Crystal and Molecular Structure of

D-β-Glucose-p-bromo-phenylhydrazone

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The crystal and molecular structure of D-glucose-p-bromo-phenyl-hydrazone has been determined by two-dimensional X-ray crystallo-graphic methods. The sugar component occurs in the pyranose chair conformation, the compound thus being a hydrazide. The structure is quite similar to the analogous arabinose derivative. The glucose is present in its β-form with conformation 1e2e3e4e5e. The azimutal angle in hydrazine is about 100°. The compound shows mutarotation in pyridine.

A considerable amount of work has been done on the phenylhydrazones of various sugars. In the case of glucose not less than three different phenylhydrazones have been isolated, and chemical [1,2] and physical [3] evidence indicate the existence of both cyclic as well as acyclic forms. It has further been pointed out that the mutarotation performed by acyclic phenylhydrazones may be due to a rearrangement from the hydrazo- to the azo form.[4]

In connection with the studies of sugar phenylhydrazones carried out at this laboratory [5-7] we have determined the structure of D-glucose-p-bromo-phenylhydrazone in the crystalline state by X-ray methods.
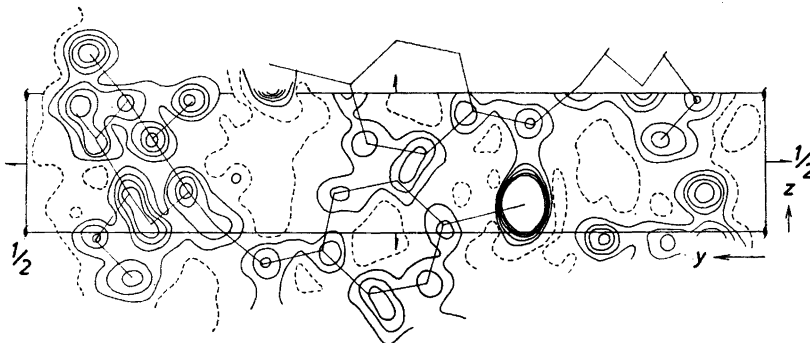

Fig. 1. Electron density projection in the direction of the *a* axis. Contours at 1, 3, 5, . . . e·Å⁻², the first one being broken. Only a few contours are drawn for the bromine atom.

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The usual method for the preparation of sugar phenylhydrazones applied in this work yielded one derivative of p-bromo-phenylhydrazone of D-glucose only.
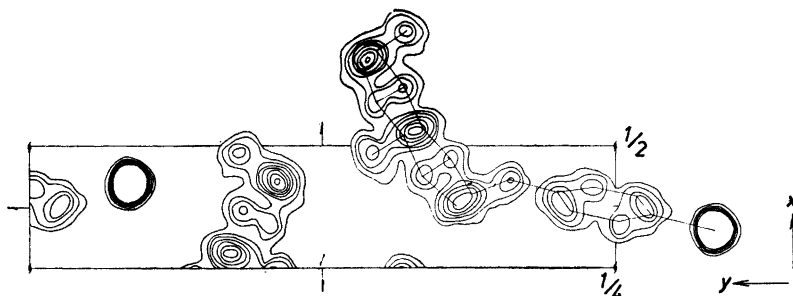

Fig. 2. Electron density projection in the direction of the c axis. Contours at 3, 5, 7, ... e·Å^{-2}.

Two-dimensional electron density maps projected along the a and c axes have been calculated (Figs. 1 and 2) and from these maps the positions of the atoms and thus the structure of the molecule were determined. The coordinates of the atoms in the two projections, and the temperature factor data collected in Table 1 were derived from difference maps and least squares calculations. The corresponding bond lengths and valence angles are given in Table 2. The reliability factor, R is a little less than 0.11 for the two zones. The standard deviations calculated by means of the Cruickshank formula [8] are about 0.03 Å
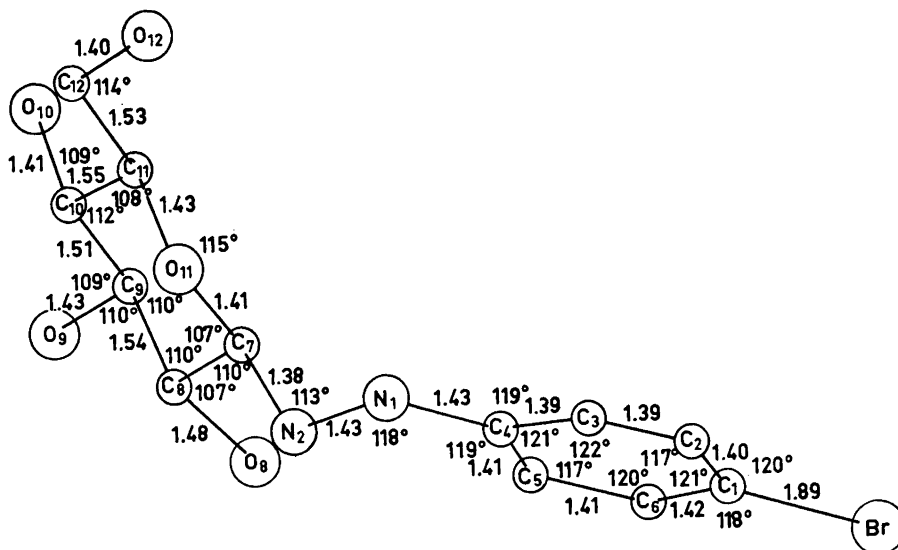

Fig. 3. The structure of the β-D-glucose-p-bromo-phenylhydrazide molecule.

Table 1. Coordinates, in fractions of the unit cell axes, and the temperature parameters.

	x	y	z	$B(hk0)$	$B(0kl)$
Br	0.153	0.1641	0.351	4.3[a]	3.6[b]
N_1	0.361	0.3413	0.137	5.0	3.5
N_2	0.298	0.3732	0.280	4.5	3.5
O_8	0.250	0.3868	0.721	4.3	3.5
O_9	0.463	0.4585	0.890	2.0	2.0
O_{10}	0.847	0.4663	0.702	3.0	3.0
O_{11}	0.570	0.4164	0.275	3.0	3.0
O_{12}	0.974	0.4280	0.080	4.9	4.9
C_1	0.221	0.2188	0.283	4.3	3.5
C_2	0.283	0.2288	0.074	4.5	3.5
C_3	0.316	0.2700	0.029	4.3	3.5
C_4	0.305	0.3000	0.187	3.5	3.5
C_5	0.228	0.2911	0.394	3.5	3.5
C_6	0.175	0.2500	0.437	3.5	3.5
C_7	0.449	0.3900	0.398	3.5	3.0
C_8	0.368	0.4151	0.587	3.0	3.0
C_9	0.537	0.4317	0.725	2.5	2.5
C_{10}	0.678	0.4555	0.584	2.5	2.5
C_{11}	0.742	0.4304	0.383	2.5	2.5
C_{12}	0.872	0.4536	0.222	2.2	2.5
H_2	0.30	0.207	−0.03	3.0	3.0
H_3	0.38	0.277	−0.13	3.0	3.0
H_5	0.20	0.314	0.51	3.0	3.0
H_6	0.12	0.243	0.60	3.0	3.0
H_7	0.50	0.363	0.43	3.0	3.0
H_8	0.32	0.442	0.56	3.0	3.0
H_9	0.58	0.406	0.76	3.0	3.0
H_{10}	0.63	0.480	0.55	3.0	3.0
H_{11}	0.79	0.403	0.41	3.0	3.0
H_{12}	0.97	0.472	0.28	3.0	3.0
H_{13}	0.78	0.469	0.15	3.0	3.0
H_{21}	0.50	0.339	0.15	3.0	3.0
H_{22}	0.17	0.392	0.20	3.0	3.0
H_{38}	0.29	0.373	0.86	3.0	3.0
H_{39}	0.49	0.444	1.02	3.0	3.0
H_{40}	0.88	0.492	0.67	3.0	3.0
H_{42}	0.94	0.441	−0.05	3.0	3.0

Anisotropy parameters:

[a] 0.00062, −0.00112, 0.04679
[b] 0.02196, −0.00152, 0.00078

for most of the bond lengths and 2—3° for the angles. A drawing of the molecule with the bond lengths and angles is given in Fig. 3.

As may be seen from the electron density maps the sugar has a cyclic structure. The compound should accordingly be represented as a hydrazide, $R-NH-NH-C_6H_4Br$. The conformation of the sugar is the well known pyranose chair form with all the substituents in equatorial positions; hence glucose occurs in its β-form. This seems to be in accordance with the mutarotation of the compound in pyridine where the rotational power changes in the direction of more dextro rotation.

Table 2. Bond lengths (Å) and angles (°) in D-glucose-p-bromophenylhydrazone.

Bonds		Angles	
$Br-C$	1.89	$Br-C_1-C_2$	120
C_1-C_2	1.40	$Br-C_1-C_6$	118
C_2-C_3	1.39	$C_2-C_1-C_6$	121
C_3-C_4	1.39	$C_1-C_2-C_3$	117
C_4-C_5	1.41	$C_2-C_3-C_4$	122
C_5-C_6	1.41	$C_3-C_4-C_5$	121
C_6-C_1	1.42	$C_4-C_5-C_6$	117
C_4-N_1	1.43	$C_5-C_6-C_1$	120
N_1-N_2	1.43	$C_3-C_4-N_1$	119
N_2-C_7	1.38	$C_5-C_4-N_1$	119
C_7-C_8	1.53	$C_4-N_1-N_2$	118
C_8-O_8	1.48	$N_1-N_2-C_7$	113
C_8-C_9	1.54	$N_2-C_7-O_{11}$	113
C_9-O_9	1.43	$N_2-C_7-C_8$	110
C_9-C_{10}	1.51	$C_7-C_8-C_9$	110
$C_{10}-O_{10}$	1.41	$C_7-C_8-O_8$	107
$C_{10}-C_{11}$	1.55	$O_8-C_8-C_9$	108
$C_{11}-C_{12}$	1.53	$C_8-C_9-C_{10}$	110
$C_{12}-O_{12}$	1.40	$C_8-C_9-O_9$	110
$C_{11}-O_{11}$	1.43	$O_9-C_9-C_{10}$	109
$O_{11}-C_7$	1.41	$C_9-C_{10}-C_{11}$	112
		$C_9-C_{10}-O_{10}$	110
		$O_{10}-C_{10}-C_{11}$	109
		$C_{10}-C_{11}-O_{11}$	108
		$C_{10}-C_{11}-C_{12}$	115
		$C_{12}-C_{11}-O_{11}$	109
		$C_{11}-C_{12}-O_{12}$	114
		$C_{11}-O_{11}-C_7$	115
		$O_{11}-C_7-C_8$	107

The C—C distances in the sugar are close to normal (mean value 1.53 Å). It is interesting to note the difference between the two C—O distances in the ring, the C_7-O_{11} distance being slightly shorter than the $C_{11}-O_{11}$ distance. Even if this difference is far too small to be significant in the present structure determination, this feature is observed in a number of pyranose structures, and the difference in the two bond lengths is found to be significant at least in the structure of sucrose.[9]

The C—(OH) distances are all close to the normal value of 1.43 Å. The mean value of the angles in the sugar component of this molecule is 110°. The only two angles which differ from this in a probably significant way are the angle at the ring oxygen ($C_{11}-O_{11}-C_7$) and the angle at C_{11} ($C_{10}-C_{11}-C_{12}$) which both are 115°. This is in accordance with what is found in β-D-glucose [10] where the corresponding angles are reported to be 113° and 115°, respectively. It also agrees with the findings in the analogous arabinose derivative where the angle at the ring oxygen is reported to be 116°.

In the hydrazine part of the molecule the azimuthal angle is found to be approximately 100°. The bond lengths in this region seems to be somewhat short compared with the normal C—N bond (1.47 Å) and N—N bond (1.46 Å) even if the estimated standard deviations prevent any conclusions. Again this part of the structure resembles the corresponding part of the arabinose-
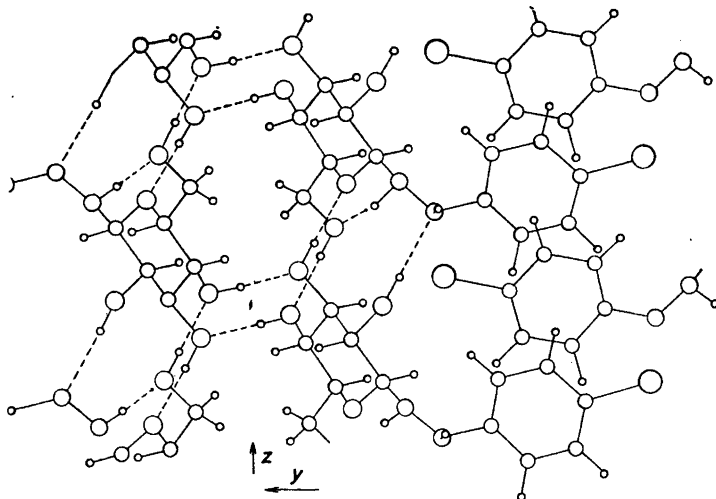
Fig. 4. The arrangement of the molecules in the crystal. Hydrogen bonds are indicated by broken lines.

p-bromo-phenylhydrazone molecule although the N—N bond in the present structure is more normal.

The aromatic part of the compound shows a mean C—C distance of 1.40 Å. All the angles are close to 120° and the atoms are coplanar within the limits of error. This plane makes an angle of about 20° with the C_2—N_1—C_6 plane.

The Br—C distance of 1.89 Å is close to those reported for other compounds such as tetrabromobenzene.[11]

Table 3. The hydrogen bonds.

Distances (Å):

O_8—(H_{38})—N_1'	3.06
O_9—(H_{39})—O_{11}'	2.84
O_{10}—(H_{40})—O_9''	2.65
O_{12}'—(H_{42}')—O_{10}	2.79
N_2'—(H_{22}')—O_{12}'''	3.09

Angles (°):

C_8—O_8—N_1'	129
C_9—O_9—O_{11}'	102
C_{10}—O_{10}—O_9''	125
C_{12}'—O_{12}'—O_{10}	125
N_1'—N_2'—O_{12}'''	110
C_7'—N_2'—O_{12}'''	125

C_4'—N_1'—O_8	125
N_2'—N_1'—O_8	113
C_9—O_9—O_{10}''	121
C_{11}'—O_{11}'—O_9	116
C_7'—O_{11}'—O_9	125

Table 4. Observed (F_o) and calculated (F_c) structure factors for D-glucose-p-bromophenylhydrazone. The signs of the F_c refer to origin at $x = 1/2$, $y = 3/4$ in the $hk0$ projection, and at $y = 0$, $z = 1/4$ in the $0kl$ projection.

$l = 0$				$h\ k$	F_o	F_c
$h\ k$		F_o	F_c			
				2 13	36	−30
1 1		7	5	2 14	14	−10
1 2		40	−43	2 15	100	−92
1 3		65	57	2 16	25	18
1 4		16	12	2 17	14	− 9
1 5		58	−51	2 18	39	38
1 6		99	−97	2 19	49	46
1 7		71	−66	2 20	< 8	− 7
1 8		125	124	2 21	50	49
1 9		32	27	2 22	17	−20
1 10		83	85	2 23	8	9
1 11		51	50	2 24	15	−14
1 12		52	−53	2 25	49	−48
1 13		35	40	2 26	< 9	− 6
1 14		98	−90	2 27	30	−30
1 15		< 6	− 4	2 28	17	18
1 16		53	−47	2 29	< 9	− 1
1 17		29	−23	2 30	11	11
1 18		10	17	2 31	28	32
1 19		30	−31	2 32	< 8	− 4
1 20		30	30	2 33	22	23
1 21		24	21	2 34	9	− 5
1 22		42	39	2 35	< 9	− 1
1 23		30	30	2 36	< 8	− 8
1 24		< 8	− 4	2 37	18	−18
1 25		17	15	2 38	< 7	1
1 26		25	−19	2 39	12	−14
1 27		7	11	2 40	< 5	0
1 28		13	−14	3 1	55	−55
1 29		20	−24	3 2	53	−45
1 30		11	9	3 3	11	11
1 31		<7	−5	3 4	< 6	− 4
1 32		32	35	3 5	35	36
1 33		12	12	3 6	15	13
1 34		<10	6	3 7	75	79
1 35		12	15	3 8	< 5	4
1 36		11	−14	3 9	31	−37
1 37		< 8	5	3 10	19	16
1 38		17	−15	3 11	47	−46
1 39		< 7	− 5	3 12	8	11
1 40		12	−14	3 13	62	−61
2 0		126	−114	3 14	6	5
2 1		119	−120	3 15	< 7	− 7
2 2		117	−116	3 16	14	7
2 3		106	−112	3 17	65	66
2 4		13	−13	3 18	< 8	− 3
2 5		61	−62	3 19	15	14
2 6		44	38	3 20	8	13
2 7		63	66	3 21	14	−17
2 8		39	−39	3 22	10	12
2 9		91	93	3 23	50	−51
2 10		< 6	− 6	3 24	11	−10
2 11		11	−10	3 25	25	−25
2 12		15	20	3 26	18	−19

h k	F_o	F_c	h k	F_o	F_c
3 27	< 7	− 5	5 9	19	−16
3 28	7	− 9	5 10	< 8	7
3 29	16	13	5 11	9	12
3 30	< 8	2	5 12	23	−22
3 31	13	13	5 13	16	20
3 32	< 9	− 2	5 14	9	9
3 33	19	−19	5 15	18	−20
3 34	< 8	5	5 16	50	58
3 35	18	−20	5 17	< 8	4
3 36	< 7	− 1	5 18	35	−35
3 37	10	−13	5 19	< 8	− 1
3 38	< 6	− 4	5 20	29	−26
3 39	10	10	5 21	< 8	6
4 0	25	−25	5 22	10	−18
4 1	33	28	5 23	7	12
4 2	15	−14	5 24	9	8
4 3	61	61	5 25	8	4
4 4	14	16	5 26	22	29
4 5	18	15	5 27	11	10
4 6	66	72	5 28	6	8
4 7	25	−21	5 29	< 6	4
4 8	15	18	5 30	< 6	3
4 9	29	−27	5 31	< 6	10
4 10	48	−47	5 32	12	−16
4 11	18	−21	5 33	< 6	0
4 12	58	−59	5 34	< 6	− 8
4 13	39	41	6 0	35	38
4 14	29	−30	6 1	14	15
4 15	23	23	6 2	16	13
4 16	47	45	6 3	10	12
4 17	< 8	− 4	6 4	< 8	− 2
4 18	19	17	6 5	< 8	7
4 19	< 8	− 2	6 6	33	−39
4 20	10	− 9	6 7	< 8	− 2
4 21	30	−32	6 8	8	−13
4 22	< 8	− 7	6 9	31	−31
4 23	< 8	− 4	6 10	35	39
4 24	33	−36	6 11	< 8	− 9
4 25	20	19	6 12	23	23
4 26	< 8	− 5	6 13	25	24
4 27	21	25	6 14	14	18
4 28	28	31	6 15	15	17
4 29	< 8	− 4	6 16	16	−19
4 30	8	10	6 17	< 8	− 2
4 31	18	−24	6 18	13	−16
4 32	< 7	− 2	6 19	10	−10
4 33	< 7	− 5	6 20	< 8	3
4 34	10	−10	6 21	8	−10
4 35	< 7	− 6	6 22	9	10
4 36	12	−17	6 23	< 7	− 3
5 1	< 8	− 1	6 24	16	22
5 2	36	41	6 25	12	10
5 3	< 8	2	6 26	< 7	1
5 4	37	33	6 27	9	10
5 5	< 8	−10	6 28	8	−15
5 6	< 8	0	6 29	< 6	− 2
5 7	< 8	7	7 1	21	25
5 8	62	−70	7 2	10	−10

h k	F_o	F_c	h k	F_o	F_c
7 3	13	−12	26 0	29	32
7 4	< 8	− 6	28 0	27	−24
7 5	12	− 9	30 0	31	33
7 6	< 8	6	32 0	11	− 9
7 7	13	−18	34 0	39	−37
7 8	8	8	36 0	17	16
7 9	< 8	8	38 0	< 7	6
7 10	12	15	40 0	18	−20
7 11	20	17	1 1	38	43
7 12	< 8	0	2 1	32	−36
7 13	12	13	3 1	35	−31
7 14	9	−11	4 1	91	83
7 15	< 8	4	5 1	63	64
7 16	< 8	− 1	6 1	8	− 8
7 17	11	−14	7 1	50	54
7 18	< 8	1	8 1	102	−99
7 19	< 7	− 9	9 1	75	−67
7 20	8	13	10 1	57	60
7 21	< 7	− 1	11 1	12	−12
7 22	6	6	12 1	35	39
7 23	6	14	13 1	19	16
7 24	< 6	− 5	14 1	59	−52
7 25	< 6	5	15 1	110	−106
8 0	< 7	2	16 1	39	40
8 1	10	−18	17 1	24	25
8 2	< 8	− 4	18 1	15	12
8 3	11	−15	19 1	44	40
8 4	< 8	− 5	20 1	36	−33
8 5	< 8	− 9	21 1	39	−43
8 6	< 7	− 5	22 1	18	16
8 7	< 7	7	23 1	16	11
8 8	< 7	− 6	24 1	19	15
8 9	11	19	25 1	19	19
8 10	< 7	3	26 1	29	−29
8 11	< 7	3	27 1	11	− 7
8 12	< 7	3	28 1	12	12
8 13	< 6	− 9	29 1	9	8
8 14	< 6	− 1	30 1	16	14
8 15	10	−23	31 1	30	28
8 16	< 6	− 4	32 1	20	−27
8 17	< 6	1	33 1	12	−16
8 18	8	− 6	34 1	< 8	5
			35 1	< 8	0
			36 1	15	9
$h = 0$			37 1	16	13
k l			38 1	14	− 9
			39 1	21	−23
4 0	57	−57	40 1	< 7	6
6 0	40	−35	0 2	70	85
8 0	98	−96	1 2	55	−68
10 0	107	−108	2 2	32	33
12 0	54	48	3 2	10	11
14 0	32	−28	4 2	60	−63
16 0	82	−80	5 2	77	82
18 0	75	72	6 2	30	35
20 0	31	−30	7 2	37	−36
22 0	56	−56	8 2	23	−15
24 0	78	82	9 2	17	−13

k l	F_o	F_c	k l	F_o	F_c
10 2	12	9	29 3	19	21
11 2	42	43	30 3	15	11
12 2	14	−14	31 3	< 8	2
13 2	38	−37	32 3	18	−20
14 2	11	−10	33 3	9	13
15 2	< 7	3	34 3	7	10
16 2	22	−19	35 3	< 7	− 1
17 2	53	49	36 3	7	12
18 2	15	11	37 3	< 6	− 2
19 2	33	−31	38 3	12	−10
20 2	18	−12	0 4	33	−35
21 2	20	−21	1 4	15	−15
22 2	14	−18	2 4	11	13
23 2	49	45	3 4	< 7	− 2
24 2	25	24	4 4	11	13
25 2	32	−36	5 4	15	19
26 2	< 8	3	6 4	37	−39
27 2	< 8	− 3	7 4	< 7	2
28 2	9	− 7	8 4	22	24
29 2	18	17	9 4	8	14
30 2	11	7	10 4	26	26
31 2	12	−13	11 4	31	35
32 2	< 8	5	12 4	27	−28
33 2	19	−17	13 4	12	− 9
34 2	8	− 4	14 4	< 8	8
35 2	23	20	15 4	19	−27
36 2	< 7	7	16 4	21	23
37 2	< 7	− 6	17 4	12	11
38 2	< 7	0	18 4	22	−23
39 2	9	− 9	19 4	18	−23
1 3	9	−13	20 4	8	− 7
2 3	35	−38	21 4	16	18
3 3	7	− 5	22 4	20	21
4 3	67	83	23 4	< 8	− 2
5 3	11	−14	24 4	15	−21
6 3	6	− 7	25 4	13	−10
7 3	15	−16	26 4	< 8	− 1
8 3	64	−69	27 4	14	−16
9 3	36	37	28 4	14	9
10 3	47	45	29 4	14	12
11 3	7	8	30 4	14	−14
12 3	< 7	13	31 4	< 7	1
13 3	< 7	4	32 4	< 7	3
14 3	43	−38	33 4	< 6	0
15 3	23	30	34 4	14	13
16 3	33	34	35 4	<10	8
17 3	14	10	36 4	<10	− 6
18 3	31	32	1 5	9	−10
19 3	< 8	− 2	2 5	< 8	4
20 3	36	−35	3 5	15	15
21 3	26	−29	4 5	20	15
22 3	11	12	5 5	< 8	− 6
23 3	39	−40	6 5	9	− 9
24 3	< 8	2	7 5	13	−14
25 3	27	−24	8 5	23	20
26 3	38	−37	9 5	20	21
27 3	20	22	10 5	< 8	− 3
28 3	12	9	11 5	< 8	− 5

h k	F_o	F_c	k l	F_o	F_c
12 5	< 8	5	11 6	< 9	1
13 5	13	−10	12 6	10	− 9
14 5	< 8	2	13 6	< 9	− 4
15 5	16	19	14 6	< 9	4
16 5	< 8	2	15 6	< 9	− 8
17 5	< 8	− 2	16 6	10	8
18 5	< 8	5	17 6	15	−11
19 5	< 8	− 6	18 6	< 9	− 6
20 5	< 8	− 6	19 6	< 9	3
21 5	< 8	6	20 6	< 9	1
22 5	< 8	− 9	21 6	< 8	2
23 5	< 9	−11	22 6	< 8	7
24 5	< 9	− 8	23 6	< 8	− 7
25 5	10	−12	24 6	< 8	3
26 5	< 9	− 3	25 6	< 7	7
27 5	10	12	1 7	< 9	− 1
28 5	< 7	− 2	2 7	17	13
29 5	< 7	3	3 7	< 9	3
30 5	< 7	− 1	4 7	< 9	1
31 5	< 6	− 4	5 7	< 9	3
32 5	< 5	3	6 7	< 9	− 3
0 6	22	21	7 7	< 8	− 1
1 6	18	13	8 7	< 8	3
2 6	20	16	9 7	< 8	− 1
3 6	18	14	10 7	< 8	− 2
4 6	< 9	4	11 7	< 8	− 4
5 6	13	12	12 7	< 8	1
6 6	33	−29	13 7	< 7	− 3
7 6	15	19	14 7	7	9
8 6	< 9	− 4	15 7	< 7	− 2
9 6	< 9	4	16 7	< 7	5
10 6	< 9	0	17 7	< 6	1

The arrangement of the molecules in the crystal is shown in Fig. 4. There are five intermolecular distances shorter than 3.1 Å. These distances are believed to represent hydrogen bonds and are listed in Table 3.

The shortest separation between O_8 and any atom of another molecule is the distance to N_1 (3.06 Å) of a molecule situated one period along the c-axis. The angles C_8—O_8—N_1' (129°) and N_2'—N_1'—O_8 (113°) seems to be in favour of the hydrogen bond in which the hydrogen in the hydroxyl-group is believed to take part. As may be seen from Table 3, the remaining of the hydroxyl-oxygen atoms are each involved in two hydrogen bonds. One of these bonds in which O_{12} is engaged is the bond between this atom and N_2 of a molecule situated one period along the a-axis. The length of this hydrogen bond is 3.09 Å. If the hydrogen at N_2'' points in the direction of O_{12} the angle N_1—N_2—H is 110°.

The set of hydrogen bonds makes firm connections between the sugar residues. One molecule is in this way connected to six other molecules resulting in a net of hydrogen bonds throughout the crystal in layers parallel to the a- and c-axis. In the direction of the b-axis the molecules are linked together by van der Waals' forces between the aromatic parts of the molecules.

The crystal structure is known also for the *p*-bromophenylhydrazone derivatives of ribose and arabinose. The ribose compound is a normal hydrazone whereas the arabinose derivative is a hydrazide like the present compound. Apart from the resemblance between the glucose and the arabinose derivatives already referred to, the molecular arrangements in the crystal are very similar for all three structures, with layers of hydrogen bonded sugar residues and layers of van der Waals' linked aromatic parts.

This molecular arrangement in the crystal seems consistent with the temperature factor data. As may be seen from Table 1, the vibrations of the bromine atom are anisotropic. In the *a*-projection we find for the temperature parameter *B*, a maximum value of 4.4 $Å^2$ and a minimum value of 2.9 $Å^2$. This gives a geometric mean value of 3.6 $Å^2$. The maximal vibration occurs in a direction at an angle of $-5.5°$ with the *a*-axis.

In the *c*-projection the corresponding values are 7.2 $Å^2$ and 2.6 $Å^2$ which gives a mean value of 4.3 $Å^2$. The direction of the maximal vibration in this projection makes an angle of 87° with the *b*-axis.

EXPERIMENTAL. STRUCTURE ANALYSIS

D-Glucose-*p*-bromo-phenylhydrazone was prepared by mixing equivalent amounts of *p*-bromo-phenylhydrazine and D-glucose. An alcoholic solution of the hydrazine and a concentrated aqueous solution of D-glucose was used. This procedure yielded one isomer of *p*-bromo-phenylhydrazone of D-glucose only (m.p. 166°C). The compound mutarotates in pyridine in which the specific rotation changes from $-43.7°$ to $+18.9°$.

The morphological form of the crystals was that of elongated flat prisms and the colour was pale yellow. For the X-ray diagrams, single crystals with cross sections of about 0.2×0.2 mm^2 were used. The diagrams were recorded on an integrating Weissenberg camera using filtered copper radiation ($\lambda = 1.542$ Å), and reflections in the *hk*0 and the 0*kl* zones were recorded only.

The diagrams showed the crystals to be orthorhombic with unit cell dimensions $a = 6.82$ Å, $b = 32.52$ Å and $c = 6.19$ Å (all within 0.5 %). The systematic absences indicated the space group $P2_12_12_1$.

The density of the crystals was measured by the flotation method. The value 1.678 g/cm^3 was found corresponding to four (calc. 3.97) molecules of $C_{12}H_{17}O_5N_2Br$ in the unit cell.

Of the 293 *hk*0 reflections and the 261 0*kl* reflections obtainable with copper radiation; 258 *hk*0 and 168 0*kl* reflections were actually observed. About half the number of observed intensities were measured on a Hilger and Watts photometer, the rest was estimated visually. No corrections for extinction or absorption were made.

The structure was solved by the standard heavy atom technique. The position of the bromine atom was derived from Patterson vector maps in the two projections. The electron density maps based on signs from the bromine atom then indicated the general outline of the molecule.

Both the α- and the β-anomer were tried as models, but only the β-anomer gave values for the *R* factor below 0.30 in the course of refinement ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$).

The refinements were carried out by difference syntheses and least square calculations down to values just below 0.11 for the *R* factor in the two projections. The hydrogen atoms were included in the course of refinement with positions partly derived from the difference maps and partly from stereochemical considerations.

The temperature factor for the bromine atom is anisotropic and the parameters for it were derived from least square calculations. The factor is expressed as $\exp[-(Ba_{11}h^2 + 2Ba_{12}hk + Ba_{22}k^2)]$ and the figures given in Table 1 are Ba_{11}, $2Ba_{12}$ and Ba_{22}. The temperature parameters for the carbon, nitrogen, and oxygen atoms given in Table 1 are derived more or less from the difference maps. For the hydrogen atoms a temperature parameter of $B = 3.0$ $Å^2$ has simply been used.

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