

- HARKEMA, S. (1971). Thesis, Twente University of Technology, Enschede, The Netherlands.
- HARVEY, K. B., MORROW, B. A. & SHURVELL, H. F. (1963). *Canad. J. Chem.* **41**, 1181-1187.
- HURST, R. P., MILLER, J. & MATSEN, F. A. (1958). *Acta Cryst.* **11**, 320-322.
- LARSON, A. C. (1969). In *Crystallographic Computing*, pp. 291-294. Edited by F. R. AHMED. Copenhagen: Munksgaard.
- MOHANA RAO, J. K. & VISWAMITRA, M. A. (1971). *Ferro-electrics*, **2**, 209-216.
- MUTHUKRISHNAN, K. & RAMAKRISHNA, J. (1971). *Curr. Sci.* **40**, 486-487.
- NITTA, I. (1928). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **9**, 151-163.
- RAMANUJAM, P. S. (1969). *Indian J. Pure Appl. Phys.* **7**, 420-423.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.

*Acta Cryst.* (1973), **B29**, 685

## The Crystal Structure of 5-Bromo-12S-tetrahydroaustamide

BY J. COETZER AND P. S. STEYN

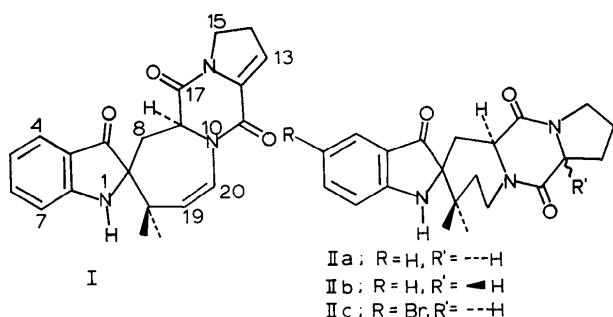
*National Physical and National Chemical Research Laboratories, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa*

(Received 13 November 1972; accepted 23 November 1972)

The crystal structure of 5-bromo-12S-tetrahydroaustamide has been determined by three-dimensional X-ray analysis. The crystals are monoclinic with space group  $P2_1$  and two molecules in the unit cell of dimensions  $a = 7.241$ ,  $b = 13.148$ ,  $c = 11.556 \text{ \AA}$  and  $\beta = 106.68^\circ$ . The absolute configuration of the molecule was derived from the known stereochemistry at the 12-position established in earlier chemical and spectroscopic studies.

### Introduction

In our continuing studies on biologically active fungal metabolites, austamide (I) was isolated as a toxic component from *Aspergillus ustus* (Steyn, 1971).



Prolonged hydrogenation of I gave two diastereoisomeric tetrahydroaustamides IIa and IIb. Acid hydrolysis of the major product, IIa, liberated S-proline, therefore establishing the 12S-configuration at this newly created chiral centre. The stereochemistry at position 9 was based on the 9S, 12S-configuration of prolyl-2-(1'1'-dimethylallyl)tryptophyldiketopiperazine, an apparent bioprecursor of I. The configuration at the spiro atom, position 2 relative to that of position 9, was based on n.m.r. shift data (Steyn, to be published).

5-Bromo-12S-tetrahydroaustamide (IIc) was prepared for an X-ray crystallographic study in an attempt to substantiate the above conclusions.

### Experimental

12S-Tetrahydroaustamide (50 mg) in tetrahydrofuran (2 ml) was treated with pyridinium hydrobromide perbromide (44 mg) in tetrahydrofuran (2 ml). The colourless mixture was concentrated in a stream of nitrogen and the residue partitioned between chloroform and water. The organic phase was concentrated and crystallized from ethanol to yield IIc. [Analysis: Found: C, 54.31; H, 5.60; Br, 17.25; N, 9.05%.  $C_{21}H_{24}BrN_3O_3 \cdot H_2O$  requires C, 54.63; H, 5.44; Br, 17.06; N, 8.97%].

The bright yellow rhombic crystals are monoclinic with space group  $P2_1$  ( $0k0$  absent for  $k$  odd).

The other crystal data are:

Molecular formula  $C_{21}H_{24}BrN_3O_3$   
 $\lambda(Mo K\alpha) = 0.70926 \text{ \AA}$

$a = 7.241 (1) \text{ \AA}$   
 $b = 13.148 (2)$   
 $c = 11.556 (1)$   
 $\beta = 106.68 (30)^\circ$   
 $d_x = 1.46 \text{ g cm}^{-3}$   
 $d_m = 1.46$  (measured by flotation in a mixture of bromoform and methanol)  
M.W.446.34  
Z=2.

Unit-cell dimensions were calculated from the accurate spot positions measured on a Hilger & Watts four-circle automatic diffractometer using a least-

Table 1. *Refined atomic parameters ( $\times 10^4$ ) (fractional coordinates and anisotropic temperature factors)*Thermal parameters are of the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$ .

(Standard deviations are given in parentheses.)

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Br	14017 (2)	0	11674 (1)	300 (3)	156 (2)	143 (2)	14 (3)	-46 (2)	10 (2)
O(1)	8713 (10)	2133 (6)	7644 (6)	292 (18)	53 (5)	81 (6)	-8 (8)	61 (9)	-2 (5)
O(2)	4511 (15)	2925 (8)	2998 (8)	503 (33)	96 (8)	132 (10)	96 (14)	102 (15)	44 (8)
O(3)	8452 (12)	-329 (7)	4371 (8)	335 (24)	64 (6)	126 (9)	54 (10)	91 (11)	1 (6)
O(4)	8150 (15)	3764 (9)	5765 (8)	497 (33)	142 (11)	135 (10)	-89 (16)	106 (15)	-5 (9)
N(1)	6288 (10)	-146 (8)	7973 (7)	220 (17)	57 (6)	83 (7)	-19 (10)	36 (9)	4 (6)
N(2)	5443 (12)	1744 (8)	4467 (7)	252 (22)	83 (7)	66 (7)	48 (10)	32 (10)	10 (6)
N(3)	8338 (13)	1202 (9)	3456 (7)	299 (24)	88 (8)	67 (7)	29 (12)	56 (11)	5 (7)
C(1)	11582 (13)	-129 (12)	10485 (8)	193 (21)	107 (11)	75 (8)	38 (17)	26 (11)	11 (10)
C(2)	10453 (19)	-965 (10)	10461 (10)	339 (34)	61 (8)	100 (12)	6 (15)	35 (16)	9 (8)
C(3)	8691 (16)	-1036 (9)	9649 (9)	277 (28)	65 (8)	75 (9)	7 (13)	37 (13)	3 (7)
C(4)	8075 (14)	-236 (8)	8831 (8)	231 (22)	48 (7)	72 (8)	-16 (11)	39 (11)	-12 (6)
C(5)	9207 (13)	618 (8)	8847 (8)	163 (19)	66 (7)	52 (7)	1 (10)	33 (10)	-9 (6)
C(6)	11046 (15)	728 (9)	9687 (9)	218 (23)	73 (8)	65 (8)	16 (11)	37 (11)	-5 (7)
C(7)	8192 (13)	1283 (8)	7894 (8)	207 (21)	41 (6)	63 (8)	0 (10)	49 (11)	-8 (6)
C(8)	6284 (13)	727 (8)	7207 (8)	186 (21)	60 (7)	66 (8)	-10 (10)	23 (11)	7 (7)
C(9)	4427 (14)	1375 (9)	7115 (9)	199 (23)	67 (8)	84 (9)	5 (11)	59 (12)	3 (7)
C(10)	2686 (14)	643 (11)	6833 (11)	152 (21)	108 (11)	118 (12)	-16 (13)	21 (13)	-3 (10)
C(11)	4631 (17)	1891 (10)	8345 (10)	287 (29)	82 (9)	117 (12)	1 (14)	111 (16)	-13 (9)
C(12)	4121 (17)	2213 (10)	6148 (11)	281 (30)	68 (9)	97 (11)	62 (14)	64 (15)	7 (8)
C(13)	3721 (16)	1851 (12)	4839 (10)	221 (27)	129 (13)	86 (11)	72 (16)	29 (14)	24 (10)
C(14)	7088 (13)	1118 (8)	5183 (8)	202 (22)	64 (7)	62 (8)	28 (11)	44 (11)	-5 (7)
C(15)	6521 (13)	326 (7)	5972 (7)	238 (22)	50 (7)	51 (7)	10 (9)	41 (10)	-6 (6)
C(16)	5712 (21)	2341 (9)	3591 (10)	445 (41)	50 (7)	72 (10)	43 (15)	73 (17)	10 (7)
C(17)	7656 (20)	2270 (11)	3374 (11)	403 (38)	73 (9)	97 (12)	34 (16)	101 (18)	12 (8)
C(18)	7611 (25)	2586 (13)	2043 (13)	631 (58)	129 (16)	128 (15)	73 (25)	211 (26)	36 (12)
C(19)	9037 (25)	1906 (14)	1796 (12)	579 (57)	136 (16)	104 (13)	64 (26)	130 (23)	9 (13)
C(20)	9092 (17)	889 (11)	2466 (10)	323 (30)	107 (12)	73 (9)	26 (16)	90 (14)	-5 (9)
C(21)	8022 (17)	587 (10)	4272 (11)	188 (24)	84 (10)	86 (10)	8 (13)	33 (13)	-15 (9)

squares procedure (Busing & Levy, 1967). A crystal with dimensions  $0.12 \times 0.14 \times 0.20$  mm was chosen to collect intensities for 2112 independent reflexions with  $\theta < 25^\circ$  using the diffractometer with graphite monochromated Mo  $K\alpha$  radiation and applying the  $\omega-2\theta$  scanning technique. Of these intensities 1656 were greater than  $3\sigma(I)$ , where  $\sigma(I)$  is given by  $[I_0 + I_b]^{1/2}$ .  $I_0$  is the total number of counts during the peak scan and  $I_b$  the number of counts for the background intensity. Background corrections were made from scans of intensity against  $\theta$ , parallel to central lattice rows. The reflexions were corrected for Lorentz and polarization factors but no absorption corrections were applied.

### Structure analysis

The structure was solved by the heavy-atom method. Refinement of the atomic parameters assigning unit weights to the 1656 observed reflexions in a full-matrix least-squares program (Busing, Martin & Levy, 1962) which minimizes the function  $\sum \omega(|F_o| - |kF_c|)^2$  gave an  $R$  index [ $R = (\sum |F_o| - |F_c|)/\sum |F_o|$ ] of 0.14 with individual isotropic thermal parameters for all the atoms. Refinement with anisotropic thermal parameters reduced the  $R$  index to 0.065. The form factors used were those of Hansen, Herman, Lea & Skillman (1964). A list of the final atomic parameters is given in Table 1. Bond lengths and angles were calculated using the function and error program ORFFE

(Busing, Martin & Levy, 1964). These values are given in Tables 2 and 3. Table 4 lists the observed and calculated structure factors.

Table 2. *Interatomic distances ( $\text{\AA}$ ) (standard deviations in parentheses)*

C=O		C=C (arom)	
C(7)—O(1)	1.24 (2) $\text{\AA}$	C(1)—C(2)	1.37 (2) $\text{\AA}$
C(16)—O(2)	1.21 (2)	C(2)—C(3)	1.35 (2)
C(21)—O(3)	1.24 (3)	C(3)—C(4)	1.40 (2)
		C(4)—C(5)	1.39 (2)
		C(5)—C(6)	1.41 (2)
		C(6)—C(1)	1.44 (3)
<i>sp</i> <sup>2</sup> C—N		<i>sp</i> <sup>2</sup> C— <i>sp</i> <sup>2</sup> C	
C(4)—N(1)	1.39 (2)	C(5)—C(7)	1.43 (2)
C(16)—N(2)	1.34 (2)		
C(21)—N(3)	1.31 (3)		
<i>sp</i> <sup>3</sup> C—N			
C(8)—N(1)	1.45 (3)	<i>sp</i> <sup>2</sup> C— <i>sp</i> <sup>3</sup> C	
C(13)—N(2)	1.44 (3)	C(7)—C(8)	1.56 (2)
C(21)—N(2)	1.49 (2)	C(16)—C(17)	1.50 (3)
C(17)—N(3)	1.48 (3)	C(14)—C(21)	1.57 (3)
C(20)—N(3)	1.46 (2)		
C—C			
C(1)—Br	1.91 (3)	C(8)—C(9)	1.57 (3)
		C(9)—C(10)	1.54 (3)
O(1)···O(4)	2.99 (4)	C(9)—C(11)	1.54 (2)
O(2)···O(4)	2.77 (4)	C(9)—C(12)	1.54 (2)
		C(12)—C(13)	1.53 (2)
		C(8)—C(15)	1.58 (3)
		C(14)—C(15)	1.52 (2)
		C(17)—C(18)	1.58 (3)
		C(18)—C(19)	1.46 (2)
		C(19)—C(20)	1.54 (3)

### Discussion

The stereo pair in Fig. 1 illustrates the molecular geometry and the atomic numbering used in the X-ray

analysis while the structure formula (I) shows the chemical numbering (Steyn, 1971). The assignment of the absolute configuration of the molecule is based on the known stereochemistry at the 12-position [C(17)]

Table 3. Bond angles (standard deviations in parentheses)

C(4)—N(1)—C(8)	109.9 (1) <sup>o</sup>	C(8)—C(9)—C(10)	107.9 (3) <sup>o</sup>
C(13)—N(2)—C(14)	120.9 (2)	C(8)—C(9)—C(11)	108.8 (2)
C(13)—N(2)—C(16)	119.7 (1)	C(8)—C(9)—C(12)	112.4 (2)
C(14)—N(2)—C(16)	118.5 (2)	C(10)—C(9)—C(11)	108.9 (2)
C(17)—N(3)—C(20)	114.2 (1)	C(10)—C(9)—C(12)	110.7 (2)
C(17)—N(3)—C(21)	120.4 (2)	C(11)—C(9)—C(12)	108.0 (3)
C(20)—N(3)—C(21)	124.8 (2)	C(9)—C(12)—C(13)	116.2 (2)
Br—C(1)—C(2)	120.7 (2)	N(2)—C(13)—C(12)	113.1 (2)
Br—C(1)—C(6)	114.6 (2)	N(2)—C(14)—C(21)	107.7 (2)
C(2)—C(1)—C(6)	124.6 (2)	N(2)—C(14)—C(15)	113.7 (2)
C(1)—C(2)—C(3)	120.7 (2)	C(15)—C(14)—C(21)	109.9 (3)
C(2)—C(3)—C(4)	118.1 (2)	C(8)—C(15)—C(14)	115.7 (2)
N(1)—C(4)—C(3)	126.6 (1)	O(2)—C(16)—N(2)	124.1 (2)
N(1)—C(4)—C(5)	111.5 (2)	O(2)—C(16)—C(17)	120.0 (2)
C(3)—C(4)—C(5)	121.8 (2)	N(2)—C(16)—C(17)	115.9 (1)
C(4)—C(5)—C(6)	121.9 (2)	N(3)—C(17)—C(16)	111.1 (1)
C(6)—C(5)—C(7)	129.8 (2)	N(3)—C(17)—C(18)	103.0 (1)
C(1)—C(6)—C(5)	112.8 (1)	C(16)—C(17)—C(18)	112.8 (2)
O(1)—C(7)—C(5)	127.2 (2)	C(17)—C(18)—C(19)	102.2 (2)
O(1)—C(7)—C(8)	125.9 (1)	C(18)—C(19)—C(20)	110.6 (2)
C(5)—C(7)—C(8)	106.8 (3)	N(3)—C(20)—C(19)	100.8 (2)
N(1)—C(8)—C(7)	102.4 (2)	O(3)—C(21)—N(3)	125.0 (2)
N(1)—C(8)—C(9)	108.9 (2)	O(3)—C(21)—C(14)	121.0 (1)
N(1)—C(8)—C(15)	107.9 (2)	N(3)—C(21)—C(14)	114.0 (3)
C(7)—C(8)—C(9)	113.3 (3)		
C(7)—C(8)—C(15)	107.9 (2)		
C(9)—C(8)—C(15)	115.7 (2)		

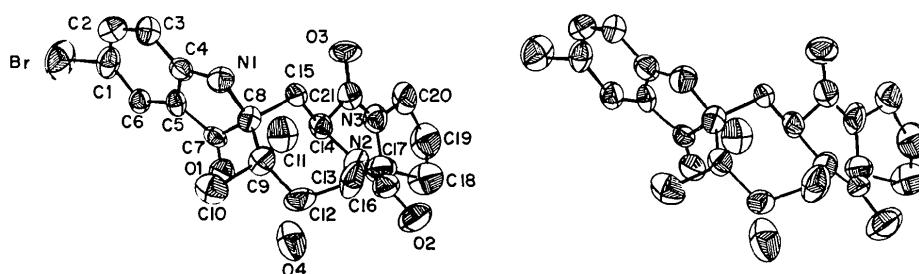


Fig. 1. Stereoscopic drawing of 5-bromo-12S-tetrahydroaustamide showing the atomic numbering used in the X-ray analysis.

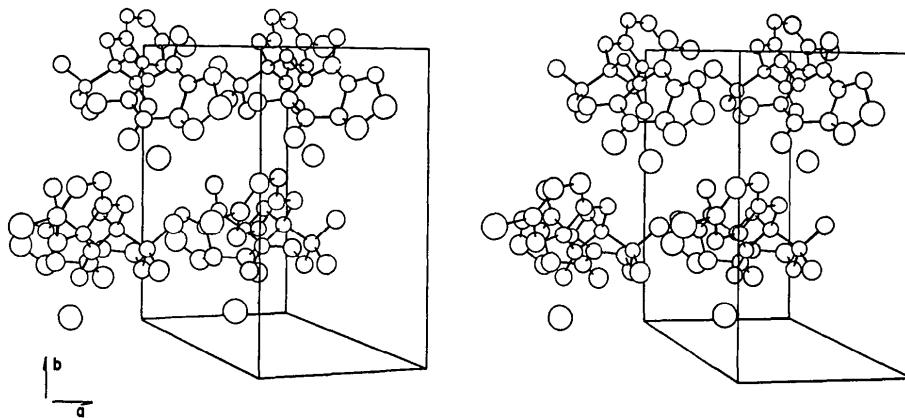


Fig. 2. Stereoscopic diagram of the molecular packing in the unit cell.

Table 4. Observed and calculated structure factors

The columns are  $k$ ,  $l$ ,  $F_{\text{obs}} \times 10$  and  $F_{\text{calc}} \times 10$ .

$N + O$	$k$	$l$	$F_{\text{obs}} \times 10$	$F_{\text{calc}} \times 10$
0	0	471	473	-
0	0	150	86	-
0	2	472	493	-
0	2	265	215	-
0	2	150	75	-
0	9	112	359	-
0	9	370	92	-
0	7	108	110	-
0	7	179	183	-
0	8	184	191	-
0	10	58	59	-
0	11	155	154	-
0	12	67	80	-
0	13	115	73	-
0	14	148	207	-
0	15	150	116	-
0	2	223	241	-
0	2	8	8	-
0	4	171	194	-
0	4	245	230	-
0	6	23	21	-
0	6	33	32	-
0	7	322	311	-
0	7	304	328	-
0	8	8	2	-
0	8	2	227	-
0	9	240	75	-
0	10	2	9	-
0	11	379	641	-
0	12	223	29	-
0	13	424	466	-
0	14	1071	1126	-
0	15	693	707	-
0	16	2	775	-
0	17	304	510	-
0	18	424	426	-
0	19	179	194	-
0	20	443	456	-
0	21	644	133	-
0	22	163	170	-
0	23	22	26	-
0	24	99	88	-
0	25	109	112	-
0	26	28	26	-
0	27	9	9	-
0	28	134	135	-
0	29	152	153	-
0	30	126	125	-
0	31	35	31	-
0	32	137	137	-
0	33	12	12	-
0	34	12	12	-
0	35	12	12	-
0	36	12	12	-
0	37	12	12	-
0	38	12	12	-
0	39	12	12	-
0	40	12	12	-
0	41	12	12	-
0	42	12	12	-
0	43	12	12	-
0	44	12	12	-
0	45	12	12	-
0	46	12	12	-
0	47	12	12	-
0	48	12	12	-
0	49	12	12	-
0	50	12	12	-
0	51	12	12	-
0	52	12	12	-
0	53	12	12	-
0	54	12	12	-
0	55	12	12	-
0	56	12	12	-
0	57	12	12	-
0	58	12	12	-
0	59	12	12	-
0	60	12	12	-
0	61	12	12	-
0	62	12	12	-
0	63	12	12	-
0	64	12	12	-
0	65	12	12	-
0	66	12	12	-
0	67	12	12	-
0	68	12	12	-
0	69	12	12	-
0	70	12	12	-
0	71	12	12	-
0	72	12	12	-
0	73	12	12	-
0	74	12	12	-
0	75	12	12	-
0	76	12	12	-
0	77	12	12	-
0	78	12	12	-
0	79	12	12	-
0	80	12	12	-
0	81	12	12	-
0	82	12	12	-
0	83	12	12	-
0	84	12	12	-
0	85	12	12	-
0	86	12	12	-
0	87	12	12	-
0	88	12	12	-
0	89	12	12	-
0	90	12	12	-
0	91	12	12	-
0	92	12	12	-
0	93	12	12	-
0	94	12	12	-
0	95	12	12	-
0	96	12	12	-
0	97	12	12	-
0	98	12	12	-
0	99	12	12	-
0	100	12	12	-
0	101	12	12	-
0	102	12	12	-
0	103	12	12	-
0	104	12	12	-
0	105	12	12	-
0	106	12	12	-
0	107	12	12	-
0	108	12	12	-
0	109	12	12	-
0	110	12	12	-
0	111	12	12	-
0	112	12	12	-
0	113	12	12	-
0	114	12	12	-
0	115	12	12	-
0	116	12	12	-
0	117	12	12	-
0	118	12	12	-
0	119	12	12	-
0	120	12	12	-
0	121	12	12	-
0	122	12	12	-
0	123	12	12	-
0	124	12	12	-
0	125	12	12	-
0	126	12	12	-
0	127	12	12	-
0	128	12	12	-
0	129	12	12	-
0	130	12	12	-
0	131	12	12	-
0	132	12	12	-
0	133	12	12	-
0	134	12	12	-
0	135	12	12	-
0	136	12	12	-
0	137	12	12	-
0	138	12	12	-
0	139	12	12	-
0	140	12	12	-
0	141	12	12	-
0	142	12	12	-
0	143	12	12	-
0	144	12	12	-
0	145	12	12	-
0	146	12	12	-
0	147	12	12	-
0	148	12	12	-
0	149	12	12	-
0	150	12	12	-
0	151	12	12	-
0	152	12	12	-
0	153	12	12	-
0	154	12	12	-
0	155	12	12	-
0	156	12	12	-
0	157	12	12	-
0	158	12	12	-
0	159	12	12	-
0	160	12	12	-
0	161	12	12	-
0	162	12	12	-
0	163	12	12	-
0	164	12	12	-
0	165	12	12	-
0	166	12	12	-
0	167	12	12	-
0	168	12	12	-
0	169	12	12	-
0	170	12	12	-
0	171	12	12	-
0	172	12	12	-
0	173	12	12	-
0	174	12	12	-
0	175	12	12	-
0	176	12	12	-
0	177	12	12	-
0	178	12	12	-
0	179	12	12	-
0	180	12	12	-
0	181	12	12	-
0	182	12	12	-
0	183	12	12	-
0	184	12	12	-
0	185	12	12	-
0	186	12	12	-
0	187	12	12	-
0	188	12	12	-
0	189	12	12	-
0	190	12	12	-
0	191	12	12	-
0	192	12	12	-
0	193	12	12	-
0	194	12	12	-
0	195	12	12	-
0	196	12	12	-
0	197	12	12	-
0	198	12	12	-
0	199	12	12	-
0	200	12	12	-
0	201	12	12	-
0	202	12	12	-
0	203	12	12	-
0	204	12	12	-
0	205	12	12	-
0	206	12	12	-
0	207	12	12	-
0	208	12	12	-
0	209	12	12	-
0	210	12	12	-
0	211	12	12	-
0	212	12	12	-
0	213	12	12	-
0	214	12	12	-
0	215	12	12	-
0	216	12	12	-
0	217	12	12	-
0	218	12	12	-
0	219	12	12	-
0	220	12	12	-
0	221	12	12	-
0	222	12	12	-
0	223	12	12	-
0	224	12	12	-
0	225	12	12	-
0	226	12	12	-
0	227	12	12	-
0	228	12	12	-
0	229	12	12	-
0	230	12	12	-
0	231	12	12	-
0	232	12	12	-
0	233	12	12	-
0	234	12	12	-
0	235	12	12	-
0	236	12	12	-
0	237	12	12	-
0	238	12	12	-
0	239	12	12	-
0	240	12	12	-
0	241	12	12	-
0	242	12	12	-
0	243	12	12	-
0	244	12	12	-
0	245	12	12	-
0	246	12	12	-
0	247	12	12	-
0	248	12	12	-
0	249	12	12	-
0	250	12	12	-
0	251	12	12	-
0	252	12	12	-
0	253	12	12	-
0	254	12	12	-
0	255	12	12	-
0	256	12	12	-
0	257	12	12	-
0	258	12	12	-
0	259	12	12	-
0	260	12	12	-
0	261	12	12	-
0	262	12	12	-
0	263	12	12	-
0	264	12	12	-
0	265	12	12	-
0	266	12	12	-
0	267	12	12	-
0	268	12	12	-
0	269	12	12	-
0	270	12	12	-
0	271	12	12	-
0	272	12	12	-
0	273	12	12	-
0	274	12	12	-
0	275	12	12	-
0	276	12	12	-
0	277	12	12	-
0	278	12	12	-
0	279	12	12	-
0	280	12	12	-
0	281	12	12	-
0	282	12	12	-
0	283	12	12	-
0	284	12	12	-
0	285	12	12	-
0	286	12	12	-
0	287	12	12	-
0	288	12	12	-
0				

Table 5. Equations of least-squares planes

Atoms	Equation	Maximum deviation from plane (Å)
C(1), C(2), C(3), C(4), C(5), C(6)	$-0.6236x + 0.4431y + 0.6441z = 4.3421^*$	0.005 (1)
O(3), C(21), C(14), N(3)	$0.7659x + 0.2199y + 0.6042z = 6.4011$	0.01 (2)
O(2), C(16), C(17), N(2)	$0.1592x + 0.7232y + 0.6721z = 5.3713$	0.005 (3)
O(1), C(7), C(5), C(8)	$0.6684x - 0.4228y - 0.6120z = -3.8434$	0.003 (4)

\*  $x$ ,  $y$  and  $z$  (in Å) refer to the crystallographic axes  $a$ ,  $b$  and  $c$ , respectively.

in the X-ray numbering] from chemical data. The predicted stereochemistry of the *spiro* atom and carbon 9 [C(14)] is shown to be in agreement with the X-ray structure.

As expected the six benzene carbon atoms are all coplanar. This is shown by the maximum atomic deviation of 0.005 Å from the least-squares plane (Equation 1, Table 5) passing through the benzene ring. The three aromatic substituent atoms, Br, N(1) and C(7), show insignificant deviations of 0.07, 0.07 and 0.03 Å, respectively, from this plane.

The mean C=C aromatic bond length is 1.39 Å while the distances of 1.43 and 1.39 Å for the pairs C(5)-C(7) and C(4)-N(1) are typical of C(aromatic)-C and C(aromatic)-N bond types (Sutton, 1965).

Equations 2, 3 and 4 in Table 5 give the respective least-squares planes through the trigonal arrangements associated with the carbonyl carbon atoms C(7), C(16) and C(21). The respective maximum atomic deviations are 0.003, 0.005 and 0.01 Å, making all three sets of atoms planar.

Despite the planarity of the latter two groups of atoms the diketopiperazine ring is folded and assumes the boat conformation as shown in Fig. 1.

The carbonyl bond lengths are 1.24 [C(7)-O(1)], 1.24 [C(21)-O(3)] and 1.21 Å [C(16)-O(2)], respectively, and show good agreement with the values quoted by Sutton (1965) for these distances, *viz.* 1.235 (O=C-N) and 1.25 Å (in 3,3'-dibromobenzophenone).

The mean  $sp^3$ C- $sp^3$ C bond length of 1.54 Å compares favourably with the value of 1.545 Å in diamond. The crystals of 5-bromo-12*S*-tetrahydroaustamide contain one molecule of crystal water per formula unit. The oxygen atom of the water molecule, O(4), is removed from the two carbonyl oxygen atoms O(1) and O(3) by distances of 2.99 and 2.77 Å, respectively, indicating hydrogen bonding to both carbonyl oxygens.

The molecular packing in the unit cell is shown in Fig. 2. The shortest contact distance of 3.53 Å occurs between the atoms C(6) and C(19) in molecules which are separated by a unit-cell translation in the  $c$  direction.

#### References

- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457-464.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORFFE. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040-1044.
- STEYN, P. S. (1971). *Tetrahedron Lett.* pp. 3331-3334.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration of Molecules and Ions*, Supplement 1956-1959. London: The Chemical Society.