

## Crystal and Molecular Structure of the *p*-Bromophenylhydrazone of Arabinose

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The structure of the *p*-bromophenylhydrazone of arabinose in the crystalline state has been determined by X-ray crystallographic methods. It is shown that the sugar occurs in the pyranose ring form. The compound is therefore a N,N'-derivative of hydrazine, R-NH-NH-C<sub>6</sub>H<sub>4</sub>Br. The azimuthal angle in hydrazine is about 90°. The bond C(1)-N(1) connecting sugar and hydrazine appears to be significantly shorter than a normal C-N single bond. The arabinose is present in its  $\alpha$ -form, with conformation 1e2e3e4a.

The phenylhydrazone and phenylosazone derivatives were originally represented as open-chain compounds, but as they show mutarotation in many cases, other structures have to be considered. In the case of glucose at least two isomeric phenylhydrazones have been isolated. Several types of isomerism are possible, and it has been suggested that they are  $\alpha$ -/ $\beta$ -anomers, *syn*- and *anti*-forms, and cyclic-/acyclic isomers<sup>1,2</sup>. Mester<sup>2</sup> applied the formazan reaction to study these compounds. The phenylhydrazone can only yield a formazan when the sugar is present in its acyclic (aldehydo) form. It was found that one of the glucose isomers was acyclic, the others cyclic. Arabinose gave formazan in good yield<sup>3</sup> and its phenylhydrazone therefore probably occurs predominantly in the acyclic form in solution. These results were confirmed by Percival<sup>4</sup> who studied the ultraviolet spectra of the phenylhydrazones. She found that the phenylhydrazone of arabinose and a number of other sugars had absorption characteristics similar to those of the acyclic isomer of glucose. The available evidence thus indicates that acyclic structure is the predominant form of arabinose phenylhydrazone in solution. As for the *p*-bromoderivative, no information on the structure of the sugar in this compound was found in the literature.

We have now determined the structure of the *p*-bromophenylhydrazone of arabinose in the crystalline state, using the methods of X-ray crystallography. Details of the structure analysis are given below. Projections of the electron density in two directions have been calculated (Figs. 1 and 2), from which the positions of the atoms and the molecular structure (Fig. 3) were

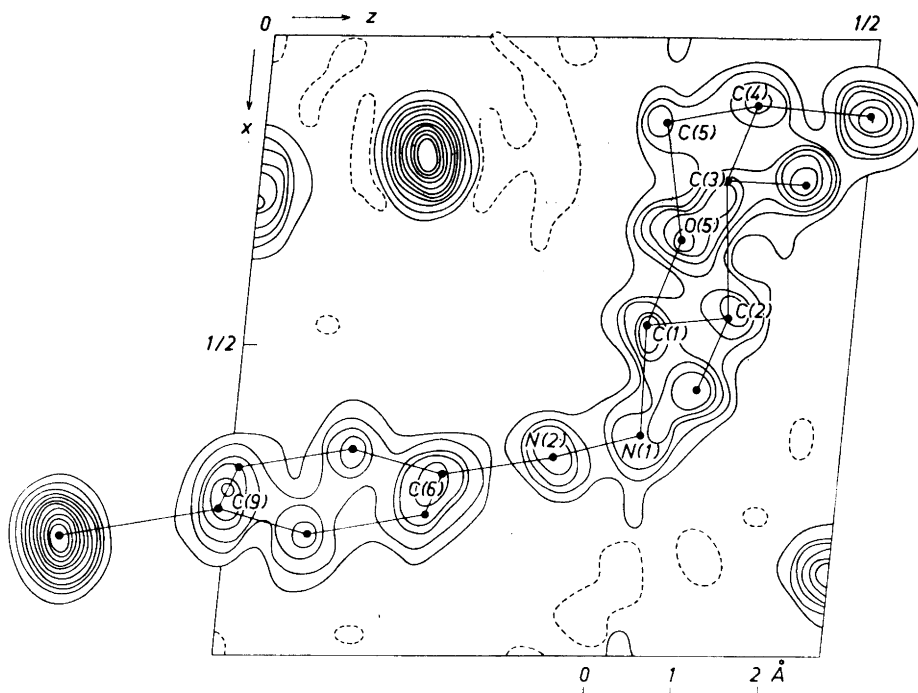


Fig. 1. Electron density projection in direction of  $b$  axis. Contours at intervals of  $5e \cdot \text{\AA}^{-2}$  for bromine,  $2e \cdot \text{\AA}^{-2}$  for the other atoms. The zero contour line is dotted.

determined. As is seen from the figures, the sugar has a cyclic structure, a somewhat unexpected result in view of the investigations referred to above. The compound accordingly should be represented as  $\text{R}-\text{NH}-\text{NH}-\text{C}_6\text{H}_4\text{Br}$ .

The sugar occurs in its normal pyranose chair form. The  $\text{C}(1)-\text{N}(1)$  bond is equatorial and the conformation is  $1e2e3e4a$ . The compound is therefore a derivative of  $\alpha$ -arabinose. The sugar itself crystallizes only in the  $\beta$ -form, with conformation  $1a2e3e4a$ . There are four possible pyranose structures of arabinose,  $1e2e3e4a \rightleftharpoons 1a2a3a4e$  ( $\alpha$ -arabinose) and  $1a2e3e4a \rightleftharpoons 1e2a3a4e$  ( $\beta$ -arabinose). According to the stability rules of Reeves<sup>5</sup>  $1e2e3e4a$  is the most stable of these structures. The mutarotation data, although difficult to interpret, also show that the  $\alpha$ -form predominates in the equilibrium mixture<sup>6</sup>. In addition, the reactivity of an equatorial hydroxyl group at  $\text{C}(1)$  is greater, in general, than that of an axial group. It is therefore to be expected that the reaction preferably gives a product in which arabinose has the  $1e2e3e4a$  conformation. Only one isomer of the compound is known, and we have also observed only one crystalline form in our experiments.

The bond lengths and bond angles derived from the final atomic coordinates are given in Table 2 and Fig. 3. No great accuracy can be claimed because of overlap of atoms, lack of centre of symmetry, and the presence of a heavy

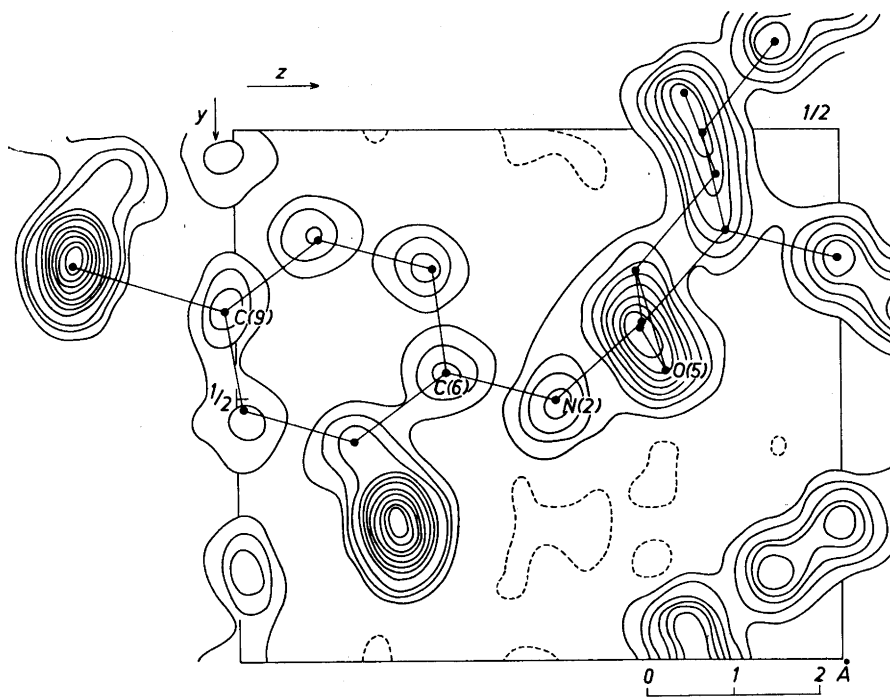


Fig. 2. Electron density projection in direction of *a* axis. Contours as in Fig. 1.

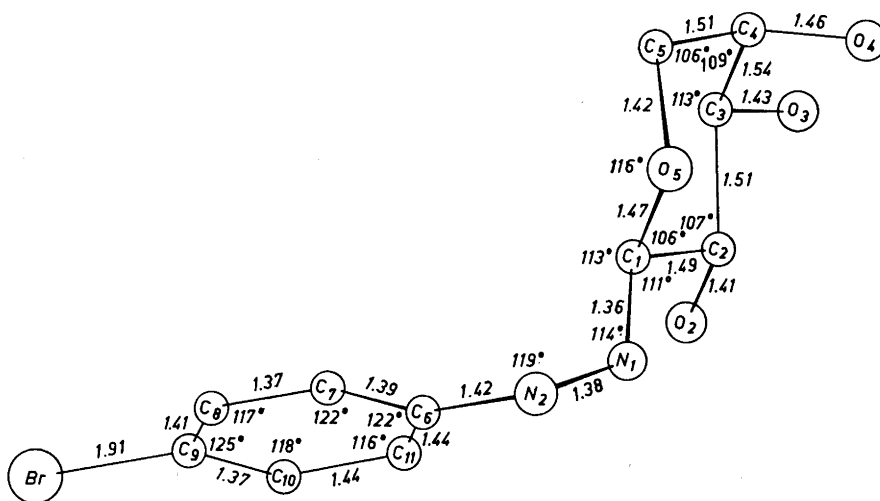


Fig. 3. The molecular structure of arabinose-*p*-bromophenylhydrazone. Bond lengths in Å units.

atom. The standard deviation is estimated to be about 0.02 Å for most distances and 1°–2° for the angles (see below).

The *hydrazine* part of the molecule exhibits some interesting features. The azimuthal angle between the planes N–N–C(6) and N–N–C(1) is close to 90°, in agreement with the calculations of Penny and Sutherland<sup>7</sup> who concluded that the only stable form of hydrazine is that in which the azimuth of one-half of the molecule with respect to the other is approximately 90°. In crystalline diformyl-<sup>8</sup> and diacetyl-hydrazine<sup>9</sup> this angle is 180°, in diacetyl-hydrazine monohydrate<sup>9</sup> 135°, whereas an eclipsed configuration is reported for crystalline hydrazine<sup>10</sup>. The influence of external forces upon the molecular structure is evidently of importance. Gaseous N,N'-dimethylhydrazine has been studied by electron diffraction<sup>11</sup>, but the relative position of the methyl groups with respect to each other could not be ascertained. The C–N and N–N bond lengths are all more or less short in the present investigation, the values found being 1.42 Å (N(2)–C(6)), 1.36 Å (N(1)–C(1)) and 1.38 Å (N(1)–N(2)). The N–N bond in hydrazine is 1.46 Å and a normal single bond C–N about 1.49 Å. The calculated standard deviations for the three bonds are in the order of 0.02 Å, but lack of resolution, especially of N(1) and C(1), makes it difficult to estimate whether the deviations are significant or not. We consider the shortening of N(2)–C(6) and N(1)–N(2) possibly significant and that of N(1)–C(1) probably significant. The latter bond connects sugar and hydrazine and is of interest, as in the usual acyclic formulae of sugar phenylhydrazones it is a double bond, whereas the cyclic formula established in the present work gives a single bond. It is noteworthy that the C(1)–O(1) bond in arabinose<sup>12</sup> and other sugars<sup>13</sup> is found to be considerably shorter (1.38 Å) than normal C–O bonds in sugars (1.43 Å). The angles N–N–C(1) and N–N–C(6) are found to be 114° and 119°, respectively.

The dimensions of hydrazine derived in the present work resemble those found in diacetyl-hydrazine, in which there is a significant shortening of both the N–N bond (1.396 Å) and the C–N bond (1.341 Å) due to conjugation effects. In view of the neighbouring benzene ring a similar effect might possibly to a small extent be present also in the phenylhydrazones.

In the *sugar* part of the molecule the only significant deviation from normal molecular dimensions (1.43 Å for C–O, 1.53 Å for C–C and 110° for the angles) occurs in the angle at the ring oxygen atom O(5), which is found to be 116°. In crystalline arabinose<sup>12</sup> this angle is reported to be 113°, in  $\alpha$ -rhamnose<sup>13</sup> 120°.

In the *aromatic* part of the molecule the mean C–C distance is 1.40 Å, and all the ring atoms as well as N(2) and the bromine atom lie in the same plane within the limits of error. This plane forms an angle of about 20° with the plane N–N–C(6). The length of the C–Br bond is 1.91 Å, close to the value found in, *e.g.*, tetrabromobenzene<sup>14</sup>, where the mean C–Br distance is 1.896 Å. The ring angle at C(9), the carbon atom to which bromine is attached, is possibly significantly greater than 120°. It is interesting to note that this angle is found to be slightly greater than 120° in many cases, such as tetrabromobenzene<sup>14</sup> (122°) and *p*-dichlorobenzene<sup>15</sup> (121°30'). This indicates that the effect possibly is real.

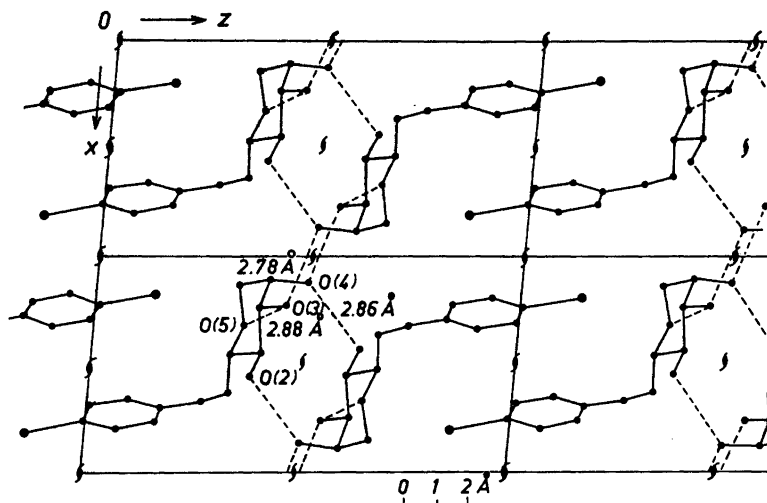


Fig. 4. The  $b$  projection of the structure. Broken lines indicate hydrogen bonds.

The arrangement of the molecules in the crystal is shown in Fig. 4. Only three intermolecular distances, all involving the oxygen atoms of the sugar, are shorter than 3.2 Å. As there are three hydroxyl hydrogens in the molecule, these interactions are likely to be hydrogen bonds. The atom O(3) is linked to O(5) and O(4) in different molecules by bonds of lengths 2.88 Å and 2.78 Å, respectively. A third bond (2.86 Å) connects O(2) and O(4) in neighbouring molecules, the arabinose residues being linked together in layers parallel to the  $xy$ -plane. The nitrogen atoms of the hydrazine are not engaged in hydrogen bond formation, apart from a possible weak intramolecular interaction between N(1) and O(2).

#### EXPERIMENTAL. STRUCTURE ANALYSIS

The compound was prepared by mixing equivalent amounts of *p*-bromophenylhydrazine and  $\beta$ -D-arabinose at room temperature. Acetic acid or 60% alcohol was used as solvent. In both cases thin long needles melting at 155°–160°C were obtained. The needle axis corresponds to the crystallographic  $b$  axis.

X-Ray single crystal diagrams of the Weissenberg type were taken around the  $a$  and  $b$  axes, using copper radiation ( $\lambda = 1.542$  Å). Small crystals of cross-section about  $0.1 \times 0.2$  mm were used. The diagrams showed that the crystals are monoclinic, with unit cell dimensions  $a = 7.12$  Å,  $b = 6.15$  Å,  $c = 14.09$  Å and  $\beta = 96^\circ$  (all  $\pm 0.5\%$ ). The only systematic absences occur in the  $0k0$  reflexions for odd values of  $k$ . The space group is  $P2_1$ . The density, measured in a carbon tetrachloride-bromoform mixture, was 1.70 g/cm<sup>3</sup>, giving two (calc. 1.97) molecules of C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Br in the unit cell.

The reflexions were recorded on an integrating Weissenberg camera and their intensities measured by a Hilger & Watts photometer. 208 of the 282  $h0l$  reflexions and 105 of the 122  $0kl$  reflexions obtainable with copper radiation were recorded with measurable intensities. Corrections for absorption and extinction were not applied.

The structure was solved by the standard heavy atom technique.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>hot</sub>	Atom	<i>x</i>	<i>z</i>
Br	0.189	0.756	0.1348	2.8	H(1)	0.484	0.257
O(2)	0.566	0.951	0.3698	3.0	H(2)	0.480	0.460
O(3)	0.226	0.860	0.4461	1.9	H(3)	0.250	0.319
O(4)	0.133	0.290	0.4993	1.7	H(4)	0.970	0.398
O(5)	0.327	0.467	0.3521	2.4	H(5)	0.052	0.351
N(1)	0.645	0.377	0.3334	2.0	H(5)'	0.157	0.273
N(2)	0.676	0.532	0.2655	2.2	H(7)	0.603	0.114
C(1)	0.464	0.302	0.3280	2.1	H(8)	0.320	0.057
C(2)	0.448	0.120	0.3965	1.8	H(10)	0.863	0.046
C(3)	0.247	0.041	0.3839	2.3	H(11)	0.787	0.220
C(4)	0.104	0.221	0.4000	2.2	H(N(1))	0.652	0.387
C(5)	0.134	0.409	0.3342	2.3	H(N(2))	0.596	0.262
C(6)	0.703	0.464	0.1714	1.5	H(O(2))	0.677	0.417
C(7)	0.673	0.608	0.0957	3.2	H(O(3))	0.270	0.410
C(8)	0.704	0.550	0.0050	2.9	H(O(4))	0.981	0.480
C(9)	0.233	0.836	0.0078	1.9			
C(10)	0.801	0.185	0.0634	2.3			
C(11)	0.764	0.244	0.1587	2.3			

The *b* projection was first determined. The position of the bromine atom was derived from the Patterson synthesis, and the electron density map based on the corresponding signs clearly showed where the benzene ring and the nitrogen atoms had to be placed. The location of the atoms of the arabinose caused considerable difficulties because of overlap of atoms and ambiguity of molecular structure. Several possibilities were tried,

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

Bond lengths		Bond angles	
C(9)–Br	1.91	Br–C(9)–C(8)	116°
C(9)–C(8)	1.41	C(9)–C(8)–C(7)	117°
C(8)–C(7)	1.37	C(8)–C(7)–C(6)	122°
C(7)–C(6)	1.39	C(7)–C(6)–C(11)	122°
C(6)–C(11)	1.44	C(6)–C(11)–C(10)	116°
C(11)–C(10)	1.44	C(11)–C(10)–C(9)	118°
C(10)–C(9)	1.37	C(10)–C(9)–C(8)	125°
C(6)–N(2)	1.42	Br–C(9)–C(10)	119°
N(2)–N(1)	1.38	C(7)–C(6)–N(2)	120°
N(1)–C(1)	1.36	C(11)–C(6)–N(2)	118°
C(1)–C(2)	1.49	C(6)–N(2)–N(1)	119°
C(2)–C(3)	1.51	N(2)–N(1)–C(1)	114°
C(3)–C(4)	1.54	N(1)–C(1)–C(2)	111°
C(4)–C(5)	1.51	N(1)–C(1)–O(5)	113°
C(5)–O(5)	1.42	C(1)–C(2)–C(3)	107°
C(1)–O(5)	1.47	C(2)–C(3)–C(4)	113°
C(2)–O(2)	1.41	C(3)–C(4)–C(5)	109°
C(3)–O(3)	1.43	C(4)–C(5)–O(5)	106°
C(4)–O(4)	1.46	C(5)–O(5)–C(1)	116°
		O(5)–C(1)–C(2)	106°
		C(1)–C(2)–O(2)	107°
		C(3)–C(2)–O(2)	108°
		C(2)–C(3)–O(3)	110°
		C(4)–C(3)–O(3)	111°
		C(3)–C(4)–O(4)	109°
		C(5)–C(4)–O(4)	111°

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

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
00 2	18	12	20 - 9	15	15
00 3	7	1	20 - 8	9	- 9
00 4	87	- 84	20 - 7	52	- 52
00 5	13	- 14	20 - 6	52	- 52
00 6	47	47	20 - 5	25	- 26
00 7	30	28	20 - 4	16	16
00 8	53	49	20 - 3	52	59
00 9	6	5	20 - 2	7	5
00 10	21	- 21	20 - 1	8	11
00 11	22	- 21	20 0	88	-101
00 12	< 6	- 2	20 1	99	-108
00 13	< 6	2	20 2	33	- 30
00 14	15	15	20 3	12	9
00 15	24	25	20 4	29	29
00 16	12	11	20 5	38	34
00 17	10	- 8	20 6	13	13
10 -17	16	13	20 7	25	23
10 -16	23	24	20 8	30	- 29
10 -15	5	6	20 9	29	- 27
10 -14	< 6	- 2	20 10	< 6	2
10 -13	28	- 28	20 11	< 6	2
10 -12	23	- 23	20 12	11	10
10 -11	10	- 9	20 13	< 6	3
10 -10	34	34	20 14	7	- 7
10 -9	33	33	20 15	10	- 9
10 -8	21	18	20 16	18	- 19
10 -7	6	5	30 -17	6	- 5
10 -6	31	- 34	30 -16	21	- 19
10 -5	55	- 55	30 -15	15	- 16
10 -4	18	- 22	30 -14	18	- 16
10 -3	2	- 1	30 -13	15	15
10 -2	11	18	30 -12	17	16
10 -1	42	43	30 -11	31	30
10 0	12	- 3	30 -10	< 6	1
10 1	12	- 16	30 -9	22	- 21
10 2	40	32	30 -8	19	- 19
10 3	96	- 96	30 -7	19	- 18
10 4	33	25	30 -6	< 5	0
10 5	26	28	30 -5	26	27
10 6	40	37	30 -4	31	34
10 7	33	29	30 -3	24	25
10 8	4	2	30 -2	16	- 11
10 9	38	- 35	30 -1	13	- 19
10 10	35	- 33	30 0	36	- 36
10 11	30	- 28	30 1	6	- 3
10 12	9	8	30 2	21	- 19
10 13	23	23	30 3	55	55
10 14	19	21	30 4	23	20
10 15	5	4	30 5	9	9
10 16	12	- 11	30 6	21	- 20
10 17	11	- 13	30 7	29	- 26
20 -17	11	10	30 8	23	- 22
20 -16	< 5	4	30 9	19	17
20 -15	12	- 12	30 10	16	14
20 -14	26	- 27	30 11	35	35
20 -13	14	- 13	30 12	16	17
20 -12	< 6	0	30 13	18	- 20
20 -11	10	8	30 14	8	- 8
20 -10	37	37	30 15	13	- 14

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
30 16	< 4	— 5	60 -14	9	10
40 -16	16	— 15	60 -13	26	— 22
40 -15	< 5	1	60 -12	5	2
40 -14	12	10	60 -11	5	— 5
40 -13	21	20	60 -10	6	— 5
40 -12	< 6	5	60 -9	23	21
40 -11	6	6	60 -8	16	15
40 -10	29	— 27	60 -7	< 6	— 2
40 -9	18	— 17	60 -6	8	— 9
40 -8	23	— 21	60 -5	25	— 25
40 -7	26	24	60 -4	21	— 19
40 -6	40	39	60 -3	< 6	— 3
40 -5	37	35	60 -2	13	12
40 -4	12	12	60 -1	13	14
40 -3	17	— 16	60 0	13	12
40 -2	28	— 30	60 1	8	6
40 -1	19	— 16	60 2	26	— 26
40 0	< 5	3	60 3	10	— 9
40 1	46	44	60 4	5	6
40 2	39	39	60 5	14	— 14
40 3	7	6	60 6	17	17
40 4	13	— 11	60 7	< 6	3
40 5	< 5	1	60 8	< 5	— 2
40 6	37	— 37	60 9	< 5	— 5
40 7	11	10	60 10	8	— 8
40 8	11	10	60 11	8	— 8
40 9	15	14	70 -11	4	1
40 10	16	14	70 -10	23	20
40 11	9	10	70 -9	< 5	3
40 12	11	— 11	70 -8	< 5	4
40 13	8	9	70 -7	7	— 8
40 14	7	— 7	70 -6	6	— 7
40 15	< 3	— 2	70 -5	14	— 13
50 -14	17	16	70 -4	5	3
50 -13	18	16	50 -3	5	5
50 -12	17	— 17	70 -2	9	10
50 -11	16	— 14	70 -1	< 6	— 2
50 -10	19	— 18	70 0	< 6	— 4
50 -9	5	— 6	70 1	11	— 11
50 -8	10	9	70 2	9	— 8
50 -7	21	20	70 3	< 6	— 1
50 -6	< 6	4	70 4	< 6	5
50 -5	10	9	70 5	15	16
50 -4	18	— 18	70 6	10	9
50 -3	21	— 21	70 7	8	— 7
50 -2	11	— 12	70 8	< 4	2
50 -1	17	16	70 9	11	— 12
50 0	12	11	80 -9	< 4	— 0
50 1	19	18	80 -8	10	— 8
50 2	16	17	80 -7	8	— 7
50 3	18	— 18	80 -6	< 5	1
50 4	19	— 20	80 -5	< 5	2
50 5	24	— 21	80 -4	17	16
50 6	< 6	— 2	80 -3	< 5	— 1
50 7	16	15	80 -2	10	9
50 8	10	8	80 -1	10	— 11
50 9	13	14	80 0	9	— 9
50 10	11	— 11	80 1	6	— 6
50 11	12	— 13	80 2	< 5	— 1
50 12	13	— 15	80 3	7	7
50 13	< 4	— 3	80 4	< 4	4



ARABINOSE *p*-BROMOPHENYLHYDRAZONE

1547

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
80 5	< 5	0	02 7	33	34
90 - 3	5	5	03 7	4	4
90 - 2	3	- 3	04 7	18	17
90 - 1	6	- 6	05 7	7	8
90 0	11	11	06 7	4	8
90 1	7	- 7	00 8	51	48
01 0	0	0	01 8	19	18
02 0	48	45	02 8	17	16
03 0	0	0	03 8	10	12
04 0	23	23	04 8	18	23
05 0	0	0	05 8	3	3
06 0	7	6	06 8	8	7
07 0	0	0	00 9	5	6
01 1	31	28	01 9	36	35
02 1	43	43	02 9	17	15
03 1	21	23	03 9	16	19
04 1	15	13	04 9	12	11
05 1	8	6	05 9	8	8
06 1	5	4	06 9	1	3
07 1	2	2	00 10	20	20
00 2	15	13	01 10	25	23
01 2	77	79	02 10	20	16
02 2	24	19	03 10	18	19
03 2	16	21	04 10	8	10
04 2	9	13	05 10	6	6
05 2	7	11	06 10	1	1
06 2	4	3	00 11	21	19
07 2	4	6	01 11	18	15
00 3	7	0	02 11	37	38
01 3	46	40	03 11	5	6
02 3	73	64	04 11	11	11
03 3	19	12	05 11	2	3
04 3	26	21	06 11	6	6
05 3	5	6	00 12	5	3
06 3	7	8	01 12	13	11
07 3	4	4	02 12	10	10
00 4	79	88	03 12	12	11
01 4	40	40	04 12	7	8
02 4	22	25	05 12	6	6
03 4	19	12	00 13	3	2
04 4	24	24	01 13	29	30
05 4	6	7	02 13	3	4
06 4	9	12	03 13	12	12
07 4	1	0	04 13	4	3
00 5	12	12	05 13	4	6
01 5	20	20	00 14	14	15
02 5	37	32	01 14	9	9
03 5	39	38	02 14	15	13
04 5	8	7	03 14	12	13
05 5	9	7	04 14	9	9
06 5	4	4	00 15	23	21
07 5	3	4	01 15	5	5
00 6	43	47	02 15	14	15
01 6	55	55	03 15	1	3
02 6	40	38	04 15	3	5
03 6	19	18	00 16	10	10
04 6	13	12	01 16	10	11
05 6	8	7	02 16	6	7
06 6	7	7	03 16	7	8
07 6	3	3	00 17	7	7
00 7	26	27	01 17	19	17
01 7	26	25			

using the agreement factor  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  as a criterion. A ring structure gave the lowest  $R$  value ( $R = 0.23$ ). This structure was refined, first by difference syntheses ( $R = 0.17$ ), then by least squares calculations ( $R = 0.10$ ) and finally by two more difference syntheses ( $R = 0.08$ ). In the course of the refinement the contributions from the 15 hydrogen atoms were included, their positions being derived partly from the difference syntheses, partly by stereochemical considerations. Isotropic temperature factors  $\exp(-B \sin^2\theta/\lambda^2)$  with  $B$ -values between 1.5 and 3.2 were applied to the lighter atoms whereas for bromine  $B = 1.5 + 2.9 \cos^2\varphi$ ,  $\varphi$  being the angle between the normal to the reflecting plane and the direction of maximum vibration. This direction is approximately perpendicular to the Br—C(9) bond. The atomic scattering factors of Hartree (for bromine) and Berghuis *et al.*<sup>16</sup> (for the lighter atoms) were used.

In the  $a$  projection, which has no centre of symmetry, the first trial structure was derived from the  $b$  projection and approximately known bond lengths and angles. The structure was first refined by trial, and then by least squares calculations. Four of the atoms, N(1), C(1), O(5) and C(2), lie so close together in this projection that their positions cannot be refined effectively. The final  $y$  coordinates of these atoms were derived by trial and are less accurate than those of the other atoms. The final value of  $R$  was 0.10. The contributions from the hydrogen atoms were not included in this projection. The value used for  $B$  was 2.3 for the oxygens, 2.6 for the nitrogens, 2.7 for aliphatic carbons, 3.0 for aromatic carbons, and 3.8 for bromine, the latter being the mean value of the anisotropic factor. In Table 3 observed ( $F_o$ ) and calculated ( $F_c$ ) values for the structure factors are compared. The final coordinates are given in Table 1, and the corresponding bond lengths and angles in Table 2. The  $z$  coordinates are those derived from the  $b$  projection.

The standard deviations of the atomic coordinates were estimated by the Cruickshank formula<sup>17</sup>. The following values were found:  $\sigma(x) = \sigma(z) = 0.012 \text{ \AA}$ ,  $\sigma(y) = 0.035 \text{ \AA}$  for the carbon and nitrogen atoms;  $\sigma(x) = \sigma(z) = 0.009 \text{ \AA}$ ,  $\sigma(y) = 0.025 \text{ \AA}$  for the oxygen atoms. For  $\sigma(y)$  the lack of centre of symmetry is taken into account by multiplication by 2. The standard deviations in the bond lengths (apart from C—Br) vary between 0.015  $\text{\AA}$  (for C(4)—O(4)) and about 0.04  $\text{\AA}$  (for C(6)—C(11) and C(8)—C(9)). If three times the probable error is taken as a limit of error, the corresponding values for this quantity are 0.03  $\text{\AA}$  and 0.08  $\text{\AA}$ . For unresolved atoms the error may be even greater, but for all bonds of known length, such as the C—C bonds, the values derived lie well within those limits. The standard deviation of the angles lies in the range 1.0°—2.3°.

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