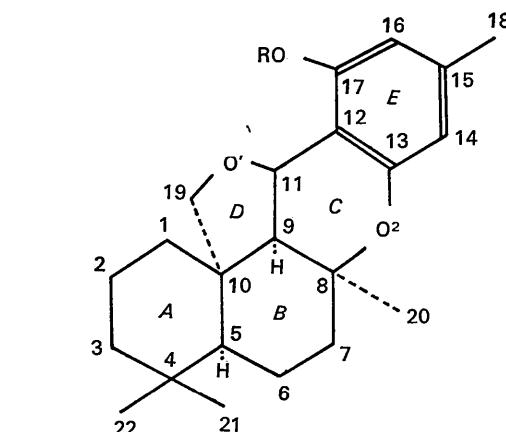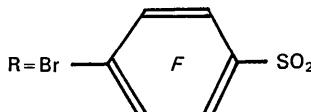
(*c*)
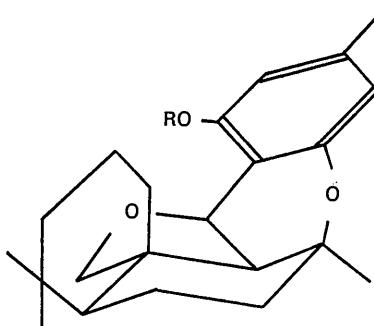
Fig. 1. Chemical formulae (*a*) siccanin (*b*) siccanin *p*-bromo-benzensulphonate (*c*) stereo-structure of siccanin.

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Table 1 (*cont.*)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BR	0.6401 (3)	0.3805 (2)	-0.2222 (3)	0.0150 (3)	0.0067 (1)	0.0099 (2)	-0.0002 (2)	0.0009 (3)	0.0004 (3)
S	0.5846 (5)	0.4268 (2)	0.3824 (5)	0.0083 (4)	0.0018 (1)	0.0095 (4)	-0.0002 (2)	-0.0015 (5)	-0.0007 (1)
O(1)	0.3415 (10)	0.4485 (5)	0.1453 (11)	0.0055 (11)	0.0014 (2)	0.0078 (12)	-0.0007 (4)	-0.0024 (11)	0.0008 (2)
O(2)	0.0814 (11)	0.3359 (4)	0.2659 (11)	0.0071 (11)	0.0013 (2)	0.0067 (10)	-0.0005 (5)	0.0005 (10)	0.0000 (4)
O(3)	0.4458 (10)	0.4262 (5)	0.4076 (11)	0.0057 (10)	0.0019 (2)	0.0071 (11)	-0.0007 (5)	-0.0015 (10)	-0.0010 (4)
O(4)	0.6304 (17)	0.3800 (7)	0.4540 (15)	0.0144 (19)	0.0038 (4)	0.0104 (15)	0.0004 (9)	-0.0036 (17)	-0.0002 (7)
O(5)	0.6218 (16)	0.4861 (6)	0.4074 (17)	0.0134 (18)	0.0027 (3)	0.0155 (20)	-0.0011 (7)	0.0045 (18)	-0.0015 (7)
C(1)	0.2442 (21)	0.3276 (7)	0.0374 (17)	0.0123 (19)	0.0013 (3)	0.0062 (16)	0.0016 (8)	0.0017 (18)	0.0001 (6)
C(2)	0.2877 (24)	0.3111 (7)	-0.0973 (17)	0.0096 (19)	0.0014 (3)	0.0076 (16)	0.0004 (8)	-0.0019 (18)	-0.0007 (6)
C(3)	0.1869 (26)	0.3065 (7)	-0.1946 (20)	0.0202 (32)	0.0006 (3)	0.0107 (22)	0.0016 (9)	0.0016 (24)	0.0004 (7)
C(4)	0.1152 (21)	0.3665 (8)	-0.2031 (19)	0.0120 (24)	0.0016 (4)	0.0088 (20)	-0.0001 (9)	-0.0017 (20)	0.0002 (7)
C(5)	0.0854 (14)	0.3982 (6)	-0.0737 (14)	0.0065 (14)	0.0015 (3)	0.0057 (13)	0.0008 (7)	-0.0003 (14)	0.0001 (5)
C(6)	-0.0219 (19)	0.3535 (8)	-0.0155 (18)	0.0094 (18)	0.0023 (4)	0.0079 (18)	0.0003 (8)	-0.0035 (18)	0.0004 (7)
C(7)	-0.0659 (16)	0.3749 (7)	0.1226 (19)	0.0052 (15)	0.0019 (4)	0.0112 (20)	-0.0006 (7)	0.0003 (17)	0.0001 (8)
C(8)	0.0350 (19)	0.3856 (7)	0.2148 (17)	0.0088 (19)	0.0018 (3)	0.0078 (17)	0.0011 (8)	0.0011 (18)	0.0004 (7)
C(9)	0.1404 (17)	0.4182 (8)	0.1514 (15)	0.0060 (15)	0.0012 (3)	0.0067 (15)	0.0004 (7)	-0.0006 (15)	0.0002 (6)
C(10)	0.1879 (16)	0.3907 (7)	0.0275 (14)	0.0065 (15)	0.0012 (3)	0.0057 (13)	-0.0011 (6)	-0.0006 (14)	0.0012 (6)
C(11)	0.2474 (16)	0.4307 (7)	0.2367 (17)	0.0064 (17)	0.0016 (3)	0.0081 (17)	-0.0004 (7)	0.0041 (16)	0.0007 (7)
C(12)	0.2674 (17)	0.3798 (6)	0.3213 (15)	0.0094 (17)	0.0007 (2)	0.0059 (13)	0.0014 (6)	-0.0008 (14)	-0.0009 (5)
C(13)	0.1875 (19)	0.3329 (7)	0.3290 (17)	0.0084 (19)	0.0015 (3)	0.0061 (15)	-0.0001 (7)	0.0024 (16)	0.0012 (6)
C(14)	0.2114 (19)	0.2831 (7)	0.4031 (19)	0.0082 (19)	0.0014 (3)	0.0097 (19)	-0.0001 (7)	0.0001 (18)	-0.0002 (7)
C(15)	0.3190 (18)	0.2812 (7)	0.4729 (16)	0.0080 (18)	0.0019 (4)	0.0060 (16)	0.0003 (7)	-0.0003 (18)	0.0005 (7)
C(16)	0.3974 (17)	0.3275 (7)	0.4767 (17)	0.0056 (17)	0.0019 (3)	0.0071 (16)	0.0002 (7)	-0.0001 (15)	-0.0009 (6)
C(17)	0.3722 (18)	0.3746 (7)	0.4009 (15)	0.0087 (17)	0.0018 (3)	0.0055 (13)	0.0014 (7)	0.0005 (16)	-0.0007 (6)
C(18)	0.3489 (25)	0.2260 (10)	0.5534 (21)	0.0132 (27)	0.0030 (5)	0.0097 (21)	0.0007 (11)	0.0002 (24)	0.0033 (9)
C(19)	0.2933 (19)	0.4353 (8)	0.0109 (17)	0.0073 (19)	0.0027 (4)	0.0060 (17)	-0.0008 (9)	0.0013 (16)	0.0008 (7)
C(20)	-0.0182 (23)	0.4225 (9)	0.3338 (20)	0.0126 (24)	0.0023 (4)	0.0096 (19)	0.0014 (10)	0.0012 (21)	-0.0000 (8)
C(21)	0.2018 (26)	0.4109 (8)	-0.2811 (18)	0.0124 (24)	0.0022 (5)	0.0057 (15)	-0.0000 (9)	0.0027 (20)	0.0012 (7)
C(22)	0.0085 (26)	0.3630 (8)	-0.2951 (22)	0.0163 (31)	0.0028 (6)	0.0112 (25)	-0.0008 (12)	-0.0072 (28)	-0.0006 (10)
C(23)	0.6237 (24)	0.3972 (11)	-0.0400 (24)	0.0105 (25)	0.0036 (6)	0.0116 (25)	0.0018 (12)	0.0012 (25)	0.0009 (11)
C(24)	0.6439 (25)	0.4502 (10)	0.0046 (23)	0.0122 (27)	0.0027 (5)	0.0119 (23)	-0.0003 (11)	-0.0004 (25)	0.0004 (9)
C(25)	0.6284 (19)	0.4588 (8)	0.1394 (23)	0.0061 (17)	0.0020 (4)	0.0173 (29)	-0.0020 (8)	-0.0037 (21)	0.0028 (9)
C(26)	0.6064 (18)	0.4115 (7)	0.2212 (18)	0.0075 (18)	0.0014 (3)	0.0096 (18)	0.0002 (7)	-0.0002 (18)	0.0014 (7)
C(27)	0.5915 (21)	0.3570 (8)	0.1722 (19)	0.0112 (21)	0.0021 (5)	0.0087 (18)	0.0008 (9)	-0.0028 (18)	0.0012 (8)
C(28)	0.6059 (16)	0.3461 (6)	0.0417 (16)	0.0073 (17)	0.0016 (3)	0.0086 (16)	0.0007 (7)	-0.0015 (15)	0.0001 (6)

made by visual comparison with the standard intensity scales prepared for each axis. Lorentz and polarization corrections were applied in the usual way and the structure factors obtained were put on a common scale by comparing the values of the equivalent reflexions appearing on various layers. The total number of independent non-zero structure factors was 1537 out of about 1900 possible reflexions within a range $0° < 2\theta < 120°$.

Determination of the structure

The crystal structure was determined by the heavy atom method with the bromine atom of the *p*-bromobenzenesulphonyl group as the phasing atom. The *R* value was 0·30 at the stage when all the thirty-five atoms were properly located.

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
2	0	0	41.09	49.08
4	0	0	153.51	194.61
8	0	0	32.25	26.78
1	1	0	20.44	7.92
2	1	0	124.57	185.76
3	1	0	142.76	168.30
5	1	0	75.69	80.38
6	1	0	49.88	51.97
7	1	0	39.73	41.75
9	1	0	11.53	14.82
0	2	0	62.90	76.45
1	2	0	73.82	97.18
2	2	0	44.49	46.47
3	2	0	145.14	182.03
4	2	0	53.51	54.39
5	2	0	98.59	107.73
7	2	0	50.62	45.61
8	2	0	17.06	14.87
11	2	0	16.46	14.71
1	3	0	74.42	83.14
2	3	0	154.87	241.51
3	3	0	44.87	36.70
5	3	0	35.82	42.11
6	3	0	91.29	92.06
9	3	0	24.64	25.28
0	4	0	182.72	381.96
1	4	0	102.10	127.87
2	4	0	67.09	53.96
3	4	0	69.49	65.22
4	4	0	79.88	84.15
5	4	0	30.17	30.56
8	4	0	21.92	23.17
1	5	0	74.23	78.70
2	5	0	69.11	78.73
3	5	0	49.05	49.82
4	5	0	32.52	32.34
5	5	0	35.56	33.65
7	5	0	19.03	15.86
8	5	0	25.96	23.17
0	6	0	80.88	104.20
1	6	0	29.61	30.08
2	6	0	10.90	5.90
3	6	0	81.41	79.42
4	6	0	26.98	23.04
5	6	0	19.91	23.06
7	6	0	41.38	40.69
11	6	0	16.06	15.08
1	7	0	103.20	93.69
2	7	0	67.94	73.69
3	7	0	23.67	26.52
4	7	0	28.08	25.33
5	7	0	27.04	27.58
6	7	0	22.62	25.82
7	7	0	23.54	24.72
9	7	0	14.49	16.62
0	8	0	15.15	12.36
2	8	0	31.02	33.15
3	8	0	31.44	31.20
4	8	0	53.32	54.86
6	8	0	32.12	30.38
7	8	0	10.73	10.06
8	8	0	26.90	31.45
1	9	0	67.34	65.77
2	9	0	20.56	19.71
3	9	0	29.34	23.60
5	9	0	34.48	40.27
6	9	0	16.10	14.49
8	9	0	14.23	16.82
10	9	0	14.36	12.67
0	10	0	12.53	14.55
1	10	0	16.87	13.38
2	10	0	33.93	32.77
3	10	0	69.28	66.88
7	10	0	47.50	50.85
10	10	0	14.21	5.56
1	11	0	47.78	44.63
2	11	0	47.20	42.77
3	11	0	5.69	11.61
4	11	0	34.56	31.80
8	11	0	27.79	33.44
10	11	0	19.76	15.85
1	12	0	18.12	17.08
2	12	0	32.59	29.20
3	12	0	5.18	9.21
4	12	0	13.87	17.97
6	12	0	37.50	41.58
7	12	0	32.84	30.51
8	12	0	14.59	13.40
9	12	0	18.69	19.21
1	13	0	4.93	5.13
2	13	0	31.89	30.32
3	13	0	7.31	12.29
4	13	0	12.49	11.17
5	13	0	26.39	32.94
9	13	0	20.24	22.65
0	14	0	26.92	28.50
1	14	0	13.15	11.09
2	14	0	22.46	24.95
3	14	0	45.42	46.28
5	14	0	13.60	18.56
7	14	0	18.80	18.42
3	15	0	24.24	25.27
5	15	0	18.06	18.25
8	15	0	24.98	28.71
9	15	0	22.37	24.13
0	16	0	38.11	43.54
1	16	0	22.79	17.60
3	16	0	8.18	9.31
5	16	0	20.22	21.47
7	16	0	27.92	35.30
1	17	0	23.30	22.59
3	17	0	8.48	4.61
6	17	0	14.62	16.48
0	18	0	19.29	19.41
1	18	0	22.29	16.04
2	18	0	21.77	20.43
3	18	0	15.74	12.71
7	18	0	11.53	8.61
2	19	0	7.26	5.65
3	19	0	11.79	11.17
0	20	0	43.59	46.15
1	20	0	6.99	6.34
3	20	0	11.01	9.83
1	21	0	20.73	15.30
3	21	0	7.75	6.02
0	22	0	14.36	16.31
2	23	0	13.55	10.47
0	24	0	13.49	8.58
2	24	0	6.75	2.88
2	25	0	6.33	2.66
2	27	0	5.14	4.65
2	28	0	5.59	5.90
3	28	0	4.80	2.02
2	29	0	2.99	7.20
1	0	1	13.23	11.40
2	0	1	85.15	87.32
3	0	1	28.34	24.38
4	0	1	5.99	0.48
5	0	1	30.89	26.85
6	0	1	36.73	41.00
7	0	1	33.54	35.37
8	0	1	16.66	14.14
9	0	1	15.76	14.27
11	0	1	18.95	16.40
0	1	1	32.14	20.15
1	1	1	79.15	93.91
2	1	1	35.99	34.95
3	1	1	40.15	34.79
4	1	1	53.87	55.55
5	1	1	53.70	50.25
6	1	1	7.82	7.79
7	1	1	29.95	28.49
8	1	1	36.50	34.50
9	1	1	21.50	25.12
10	1	1	10.64	7.84
12	1	1	9.39	10.05
0	2	1	69.23	78.96
1	2	1	52.34	54.66
2	2	1	64.98	61.86
3	2	1	71.85	66.55
4	2	1	37.28	39.56
5	2	1	21.37	19.99
6	2	1	67.22	67.30
7	2	1	18.35	18.59
8	2	1	27.36	26.41
9	2	1	10.33	13.91
10	2	1	12.28	11.33
0	3	1	83.55	91.43
1	3	1	66.45	73.92
2	3	1	87.18	95.39
3	3	1	32.29	32.48
4	3	1	45.19	43.67
5	3	1	46.72	54.14
6	3	1	53.81	62.99
7	3	1	20.52	19.12
8	3	1	15.89	15.59
9	3	1	41.96	45.09
10	3	1	12.28	14.65
12	3	1	9.30	7.95
0	4	1	89.61	99.61
1	4	1	59.89	62.52
2	4	1	53.70	55.82
3	4	1	73.06	72.65
4	4	1	6.40	6.18
6	4	1	48.67	20.11
7	4	1	40.21	41.24
8	4	1	18.76	18.98
9	4	1	30.70	29.61
10	4	1	10.64	13.14
11	4	1	11.85	13.16
0	5	1	66.88	65.23
1	5	1	62.12	62.79
2	5	1	95.09	104.28
3	5	1	42.02	41.51
4	5	1	28.06	35.65
5	5	1	22.26	24.41
6	5	1	30.93	35.19
7	5	1	32.89	29.94
8	5	1	15.11	16.09
10	5	1	10.64	12.20
12	5	1	9.07	10.12
0	6	1	100.95	117.69
1	6	1	35.67	27.82
2	6	1	17.44	15.89
3	6	1	21.94	17.28
4	6	1	62.59	75.53
5	6	1	14.60	13.96
6	6	1	27.15	29.42
7	6	1	42.83	44.13
8	6	1	34.20	36.67
10	6	1	10.62	11.09
11	6	1	10.09	12.78
0	7	1	29.13	17.27
1	7	1	40.17	44.87
2	7	1	58.25	54.05
3	7	1	31.97	30.02
4	7	1	20.58	24.48
5	7	1	47.63	52.08
6	7	1	29.55	32.04
7	7	1	21.80	23.09
8	7	1	16.53	15.51
9	7	1	30.55	32.25
11	7	1	9.96	12.72
0	8	1	12.53	10.04
1	8	1	47.69	46.36
2	8	1	39.49	33.48
3	8	1	74.04	67.39
4	8	1	36.14	37.20
5	8	1	14.83	15.98
7	8	1	16.66	16.75
8	8	1	19.63	18.73
9	8	1	19.38	21.01
0	9	1	43.33	24.51
1	9	1	39.00	32.95
2	9	1	93.54	100.47
3	9	1	53.03	47.02
5	9	1	14.57	14.49
6	9	1	32.46	32.32
8	9	1	18.95	18.34
0	10	1	83.55	96.43
1	10	1	49.26	47.86
2	10	1	30.02	29.26
3	10	1	28.53	21.57
4	10	1	45.27	48.68
5	10	1	13.30	12.96
6	10	1	20.97	18.69
7	10	1	17.33	18.78
8	10	1	10.47	11.60
0	11	1	9.24	7.45
1	11	1	25.22	23.17
2	11	1	67.83	64.04
3	11	1	32.31	29.49
4	11	1	8.43	4.70
5	11	1	18.76	20.46
6	11	1	25.51	30.81
8	11	1	20.24	21.61
0	12	1	53.17	57.40
1	12	1	22.26	20.88
2	12	1	38.86	28.66
4	12	1	20.31	17.38
5	12	1	17.06	14.78
6	12	1	11.41	7.73
7	12	1	10.37	10.90
0	13	1	4.50	2.98
1	13	1	15.19	16.64
2	13	1	54.62	56.86
3	13	1	32.14	28.29
4	13	1	9.14	12.33
5	13	1	15.76	17.15
6	13	1	19.40	23.24
8	13	1	19.44	15.58
0	14	1	38.86	43.21
1	14	1	49.52	44.64
2	14	1	29.89	27.70
3	14	1	10.28	9.25
4	14	1	25.75	30.39
5	14	1	17.21	20.10
7	14	1	12.24	11.72
8	14	1	14.96	16.20
0	15	1	42.74	46.53
1	15	1	26.24	34.51
2	15	1	26.68	27.68
3	15	1	26.83	24.16
5	15	1	20.35	20.33
8	15	1	16.02	18.90
0	16	1	5.21	4.50
1	16	1	10.07	7.75
2	16	1	24.60	24.53
3	16	1	17.95	18.51
4	16	1	15.49	12.78
5	16	1	13.45	12.54
6	16	1	15.02	13.79
7	16	1	12.24	14.34
0	17	1	19.69	22.05
1	17	1	15.74	18.99
2	17	1	30.14	31.24
3	17	1	17.74	16.07
4	17	1	15.89	16.77
5	17	1	12.21	14.48
6	17	1	20.37	24.01
0	18	1	21.52	23.44
1	18	1	32.33	34.66
2	18	1	12.55	10.20
3	18	1	11.53	8.89
4	18	1	10.54	8.97
6	18	1	12.21	12.45
7	18	1	10.24	10.39
0	19	1	29.17	31.31
1	19	1	38.01	41.12
2	19	1	4.91	6.52
3	19	1	12.60	9.56
4	19	1	16.25	16.97
5	19	1	10.58	14.32
0	20	1	22.35	27.07
1	20	1	3.57	6.02
2	20	1	16.08	14.59
3	20	1	11.01	9.94
4	20	1	14.96	14.12
0	21	1	22.46	21.76
1	21	1	18.59	20.06
2	21	1	7.35	6.41
3	21	1	11.81	8.45
5	21	1	13.09	14.16
0	22	1	24.88	28.73
1	22	1	5.35	11.35
2	22	1	9.37	8.71
3	22	1	9.79	5.16
0	23	1	15.91	17.73
1	23	1	12.66	13.23
2	23	1	9.11	6.90
3	23	1	9.45	6.47
1	24	1	11.24	11.76
2	25	1	8.90	7.11
1	26	1	7.92	6.79
1	27	1	8.65	8.15
2	27	1	7.77	5.31
0	0	2	52.85	58.45
1	0	2	8.52	6.50
2	0	2	11.49	12.93
3	0	2	31.27	29.77
4	0	2	22.28	23.38
5	0	2	54.70	58.84
6	0	2	9.81	12.16
8	0	2	19.89	21.99
9	0	2	19.21	20.66
10	0	2	14.64	16.20
0	1	2	109.07	108.95
1	1	2	39.79	37.40
2	1	2	120.43	134.43
3	1	2	20.76	14.87
4	1	2	29.29	27.29
5	1	2	27.85	30.78
6	1	2	32.99	32.47
8	1	2	13.43	11.76
10	1	2	11.34	9.20
11	1	2	10.96	9.04
0	2	2	41.70	31.36
1	2	2	97.81	96.90
2	2	2	61.31	61.37
3	2	2	37.03	37.92
4	2	2	18.36	13.50
5	2	2	18.61	14.18
6	2	2	20.42	22.60
7	2	2	32.63	33.02
8	2	2	10.43	13.84
9	2	2	18.14	14.67
10	2	2	21.73	22.24
12	2	2	7.99	3.58
0	3	2	63.77	73.47
1	3	2	99.74	98.94
2	3	2	82.85	83.68
3	3	2	48.71	35.71
4	3	2	34.10	24.42
5	3	2	49.60	45.74
6	3	2	30.06	30.23
7	3	2	18.42	21.21
9	3	2	14.38	11.61
10	3	2	14.64	16.38
12	3	2	7.94	5.97
0	4	2	110.79	131.97
1	4	2	18.89	16.21
2	4	2	40.55	37.18
3	4	2	43.87	39.69
4	4	2	46.35	46.03
5	4	2	40.89	37.82
6	4	2	29.64	30.68
7	4	2	15.89	17.09
8	4	2	20.24	23.00
9	4	2	14.43	11.85
10	4	2	18.50	18.22
11	4	2	12.51	15.14
12	4	2	7.82	2.99
0	5	2	3.63	6.24
1	5	2	25.79	29.01
2	5	2	83.25	84.33
3	5	2	68.21	67.98
4	5	2	38.51	29.42
5	5	2	54.49	55.18
6	5	2	30.63	34.03
7	5	2	42.26	37.42
8	5	2	17.42	18.49
11	5	2	15.19	14.71
0	6	2	20.88	19.76
1	6	2	80.22	84.65
2	6	2	23.75	19.08
3	6	2	76.86	76.68
4	6	2	18.74	14.25
5	6	2	29.49	21.83
6	6	2	21.80	16.13
7	6	2	10.01	7.01
8	6	2	36.84	32.31
9	6	2	14.57	12.32
0	7	2	43.51	31.16
1	7	2	57.15	54.14
2	7	2	66.09	63.66
3	7	2	55.87	49.47
4	7	2	43.38	40.69
5	7	2	32.35	31.84
6	7	2	51.37	51.30
7	7	2	19.54	17.65
8	7	2	38.30	39.64
9	7	2	15.98	14.79
10	7	2	17.16	17.98
11	7	2	14.83	15.10
12	7	2	10.47	7.88
0	8	2	45.06	45.85
1	8	2	34.10	27.77
2	8	2	9.98	8.46
3	8	2	38.52	38.47
4	8	2	28.34	27.85
5	8	2	38.45	39.44
6	8	2	17.55	15.57
7	8	2	18.97	18.97
8	8	2	20.12	23.23
9	8	2	17.33	15.25
11	8	2	10.32	12.93
0	9	2	67.87	53.98
1	9	2	47.12	49.08
2	9	2	50.52	48.81
3	9	2	25.64	26.57
4	9	2	41.79	41.00
5	9	2	39.79	40.30
6	9	2	18.89	21.89
7	9	2	20.29	22.99
8	9	2	31.50	31.11
10	9	2	11.01	10.34
11	9	2	10.11	7.96
0	10	2	14.02	15.38
1	10	2	44.14	47.66
3	10	2	47.46	49.58
5	10	2	14.42	13.47
7	10	2	10.79	13.08
8	10	2	17.16	13.60
10	10	2	10.88	9.42
0	11	2	27.19	28.78
1	11	2	9.71	11.38
2	11	2	35.09	27.75
3	11	2	43.32	32.62
5	11	2	25.85	22.47
6	11	2	19.91	23.19
7	11	2	27.60	28.36
8	11	2	21.65	22.27
1	12	2	33.48	33.05
2	12	2	9.35	7.78
3	12	2	19.78	19.05
4	12	2	11.00	10.82
5	12	2	10.11	8.88
6	12	2	12.32	12.26
7	12	2	21.31	20.09
8	12	2	17.33	17.11
0	13	2	12.17	10.54
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2	13	2	40.39	38.80
3	13	2	26.60	25.90
4	13	2	9.90	11.68
5	13	2	14.74	15.20
6	13	2	14.09	11.66
7	13	2	11.26	14.82
8	13	2	19.63	17.91
1	14	2	19.23	18.96
2	14	2	18.84	19.00
3	14	2	19.89	23.78
7	14	2	11.34	12.54
8	14	2	17.19	16.21
0	15	2	18.36	23.92
1	15	2	12.13	6.91
2	15	2	9.94	6.62
3	15	2	12.04	12.52
4	15	2	12.26	10.21
5	15	2	4.97	13.70
6	15	2	17.19	19.46
7	15	2	11.34	9.50
0	16	2	19.18	21.97
1	16	2	2.83	6.19
2	16	2	10.66	7.47
3	16	2	14.72	17.98
6	16	2	11.34	9.72
8	16	2	10.86	13.08
0	17	2	17.95	17.25
1	17	2	35.82	36.32
2	17	2	10.37	10.47
3	17	2	13.07	11.90
4	17	2	18.21	16.85
5	17	2	17.27	17.57
6	17	2	16.02	10.71
7	17	2	15.70	14.29
0	18	2	21.20	21.16
1	18	2	13.07	10.58
2	18	2	28.49	26.66
3	18	2	8.82	9.34
4	18	2	15.98	15.69
0	19	2	21.71	20.73
1	19	2	21.61	21.43
2	19	2	3.74	6.85
3	19	2	11.87	10.85
5	19	2	14.55	18.81
6	19	2	15.53	5.63
1	20	2	3.61	5.99
2	20	2	26.32	23.82
3	20	2	16.17	14.19
0	21	2	26.96	29.37
1	21	2	9.92	10.26
2	21	2	24.24	22.37
3	21	2	8.88	5.88
1	22	2	13.53	12.48
2	22	2	7.20	4.32
3	22	2	7.50	7.96
1	23	2	12.68	14.78
2	23	2	6.95	6.28
0	24	2	11.98	11.64
1	24	2	7.35	5.38
1	25	2	8.43	8.36
2	25	2	7.94	9.65
1	26	2	7.03	6.04
2	26	2	7.88	7.68
2	27	2	5.63	3.12
3	27	2	6.82	3.98
2	28	2	7.61	7.32
3	28	2	4.76	2.34
1	0	3	120.86	155.01
2	0	3	1.83	0.02
3	0	3	50.16	51.99
4	0	3	9.41	5.50
5	0	3	90.44	89.99
6	0	3	24.50	19.14
7	0	3	22.80	26.84
8	0	3	21.99	19.59
9	0	3	9.92	10.87
10	0	3	36.73	33.09
0	1	3	22.99	24.02
1	1	3	59.89	53.48
2	1	3	76.59	73.11
3	1	3	78.88	67.26
4	1	3	91.14	87.92
5	1	3	33.73	26.77
6	1	3	48.72	42.12
7	1	3	36.09	31.39
8	1	3	11.49	7.20
9	1	3	9.92	6.63
10	1	3	17.33	13.29
11	1	3	17.82	11.94
0	2	3	145.48	185.17
1	2	3	87.91	78.85
2	2	3	39.79	23.00
3	2	3	55.96	42.59
4	2	3	89.37	93.27
5	2	3	10.98	10.07
6	2	3	34.99	32.36
7	2	3	10.60	4.92
8	2	3	17.61	13.52
10	2	3	15.83	15.37
0	3	3	35.69	25.44
1	3	3	86.29	78.71
2	3	3	10.83	10.56
3	3	3	48.69	41.79
4	3	3	86.66	80.07
5	3	3	11.13	11.84
6	3	3	15.78	12.17
7	3	3	20.48	18.99
8	3	3	24.13	23.78
10	3	3	23.47	24.33
11	3	3	11.60	11.29
0	4	3	56.96	53.46
1	4	3	78.30	73.64
2	4	3	77.35	70.51
3	4	3	65.32	55.19
4	4	3	50.54	33.63
5	4	3	23.30	25.57
6	4	3	25.98	24.45
7	4	3	24.18	22.73
8	4	3	33.67	29.90
10	4	3	18.69	14.83
11	4	3	16.29	17.44
0	5	3	24.75	11.85
1	5	3	32.91	31.31
2	5	3	40.83	43.92
3	5	3	36.63	31.32
4	5	3	43.63	40.51
5	5	3	18.01	17.79
6	5	3	40.00	36.27
7	5	3	39.49	35.03
10	5	3	14.08	10.25
0	6	3	34.18	36.47
1	6	3	85.93	84.74
2	6	3	22.26	19.49
3	6	3	31.67	26.75
4	6	3	38.52	37.82
5	6	3	33.80	32.23
6	6	3	25.00	19.62
7	6	3	19.21	12.66
8	6	3	22.73	22.23
9	6	3	12.28	13.24
10	6	3	17.16	15.20
11	6	3	15.93	13.10
0	7	3	25.56	27.39
1	7	3	48.67	42.54
2	7	3	32.18	33.30
3	7	3	20.84	16.04
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7	7	3	11.28	6.58
8	7	3	23.94	25.59
9	7	3	14.21	14.40
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11	7	3	11.07	9.07
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2	8	3	62.59	65.12
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7	8	3	39.17	37.48
8	8	3	22.05	22.57
9	8	3	12.28	10.44
11	8	3	15.38	11.58
0	9	3	18.40	20.27
1	9	3	36.69	32.00
2	9	3	33.73	36.46
3	9	3	31.36	27.74
4	9	3	34.33	32.35
5	9	3	24.86	24.50
6	9	3	17.87	18.02
7	9	3	13.49	11.24
9	9	3	12.26	12.52
0	10	3	53.56	56.11
1	10	3	45.50	45.80
2	10	3	36.07	37.82
3	10	3	48.58	43.93
4	10	3	42.70	39.44
5	10	3	22.71	19.95
6	10	3	24.28	26.61
7	10	3	21.65	19.72
8	10	3	23.47	23.51
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1	11	3	24.96	20.48
2	11	3	29.00	22.16
3	11	3	9.30	15.28
4	11	3	22.01	18.09
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6	11	3	17.55	15.06
7	11	3	17.00	18.39
9	11	3	19.72	19.40
0	12	3	37.79	37.45
1	12	3	28.85	26.86
2	12	3	39.71	38.97
3	12	3	33.80	34.61
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7	12	3	39.77	36.10
8	12	3	20.08	17.96
0	13	3	21.99	21.40
1	13	3	3.34	6.18
2	13	3	28.34	22.06
3	13	3	33.10	28.45
4	13	3	33.59	34.93
5	13	3	23.98	21.80
6	13	3	13.81	12.52
8	13	3	17.29	18.22
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1	14	3	3.91	3.16
2	14	3	5.88	9.87
3	14	3	12.04	9.50
4	14	3	27.06	26.09
6	14	3	12.15	11.25
7	14	3	12.28	14.79
0	15	3	15.30	16.20
1	15	3	26.77	26.05
2	15	3	33.80	32.29
3	15	3	46.65	17.60
4	15	3	17.87	12.84
5	15	3	12.04	6.86
7	15	3	18.70	21.45
8	15	3	11.87	12.06
0	16	3	27.00	28.46
1	16	3	30.80	31.31
2	16	3	34.24	28.11
3	16	3	17.55	16.00
4	16	3	22.96	20.57
6	16	3	18.78	16.57
1	17	3	13.40	12.89
2	17	3	22.03	18.42
3	17	3	25.22	24.40
4	17	3	14.08	10.22
7	17	3	11.87	11.82
0	18	3	24.96	24.81
1	18	3	16.70	18.02
2	18	3	36.29	33.52
3	18	3	15.59	15.45
4	18	3	22.43	23.63
0	19	3	15.08	14.75
1	19	3	14.62	15.09
2	19	3	17.67	13.41
3	19	3	25.13	22.82
0	20	3	7.22	3.61
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3	20	3	14.77	12.28
0	21	3	7.18	10.74
1	21	3	5.69	9.12
3	21	3	11.41	9.09
0	22	3	13.85	14.26
1	22	3	21.56	23.82
2	22	3	15.85	8.46
3	22	3	11.22	8.75
0	23	3	13.51	13.79
1	23	3	5.35	7.66
2	23	3	7.82	8.64
2	24	3	11.07	10.86
3	24	3	7.56	5.41
2	25	3	8.97	9.50
1	26	3	7.31	8.37
2	26	3	6.80	5.94
2	27	3	5.20	7.64
1	28	3	6.44	7.22
0	0	4	75.57	73.16
2	0	4	42.45	39.52
3	0	4	28.19	24.24
4	0	4	12.85	15.76
5	0	4	11.43	11.10
6	0	4	32.35	27.19
7	0	4	19.21	19.57
8	0	4	27.21	25.61
9	0	4	15.91	14.19
10	0	4	9.11	0.99
0	1	4	47.97	36.99
1	1	4	12.47	14.59
2	1	4	77.60	72.21
3	1	4	25.62	17.24
4	1	4	21.61	12.50
5	1	4	59.57	64.92
6	1	4	30.23	25.71
7	1	4	21.71	23.39
8	1	4	15.30	14.10
9	1	4	32.52	33.19
10	1	4	9.11	6.27
11	1	4	10.41	9.24
0	2	4	48.24	51.37
1	2	4	12.58	11.01
2	2	4	76.69	63.81
3	2	4	56.21	60.87
4	2	4	52.49	51.68
5	2	4	17.47	14.89
6	2	4	23.05	21.64
7	2	4	39.09	39.37
8	2	4	16.57	15.67
10	2	4	9.11	4.84
11	2	4	13.41	13.40
0	3	4	44.12	41.82
1	3	4	45.78	40.09
2	3	4	84.72	81.54
3	3	4	16.44	15.74
4	3	4	48.33	44.97
5	3	4	40.34	36.96
6	3	4	16.89	13.34
8	3	4	32.08	30.13
9	3	4	17.23	18.15
10	3	4	9.09	11.02
11	3	4	10.32	10.09
0	4	4	81.11	96.56
1	4	4	19.42	21.97
2	4	4	68.34	54.08
3	4	4	48.20	45.53
4	4	4	38.28	38.93
5	4	4	28.45	28.78
6	4	4	20.99	21.83

Table 2 (*cont.*)

The refinement of the structural parameters was carried out by the method of least squares. Three cycles of the full-matrix calculations (program by Busing, Martin & Levy, 1962) including isotropic temperature factor parameters, followed by three cycles of block-matrix refinement (program by Okaya & Ashida, 1967) including individual anisotropic temperature factor parameters, reduced the R value to 0·12. The weighting system adopted at the final stage of the least-squares calculations was,

$$\sqrt{w}=20/F_o, \quad \text{when } F_o > 20,$$
$$\sqrt{w}=1·0, \quad \text{when } 20 \geq F_o > 2,$$
$$\sqrt{w}=0, \quad \text{when } 2 \geq F_o.$$

Atomic scattering factors used for the calculations were taken from *International Tables for X-ray Crystallography* (1962), where the values are cited as SX–6 for carbon, SX–8 for oxygen, SXC–69 for sulphur and SX–71 for the bromine atom.

The final atomic parameters are listed in Table 1 together with their standard deviations. The observed and calculated structure factors are given in Table 2. A composite electron density map calculated with the use of the final atomic parameters is shown in Fig. 2 together with the perspective drawing of the molecule.

Absolute configuration

The absolute configuration was determined by the anomalous dispersion method. The values of the real and imaginary parts of the dispersion corrections of bro-

mine atoms for Cu $K\alpha$ radiation ($\Delta f' = -0·9$ and $\Delta f'' = 1·5$) were those given by Dauben & Templeton (1955).

Twenty Friedel pairs of reflexions showed significant intensity differences in the lth-layer Weissenberg photo-

(a)

(b)
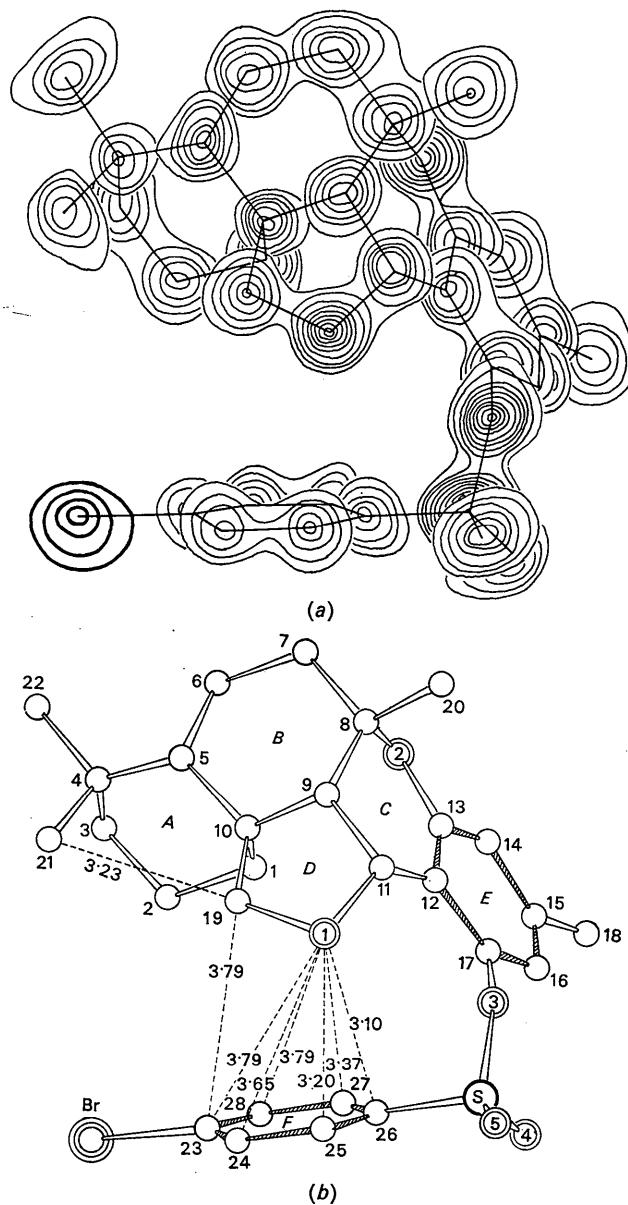
Fig. 2. (a) Composite drawing of the final electron density map viewed along the b axis. (b) The molecular structure viewed along the b axis. The short distance between two diaxial groups and the closest intramolecular contacts less than 3·8 Å found between the D and F rings are shown.

Table 3. *Comparison of the observed and calculated intensity differences used for the establishment of the absolute configuration*

h	k	l	$\|F_c(hkl)\|^2/\|F_c(\bar{h}\bar{k}\bar{l})\|^2$	$I_o(hkl)/I_o(\bar{h}\bar{k}\bar{l})$
4	5	1	1·118	<1
6	5	1	0·804	>1
6	1	2	1·259	<1
3	2	2	1·169	<1
2	3	2	1·169	<1
8	4	2	1·197	<1
1	5	2	1·211	<1
5	1	3	0·753	>1
2	5	3	0·817	>1
6	5	3	0·864	>1
4	11	3	1·214	<1
3	1	4	0·608	>1
4	1	4	0·660	>1
1	3	4	0 813	>1
3	3	4	0 779	>1
2	3	5	1·272	<1
3	3	5	0·791	>1
5	3	5	0·766	>1
4	5	5	0·792	>1
3	4	6	0·790	>1

Table 4. *The mean values of bond lengths and angles averaged for each ring*

	A	B	E	F
Bond lengths	1·535 Å	1·540	1·390	1·387
Bond angles	111·5°	111·8	—	—

graphs. The differences were in accordance with those calculated by assuming that the atomic parameters of Table 1 are referred to a left-handed set of axes. The results are shown in Table 3. All Figures shown in the present paper are drawn with the correct absolute configuration.

Discussion of the structure

The present analysis revealed that the structure of siccanin p-bromobenzenesulphonate is as shown in Fig. 1(b). Since this compound was prepared by the esterification of the phenolic hydroxyl group of siccanin with p-bromobenzenesulphonyl chloride, the structure of siccanin is deduced to be as shown in Fig. 1(a).

It is now well established that siccanin is a triprenyl-phenol compound consisting of a bicyclic sesquiterpene moiety involving the A and B rings, a phenol group involving the E ring, the C-ring which connects the two parts, and the D ring of a five-membered ether ring. From the standpoint of biogenesis, siccanin is considered to be derived from farnesyl pyrophosphate and
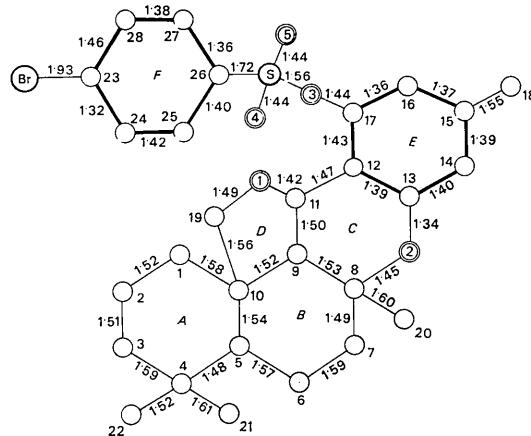
Fig. 3. Bond lengths (Å).
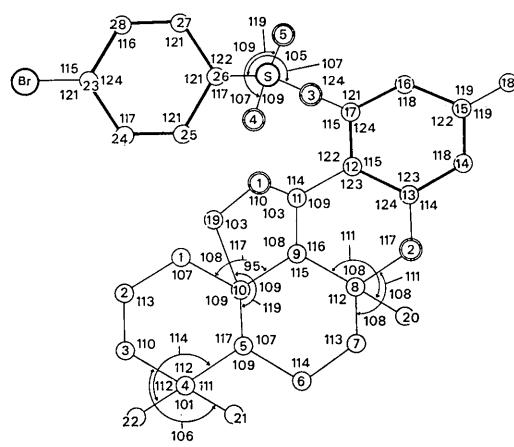
Fig. 4. Bond angles (°).

Table 5. Deviations of atoms from the least-squares planes

The atoms marked by * are not included in the least-squares calculation.

A ring		B ring		B ring alternative		C ring		D ring		E ring		F ring	
C(2)	−0·019 Å	C(5)	0·057	C(5)	−0·015	O(2)	0·007	O(1)	−0·006	C(12)	−0·023	C(23)	−0·045
C(3)	0·019	C(7)	−0·059	C(6)	0·015	C(11)	−0·007	C(9)	−0·003	C(13)	0·019	C(24)	0·035
C(5)	−0·018	C(8)	0·060	C(8)	−0·015	C(12)	0·015	C(11)	−0·006	C(14)	0·007	C(25)	−0·014
C(10)	0·019	C(10)	−0·058	C(9)	0·015	C(13)	−0·015	C(19)	0·004	C(15)	−0·029	C(26)	0·006
C(1)	0·745*	C(6)	−0·623*	C(7)	−0·549*	C(8)	0·423*	C(10)	−0·730*	C(16)	0·023	C(27)	−0·016
C(4)	−0·568*	C(9)	0·648*	C(10)	0·727*	C(9)	−0·264*			C(17)	0·003	C(28)	0·034
										O(2)	0·063*	Br	−0·011*
										O(3)	0·154*	S	−0·105*
										C(11)	−0·106*		
										C(18)	−0·073*		

Equations of the planes and dihedral angles

A ring $-0·482X - 0·671Y + 0·565Z = -1·013$
B ring $-0·123X + 0·992Y + 0·013Z = 8·808$ } dihedral angle = 126°48'
B ring (alternative choice of atoms forming the least-squares planes)
          $0·587X - 0·806Y + 0·082Z = -5·841$ } dihedral angle = 125°33'
C ring $-0·459X + 0·464Y + 0·758Z = 13·004$

X, Y and Z are parallel to the crystallographic axes a, b and c respectively, and measured in Å.

orsellinate. However, the structure is unique in that it involves a decalin system of *cis* fusion. Of the drimane type compounds so far found in nature, this may be the first example of the compounds involving such a *cis*-fused decalin system (Hirai, Nozoe, Tsuda & Iitaka, 1967).

The bond lengths and angles are shown in Figs. 3 and 4. The mean estimated standard deviations in bond lengths and angles are calculated for each type of bond and are listed in Table 1. As shown in Table 4, the mean values of C–C single bonds involved in the six-membered rings *A* and *B* are 1·54 Å, and those of C=C partial double bonds involved in the benzene rings *E* and *F* are 1·39 Å, which are in good agreement

with the usual values. However, the mean bond angles found in the *A* and *B* rings are slightly larger than the tetrahedral angle. Other bond lengths and angles are usual except the significantly small bond angle, 94·6° of C(9)–C(10)–C(19). This angle is involved in the heterocyclic five-membered ring *D*, and C(10) is at the junction of the *A* and *B* rings. The source of this distortion may be attributed to the steric repulsion between the two bulky axial groups. As shown in Fig. 2(*b*), the methyl carbon atom C(21) and the methylene carbon atom C(19) are at the 1,3-diaxial positions. The distance between the two atoms would be about 2·52 Å, if the atoms in the *A* ring took a regular tetrahedral arrangement. In the present structure, however, this
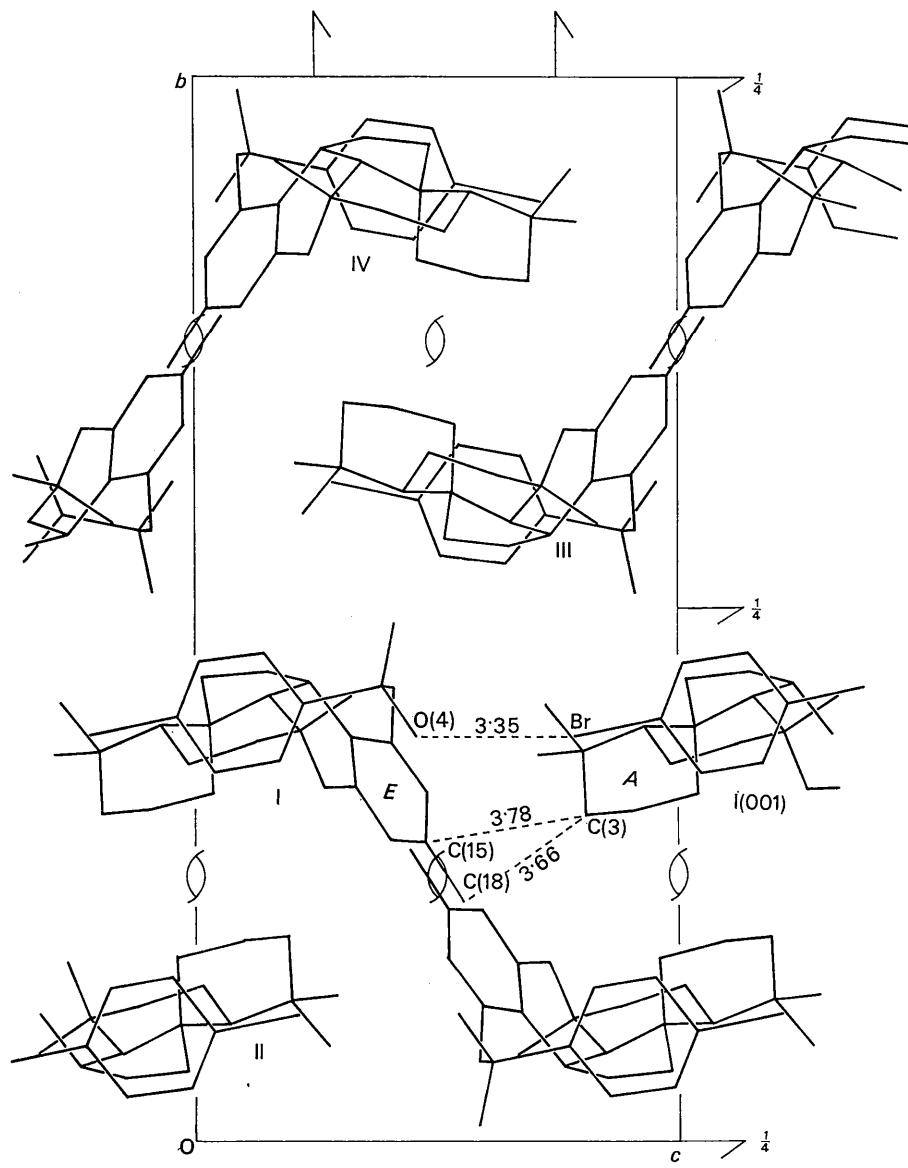

Fig. 5. Projection of the crystal structure along the *a* axis. Intermolecular short contacts less than 3·8 Å found between the molecule I and its translation equivalent along the c direction are shown.

distance is increased to 3·23 Å and results in the distortion in the bond angle C(9)–C(10)–C(19), and in the significant puckering of the D ring.

The conformation of each ring may be seen in Table 5: rings A and B both have the chair form; ring C, which involves a partial double bond at C(12)–C(13), takes a half-chair conformation. The junction between the A and B rings and that between the B and C rings are both cis fusion, the arrangement of these three rings being cis/syn/cis. The five-membered ring D takes a puckered conformation, C(10) being 0·73 Å out of

the plane formed by the remaining four atoms. Each of the benzene rings E and F is nearly exactly coplanar. The deviations of the atoms from each plane are also shown in Table 5.

The molecule has a rotational freedom about the S–O(3) bond. The internal rotation angle, C(26)–S–O(3)–C(17) is 67·8°, which implies that S–C(26) is oriented gauche with respect to O(3)–C(17) and the molecule takes a cis form, or is U shaped as a whole. The folding of the molecule seems to be caused by the strong interactions between the ether oxygen atom O(1) and
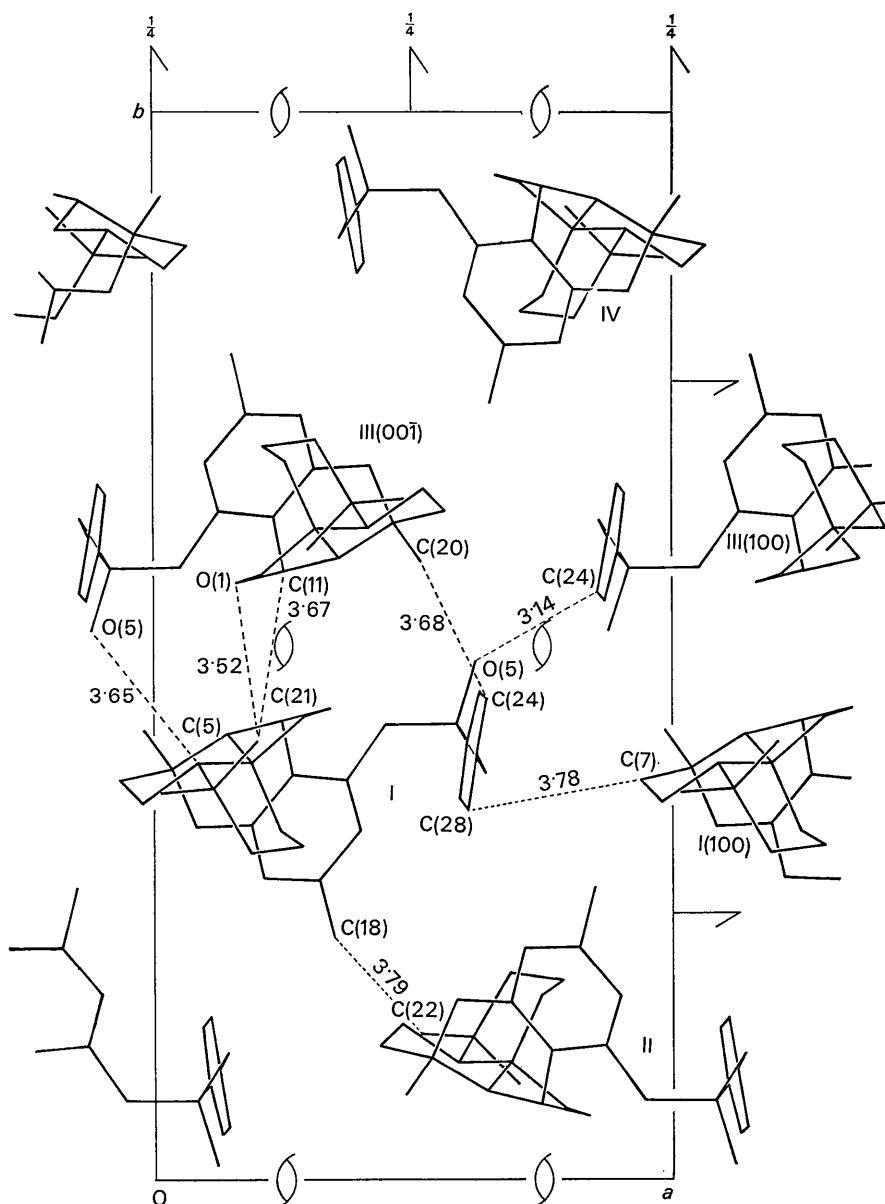

Fig. 6. Projection of the crystal structure along the c axis. Intermolecular short contacts less than 3·8 Å found between the molecular trains are shown.

the benzene ring F. Intramolecular short contacts between the D and F rings, whose distances are smaller than 3·8 Å are shown in Fig. 2(b).

The projections of the crystal structure along the a and c axes are shown in Figs. 5 and 6, respectively. The molecules are designated by the molecular numbers I to IV as follows.:

$$\text{I} \quad \text{at} \quad (x, y, z),$$
$$\text{II} \quad \text{at} \quad (\tfrac{1}{2}+x, \; -\tfrac{1}{2}+y, \; -z),$$
$$\text{III} \quad \text{at} \quad (\tfrac{1}{2}-x, \; 1-y, \; \tfrac{1}{2}+z),$$
$$\text{IV} \quad \text{at} \quad (1-x, \; \tfrac{1}{2}+y, \; \tfrac{1}{2}-z).$$

The x, y and z coordinates are as given in Table 1. The subscript attached to the molecular number in the Figures indicates translations along the three edges of the unit cell. The shortest intermolecular distances less than 3·8 Å are shown in these Figures. There are no abnormal distances between the molecules. One of the remarkable features of the packing of the molecules is the arrangement of the p-bromobenzenesulphonyl groups. As seen in Fig. 5, these groups are arranged head to tail along the c axis. The bromine atom lies on top of the sulphonyl group of the neighbouring molecule and at the same time close contacts between C(3) and the phenyl group (ring E) are produced. In this way, trains of the molecules are formed extending along the c axis. The shortest distance between the bromine atom and the sulphonyl oxygen atoms is 3·35 Å

[Br...O(4)] which corresponds to the sum of the van der Waals radii but a dipole interaction is expected for this arrangement. Fig. 6 shows the packing of the molecular trains. The shortest distance between the trains is found between the atoms O(5) of the sulphonyl oxygen atom and C(24) of the benzene ring. This distance, 3·14 Å is nearly the minimum van der Waals distance expected for this kind of contact.

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Neutron Diffraction Study of Ba(N₃)₂

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The crystal structure of anhydrous barium azide, Ba(N₃)₂, has been determined by single-crystal neutron diffraction methods. The unit cell is monoclinic, $a=9\cdot59$, $b=4\cdot39$, $c=5\cdot42$ Å, $\beta=99\cdot75°$; space group $P2_1/m$, with two molecules per cell. All atoms were shown by a Patterson map to lie on mirror planes. The trial structure was refined by the method of full-matrix least-squares to a final R index of 0·041. There are two non-equivalent azide groups, a four coordinated apparently symmetric azide and a five coordinated azide with a slight probable asymmetry. Barium atoms are surrounded by nine azides, in the form of a right triangular prism with three azides near the centers of each of the three vertical faces. The structure consists of infinite Ba–N bond chain layers, packed laterally with long Ba–N bonds. An inspection of the thermal ellipsoids suggests that the thermal vibrations of the nitrogen atoms can be described largely in terms of rigid-bar angular oscillations of the azide axis with the larger amplitude in the direction of lesser constraint.

Introduction

Barium azide [Ba(N₃)₂] crystallizes in both hydrated and anhydrous forms of which the former is the easier to

grow from aqueous solution although the hydrated crystals are subject to very slow dehydration in air. The lattice parameters of Ba(N₃)₂·H₂O were investigated some years ago by Günther, Porger & Rosboud (1929). The anhydrous barium azide, Ba(N₃)₂, was prepared and investigated for the first time in single crystal form by Torkar, Krischner & Radl, (1965). They deter-

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