

Crystal and Molecular Structure of the *p*-Bromophenyl- hydrazone of Ribose

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The crystal structure of the *p*-bromophenylhydrazone of ribose has been determined by twodimensional X-ray crystallographic methods. The sugar occurs in the open-chain form and the compound is a true hydrazone, $\text{RCH}=\text{N}-\text{NH}-\text{C}_6\text{H}_4\text{Br}$. The zig-zag chain $-\text{C}_5-\text{N}_2-\text{N}_1=\text{C}_1-\text{C}_2$ is roughly planar and coplanar with the benzene ring. Four of the atoms in the ribose carbon chain lie in one plane, but C_5 is out of this plane by 1.4 Å. This sugar conformation is stabilized by an intramolecular hydrogen bond O_5-O_2 of length 2.66 Å.

Chemical evidence indicates that the phenylhydrazones of the sugars may occur in cyclic or acyclic forms,¹ but little appears to be known about the structure of individual hydrazones. In connection with other structural studies of sugars, we are now carrying out crystal structure determinations of a number of hydrazones and osazones.² The *p*-bromophenylhydrazone of arabinose has been shown to be a hydrazide with the sugar in the 1e2e3e4a pyranose chair conformation.³ In the present paper the structure of the ribose derivative is described.

Crystals of the *p*-bromophenylhydrazone of ribose were grown and X-ray Weissenberg diagrams taken about the *c* and *a* crystallographic axes. The corresponding electron density projections (Figs. 1 and 2) were calculated, from which approximate atomic coordinates were derived. These were further refined by difference syntheses and least squares calculations. The final ones are given in Table 1 and the corresponding bond lengths and angles in Table 2 and Fig. 3. The values are inaccurate as relatively few reflections were recorded, and we do not consider deviations less than 0.1 Å in the bond lengths significant. Details of the structure analysis are given below.

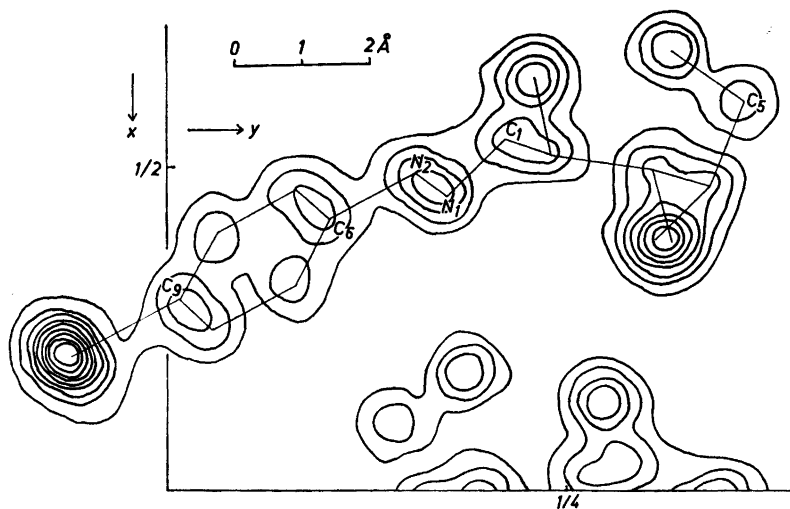


Fig. 1. Electron density projection in direction of c axis. Contours at 3, 7, 11.... $e \cdot \text{\AA}^{-2}$ for bromine; 3, 5, 7.... $e \cdot \text{\AA}^{-2}$ for the other atoms.

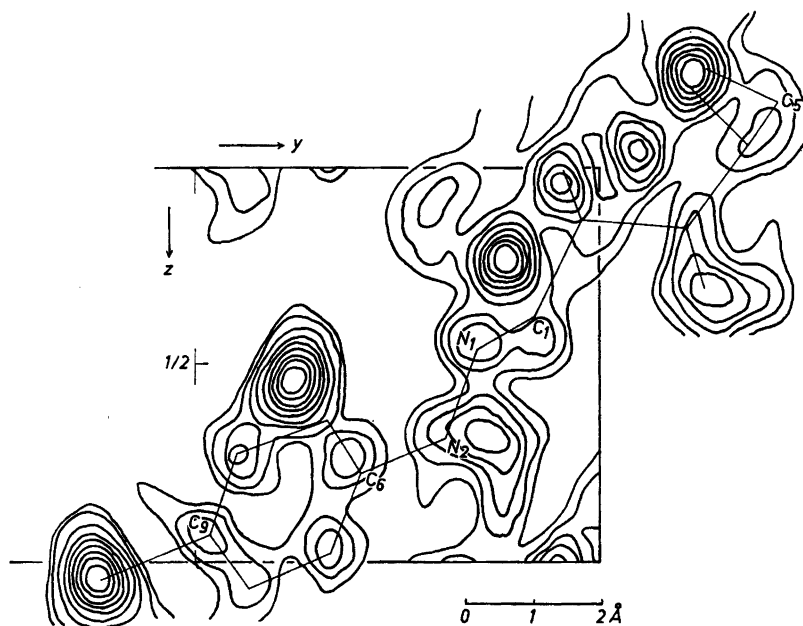


Fig. 2. Electron density projection in direction of a axis. Contours as in Fig. 1.

Table 1. Atomic coordinates as fractions of the corresponding cell edge.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{hko}</i>
Br	0.794	0.9389	0.036	4.9–9.6
C ₁	0.455	0.2111	0.384	4.9
C ₂	0.481	0.2385	0.139	5.2
C ₃	0.505	0.3029	0.155	4.6
C ₄	0.530	0.3383	0.949	5.1
C ₅	0.396	0.3610	0.838	4.8
C ₆	0.582	0.1035	0.769	5.2
C ₇	0.536	0.0811	0.975	5.5
C ₈	0.604	0.0305	0.065	4.7
C ₉	0.703	0.0073	0.926	4.9
C ₁₀	0.751	0.0277	0.713	5.7
C ₁₁	0.685	0.0790	0.634	5.9
N ₁	0.548	0.1745	0.463	5.2
N ₂	0.510	0.1538	0.686	5.8
O ₁	0.360	0.2284	0.023	4.1
O ₂	0.620	0.3144	0.309	5.2
O ₃	0.615	0.3040	0.803	5.4
O ₄	0.318	0.3153	0.740	5.4

Table 2. Bond lengths (in Å units) and bond angles.

Bond lengths	Bond angles		
C ₉ —Br	1.94	Br C ₁ C ₁₀	116°
C ₉ —C ₈	1.35	Br C ₁ C ₈	117°
C ₈ —C ₇	1.46	C ₉ C ₁ C ₇	115°
C ₇ —C ₆	1.37	C ₈ C ₁ C ₆	119°
C ₆ —C ₁₁	1.37	C ₇ C ₁ C ₁₁	123°
C ₁₁ —C ₁₀	1.44	C ₆ C ₁ C ₁₀	119°
C ₁₀ —C ₉	1.40	C ₁₁ C ₁₀ C ₉	115°
C ₉ —N ₂	1.46	C ₁₀ C ₉ C ₃	128°
N ₂ —N ₁	1.43	C ₇ C ₅ N ₂	117°
N ₁ —C ₁	1.32	C ₁₁ C ₆ N ₂	119°
C ₁ —C ₂	1.57	C ₆ N ₂ N ₁	117°
C ₂ —C ₃	1.55	N ₂ N ₁ C ₁	112°
C ₃ —C ₄	1.48	N ₁ C ₁ C ₂	119°
C ₄ —C ₅	1.52	C ₁ C ₂ C ₃	112°
C ₅ —O ₅	1.43	C ₂ C ₃ C ₄	123°
C ₄ —O ₄	1.42	C ₃ C ₄ C ₅	114°
C ₃ —O ₃	1.43	C ₄ C ₅ O ₅	109°
C ₂ —O ₂	1.34	C ₅ C ₄ O ₄	115°
O ₂ —O ₅	2.66	C ₃ C ₄ O ₄	104°
		C ₄ C ₃ O ₃	106°
		C ₂ C ₃ O ₃	110°
		C ₁ C ₂ O ₂	104°
		C ₃ C ₄ O ₂	109°

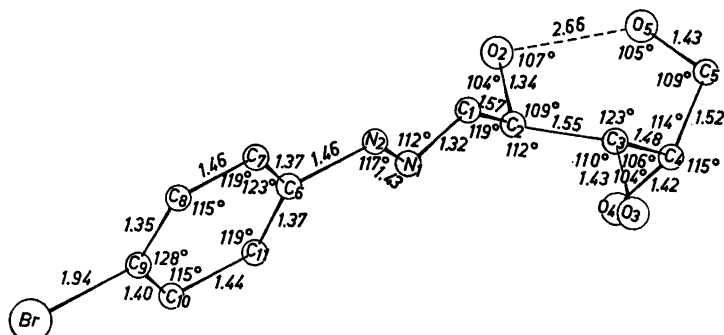


Fig. 3. The molecular structure of ribose-*p*-bromophenylhydrazone. Bond lengths in Å units.

The molecular structure derived (Fig. 3) corresponds to the conventional Fischer formula $\text{RCH}=\text{N}-\text{NH}-\text{C}_6\text{H}_5\text{Br}$ for sugar hydrazones, as shown by the following structural features: (1) The sugar is acyclic, (2) the arrangement about N_1-C_1 is planar, (3) the bond C_1-N_1 is found to be short (1.32 Å) and has a large amount of double bond character. Correspondingly, N_1-N_2 is considerably longer (1.43 Å). The compound is thus a true hydrazone, whereas the arabinose derivative was found to be a hydrazide, $\text{R}'\text{CH}-\text{NH}-\text{NH}-\text{C}_6\text{H}_5\text{Br}$. It may be expected that ribose has a greater tendency to true hydrazone formation than other sugars as it appears to occur in the acyclic (aldehydo) form to a much greater extent.⁴

Sugars generally appear to prefer a planar zig-zag carbon chain when they are in the acyclic form. This also holds for sugars as glucose and ribose in which this conformation gives unfavourable short *cis* oxygen-oxygen contacts (O_2-O_4 in ribose) if ideal bond angles are maintained. The strain appears to be relieved mainly by increase of some of the bond angles. In the present case, however, another conformation occurs. Four of the carbon atoms lie in one plane, but C_5 is brought out of the chain plane by a rotation of roughly 120° around C_3-C_4 . The strain is not relieved by this operation, as C_5 takes the place of O_4 , and the chain angle at C_3 is consequently large. The arrangement around all the C-C bonds is of the staggered type. This conformation appears to be stabilized by an intramolecular hydrogen bond between O_5 and O_2 ($\text{O}_2-\text{H}\cdots\text{O}_5$). The distance O_2-O_5 is only 2.66 Å and the angles between the line O_2-O_5 and adjacent bonds are 107° and 105° . Thus the atoms are ideally disposed for hydrogen bond formation. Further evidence for the existence of this bond is provided by the fact that there are four oxygen-bonded hydrogen atoms in the molecule, but only three intermolecular contacts which may be interpreted as hydrogen bonds. The intramolecular hydrogen bond completes a six-membered ring of the pyranose chair type in ribose, in which the bonds C_2-O_2 and C_4-C_5 are roughly coplanar, with O_5 and C_3 below and above this plane by 0.5–0.7 Å. Hydrogen bonds are known to occur between the two residues in disaccharides,⁷ but the present structure appears to be the first case of an intramolecular hydrogen bond in a crystalline monosaccharide.

The atoms N_1 , N_2 , C_1 , and C_2 are coplanar to within 0.01 Å, as is to be expected for a hydrazone structure. This plane forms an angle of 116° with the planar part of the ribose carbon chain, the bond C_1-N_1 being *trans* to the bisecting line of the angle $O_2C_2C_3$.

Another plane may be defined by N_2 , Br, and the carbon atoms of the benzene ring, none of which deviates more than 0.02 Å from the least squares plane. Furthermore, N_1 lies only 0.10 Å from this plane, which forms an angle of 3° with the plane $N_1N_2C_6$. The corresponding angle in the arabinose-*p*-bromophenylhydrazide is approximately 20° . The least squares plane through N_1, N_2, Br and the benzene carbon atoms forms an angle of 15° with the above-mentioned plane $N_1N_2C_1C_2$. The azimuthal angle about the N—N bond is consequently 165° whereas approximately 90° was found in the hydrazide of arabinose.³ In crystalline diformyl-⁵ and diacetyl-hydrazine⁶ this angle is 180° . The zig-zag chain $-C_6-N_2-N_1-C_1-C_2$ is essentially planar and coplanar with the benzene ring.

The low accuracy of the structure determination does not warrant a detailed discussion of bond lengths and angles. The largest deviations from expected values are shown by the bond C_2-O_2 (1.34 Å) and the angles $C_8C_9C_{10}$ (128°), $C_1N_1N_2$ (112°) and $C_2C_3C_4$ (123°), but only for the last-mentioned angle the deviation is definitely significant.

The arrangement of the molecules in the crystal is shown in Fig. 4. There are only three intermolecular contacts shorter than 3.0 Å, namely $O_3-H\cdots O_4$ (2.87 Å), $O_4-H\cdots O_2$ (2.64 Å), and $O_5-H\cdots N_1$ (2.82 Å). These are all likely to be hydrogen bonds. The intramolecular $O_2-H\cdots O_5$ bond is discussed above. As N_1 has no hydrogen atom, the indicated assignment of hydrogen atoms to the bonds is the most probable one.

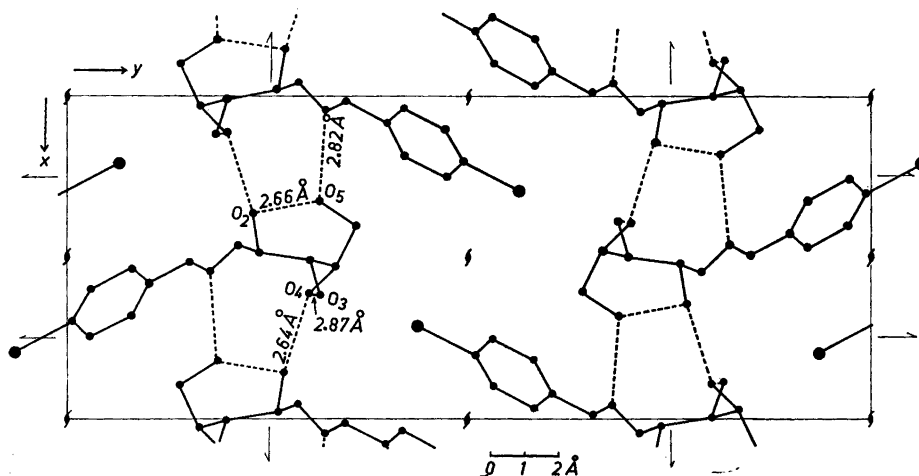


Fig. 4. The *c* projection of the structure. Broken lines indicate hydrogen bonds.

Table 3. Observed (F_o) and calculated (F_c) structure factors.

k	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	0	15	— 4	2	11	0	10	11
0	4	0	36	27	2	12	0	9	10
0	6	0	< 1	— 1	2	13	0	< 2	0
0	8	0	149	— 151	2	14	0	23	— 24
0	10	0	18	— 26	2	15	0	18	22
0	12	0	9	13	2	16	0	40	— 41
0	14	0	18	18	2	17	0	6	— 7
0	16	0	37	39	2	18	0	14	— 17
0	18	0	11	10	2	19	0	< 3	— 3
0	20	0	< 3	— 0	2	20	0	< 3	6
0	22	0	8	— 5	2	21	0	13	— 15
0	24	0	20	— 18	2	22	0	4	3
0	26	0	< 3	— 2	2	23	0	< 3	— 0
0	28	0	< 2	— 2	2	24	0	14	14
0	30	0	3	4	2	25	0	< 3	— 1
1	1	0	14	— 17	2	26	0	4	5
1	2	0	35	— 41	3	1	0	81	— 72
1	3	0	33	— 29	3	2	0	41	46
1	4	0	42	— 46	3	3	0	32	38
1	5	0	31	31	3	4	0	116	109
1	6	0	95	— 89	3	5	0	4	— 2
1	7	0	2	— 3	3	6	0	17	— 23
1	8	0	33	36	3	7	0	47	47
1	9	0	56	— 54	3	8	0	12	13
1	10	0	45	43	3	9	0	70	72
1	11	0	7	12	3	10	0	34	— 32
1	12	0	84	81	3	11	0	7	8
1	13	0	43	— 42	3	12	0	41	— 41
1	14	0	47	48	3	13	0	8	12
1	15	0	39	42	3	14	0	8	— 13
1	16	0	15	16	3	15	0	19	— 24
1	17	0	7	8	3	16	0	< 3	— 2
1	18	0	12	— 15	3	17	0	21	— 22
1	19	0	3	4	3	18	0	7	7
1	20	0	22	— 23	3	19	0	7	— 7
1	21	0	8	9	3	20	0	14	13
1	22	0	16	— 18	3	21	0	7	— 6
1	23	0	7	— 5	3	22	0	7	3
1	24	0	< 3	— 1	3	23	0	8	6
1	25	0	< 3	— 3	3	24	0	< 3	2
1	26	0	< 3	— 2	3	25	0	12	11
1	27	0	< 2	— 3	3	26	0	9	— 8
1	28	0	6	5	3	27	0	< 2	3
1	29	0	3	— 3	3	28	0	7	— 7
1	30	0	4	6	4	0	0	26	28
2	0	0	6	— 14	4	1	0	12	— 13
2	1	0	38	— 43	4	2	0	38	39
2	2	0	152	— 154	4	3	0	55	53
2	3	0	118	— 107	4	4	0	4	— 6
2	4	0	51	— 43	4	5	0	72	78
2	5	0	48	— 43	4	6	0	16	— 17
2	6	0	65	61	4	7	0	< 2	— 1
2	7	0	82	— 74	4	8	0	16	— 18
2	8	0	53	54	4	9	0	< 2	7
2	9	0	46	47	4	10	0	20	— 25
2	10	0	21	29	4	11	0	26	— 30

<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
4 12 0	20	22	6 15 0	< 3	— 3
4 13 0	48	— 52	6 16 0	< 3	— 5
4 14 0	17	22	6 17 0	< 3	0
4 15 0	4	— 3	6 18 0	< 3	6
4 16 0	9	5	6 19 0	23	— 18
4 17 0	9	7	6 20 0	7	7
4 18 0	7	8	6 21 0	10	— 7
4 19 0	14	12	7 1 0	15	— 13
4 20 0	< 3	— 0	7 2 0	3	4
4 21 0	18	18	7 3 0	8	— 11
4 22 0	17	— 16	7 4 0	20	— 20
4 23 0	6	6	7 5 0	12	14
4 24 0	< 3	2	7 6 0	< 3	— 3
4 25 0	< 2	5	7 7 0	20	18
4 26 0	3	— 2	7 8 0	12	— 14
4 27 0	3	— 3	7 9 0	17	17
5 1 0	33	36	7 10 0	24	— 24
5 2 0	10	7	7 11 0	25	23
5 3 0	30	32	7 12 0	11	13
5 4 0	12	— 10	7 13 0	19	— 17
5 5 0	14	— 17	7 14 0	< 3	3
5 6 0	5	6	7 15 0	10	— 5
5 7 0	44	— 44	7 16 0	9	8
5 8 0	6	6	7 17 0	13	— 12
5 9 0	36	— 36	7 18 0	14	10
5 10 0	10	12	7 19 0	< 3	— 0
5 11 0	17	— 19	7 20 0	< 2	— 5
5 12 0	16	13	7 21 0	< 2	2
5 13 0	10	— 10	7 22 0	< 2	— 3
5 14 0	10	6	7 23 0	7	6
5 15 0	8	6	8 0 0	< 3	— 0
5 16 0	10	— 12	8 1 0	12	10
5 17 0	22	19	8 2 0	17	— 17
5 18 0	5	— 2	8 3 0	3	3
5 19 0	14	12	8 4 0	3	4
5 20 0	8	— 9	8 5 0	26	25
5 21 0	6	— 5	8 6 0	9	8
5 22 0	< 3	2	8 7 0	< 3	— 0
5 23 0	11	— 8	8 8 0	10	9
5 24 0	5	4	8 9 0	8	— 5
5 25 0	11	— 8	8 10 0	< 3	4
5 26 0	< 2	1	8 11 0	4	0
5 27 0	3	— 4	8 12 0	< 3	— 2
6 0 0	10	14	8 13 0	10	— 6
6 1 0	14	— 13	8 14 0	< 3	— 2
6 2 0	19	— 19	8 15 0	3	— 3
6 3 0	50	— 50	8 16 0	6	— 6
6 4 0	7	8	8 17 0	7	3
6 5 0	26	— 28	8 18 0	11	— 10
6 6 0	< 3	1	8 19 0	10	6
6 7 0	4	— 1	8 20 0	< 2	— 3
6 8 0	9	— 9	8 21 0	4	4
6 9 0	< 3	— 2	9 1 0	9	8
6 10 0	8	— 9	9 2 0	< 3	— 3
6 11 0	41	41	9 3 0	8	— 9
6 12 0	< 3	4	9 4 0	18	16
6 13 0	19	17	9 5 0	< 3	0
6 14 0	< 3	1	9 6 0	< 3	2

<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
9 7 0	14	- 13	0 3 2	10	- 5
9 8 0	8	8	0 4 2	19	23
9 9 0	8	- 4	0 5 2	< 7	7
9 10 0	6	- 5	0 6 2	78	86
9 11 0	< 3	- 4	0 7 2	19	- 18
9 12 0	5	- 6	0 8 2	44	- 40
9 13 0	< 3	1	0 9 2	53	53
9 14 0	6	- 8	0 10 2	65	67
9 15 0	8	10	0 11 2	43	- 47
10 0 0	10	10	0 12 2	22	23
10 1 0	4	- 4	0 13 2	< 10	- 4
10 2 0	6	7	0 14 2	66	- 61
10 3 0	4	- 3	0 15 2	11	- 2
10 4 0	< 3	- 1	0 16 2	25	24
10 5 0	< 3	4	0 17 2	< 11	- 16
10 6 0	< 3	1	0 18 2	59	- 48
10 7 0	11	- 9	0 19 2	< 12	2
10 8 0	5	- 5	0 20 2	26	- 23
10 9 0	8	7	0 1 3	< 8	9
10 10 0	3	- 3	0 2 3	10	- 8
10 11 0	3	2	0 3 3	23	- 33
11 1 0	< 2	- 1	0 4 3	44	43
11 2 0	4	- 4	0 5 3	27	28
11 3 0	5	- 4	0 6 3	29	- 31
11 4 0	< 2	0	0 7 3	< 9	- 4
11 5 0	7	5	0 8 3	< 10	1
11 6 0	5	- 5	0 9 3	22	- 25
0 1 1	10	7	0 10 3	38	35
0 2 1	25	- 31	0 11 3	37	32
0 3 1	95	- 113	0 12 3	27	- 22
0 4 1	81	88	0 13 3	37	- 36
0 5 1	63	60	0 14 3	45	51
0 6 1	< 6	0	0 15 3	26	27
0 7 1	76	- 62	0 16 3	< 12	- 5
0 8 1	21	16	0 17 3	24	32
0 9 1	75	- 66	0 18 3	17	- 15
0 10 1	21	17	0 19 3	< 12	- 22
0 11 1	84	76	0 20 3	< 12	13
0 12 1	< 9	- 1	0 21 3	16	27
0 13 1	64	- 58	0 22 3	15	- 28
0 14 1	< 10	- 3	0 0 4	38	40
0 15 1	44	41	0 1 4	< 10	- 12
0 16 1	< 10	- 6	0 2 4	< 10	- 14
0 17 1	< 11	18	0 3 4	30	33
0 18 1	< 11	10	0 4 4	< 11	- 11
0 19 1	41	- 41	0 5 4	23	22
0 20 1	< 12	16	0 6 4	15	16
0 21 1	36	33	0 7 4	30	- 30
0 22 1	< 12	- 12	0 8 4	33	- 35
0 23 1	< 12	- 7	0 9 4	29	25
0 24 1	< 11	5	0 10 4	< 12	2
0 25 1	< 11	- 1	0 11 4	42	- 38
0 26 1	< 10	- 1	0 1 5	12	1
0 27 1	24	29	0 2 5	12	- 4
0 0 2	43	57	0 3 5	12	- 14
0 1 2	56	- 70	0 4 5	43	42
0 2 2	65	- 83			

EXPERIMENTAL. STRUCTURE ANALYSIS

The compound was prepared by mixing equivalent amounts of *p*-bromophenylhydrazine dissolved in alcohol and D-ribose in water at room temperature. Very small crystals elongated in the *c* direction were obtained. (010) is the predominant face. Only one isomer was observed.

Non-integrated Weissenberg diagrams of the *hk*0 and *0kl* zones were taken, using copper radiation ($\lambda = 1.542 \text{ \AA}$). The crystals are orthorhombic, with $a = 9.46 \text{ \AA}$, $b = 23.71 \text{ \AA}$, and $c = 5.78 \text{ \AA}$. The systematic absences show the space group to be $P2_12_12_1$. By flotation the density was found to be 1.63 g/cm^3 , corresponding to four (calc. 3.98) molecules $\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}_2\text{Br}$ in the unit cell. The diagrams were weak due to the smallness of the crystals. 199 *hk*0 reflexions and only 64 *0kl* were recorded with measurable intensities, the numbers attainable by copper radiation being 282 and 173, respectively. The intensities were estimated visually.

The structure was solved by the standard heavy atom procedure. However, the location of the atoms in the sugar part of the molecule was a matter of considerable difficulty because of overlap of atoms and ambiguity of molecular structure. A pyranose ring structure seemed to fit the first electron density maps quite well, but had finally to be abandoned in favour of the curved, open-chain structure described above. The *c* and *a* projections were refined by difference syntheses and least squares calculations to $R = 0.11$ and $R = 0.14$, respectively.

The anisotropy of the vibrations of the bromine atom was taken into account, whereas individual isotropic temperature factors were assigned to the light atoms. The direction of maximum vibration of the bromine atom is approximately perpendicular to the C—Br bond. No attempts to locate the hydrogen atoms were carried out. In Table 3 observed and calculated structure factors are compared.

Because of the low number of reflexions available the coordinates are inaccurate, especially in the *z* direction, but there should be no reason to doubt the general correctness of the structure. A rough estimate of the standard deviations may be obtained by considering the deviations from normal values in the stereochemically known part of the molecule, mainly the benzene ring. Standard deviations of $0.03\text{--}0.04 \text{ \AA}$ in the bond lengths and $3\text{--}4^\circ$ in the bond angles are indicated.

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