BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1239—1247 (1969)

The Crystal and Molecular Structure of *N*-(*p*-Bromophenyl)-α-D-ribopyranosylamine 2,4-Phenylboronate

Hirotaka SHIMANOUCHI, Norio SAITO[*1] and Yoshio SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

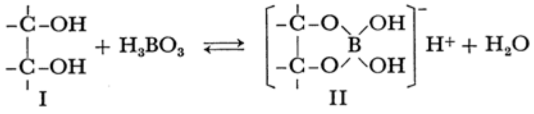
(Received September 9, 1968)

Crystals of *N*-(*p*-bromophenyl)-α-D-ribopyranosylamine 2,4-phenylboronate, $C_{17}H_{17}O_4NBBr$, are monoclinic, with two molecules in a unit cell of the dimensions, $a=12.98$, $b=10.80$, $c=6.34$Å, and $\beta=99.4°$, and with the space group of $P2_1$. The intensity data were collected by a photographic method and the structure was solved by the heavy atom method. The final R factor is 0.100. The absolute configuration was also determined.

1,2-Diols (I) have been well known to enhance the conductivity of boric acid, suggesting that they form the borate complex of the type (II) in solution.[1] T. Sato obtained a crystalline borate complex, *N*-arylribosylamine borate, by the reaction of *N*-arylribosylamine and boric acid.[2] *N*-Arylribosylamine also forms a complex with phenylboronic acid. However, the organic chemical and spectral studies failed to reveal whether the ribose is α or β, whether it is a five- or six-membered ring, and to which oxygen atoms the boron is attached.

The present X-ray diffraction study establishes the conformation of the molecule in the crystalline state, and furthermore gives the bond lengths and angles about the boron atom.

A heavy atom derivative for the X-ray work, prepared by the reaction of D-ribose, phenylboronic acid and *p*-bromoaniline, was supplied by Y. Sato.[3]


I

II

[*1] On leave from Chemical Laboratory, Meijigakuin University.

[1] J. W. Knowlton, N. C. Schieltz and D. MacMillan, *J. Am. Chem. Soc.*, **68**, 208 (1946).

[2] T. Sato, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **71**, 73 (1950).

[3] Y. Sato, M. Sc. thesis submitted to Tokyo Institute of Technology in 1968 (under supervision of Professor T. Sato).

Experimental

Colorless scale-like crystals were obtained from a methanol solution, (100) plane being well developed. The unit cell dimensions were determined from zero-layer Weissenberg photographs about the *b* and the *c* axes, calibrated with superimposed aluminum powder lines.

Multiple-film equi-inclination Weissenberg photographs were taken at room temperature for the layer lines from 0 to 7 about the *b* axis and from 0 to 4 about *c*, using CuKα radiation. The crystals used were square in cross-section with rectangular dimensions of 0.03×0.10 cm and 0.06×0.03 cm for the *b* and *c* axis rotation, respectively. By visual comparison with a standard scale prepared with the same crystal, intensities were estimated, which ranged from 1 to 11900. Out of 1873 reflections recorded, about 290 were too weak to be measured. The corrections for the Lorentz and polarization factors were made in the usual way and those for spot-size variation in high layer photographs by the method of Phillips.[4] The correction for absorption was neglected.

Crystal Data

The crystallographic and physical data obtained are: *N*-(*p*-Bromophenyl)-α-D-ribopyranosylamine 2,4-phenylboronate $C_{17}H_{17}O_4NBBr$, mp 150—150.5°C. Monoclinic, $a=12.98$, $b=10.80$, $c=6.34$ Å, $\beta=99.4°$. Absent spectra, $(0k0)$ when k is odd. Space group, $P2_1$. Two molecules per unit cell. Volume of the unit cell, 876.3 Å^3. Density (by flotation), 1.461 g·cm^{-3}. Density (calculated), 1.478 g·cm^{-3}. Linear absorption coefficient for Cu*K*α radiation, $\mu=36.9$ cm^{-1}. Total number of electrons per unit cell, $F(000)=396$.

Structure Determination

Three-dimensional sharpened Patterson function was synthesized with factors $\exp(2B\sin^2\theta/\lambda^2)$ where $B=5.0$ Å^2, and the bromine atom was located almost on the screw axis. The first three-dimensional Fourier synthesis was made with phases based on the bromine atom. In the resulting electron density distribution, a false mirror plane at $y=1/4$, in addition to that at $y=0$, appeared as a result of the special values of the bromine coordinates. In spite of a disturbance caused by additional mirrors, it was possible to pick out the atoms in the *p*-bromoanilino group. Minimum function, based on the Br–Br vector, also supported this interpretation.

Phases for the second Fourier synthesis were based on the eight atoms in the *p*-bromoanilino group. Although the false mirrors were not yet completely excluded, all the light atoms were picked out from the electron density distribution, so that a reasonable molecular model was constructed. Two successive three-dimensional Fourier syntheses with revised phases confirmed the positions of all the light atoms and considerably reduced the false details which had appeared in the earlier stages. The coordinates of all the atoms obtained from the fourth map gave a discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.42.

TABLE 1. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

The anisotropic temperature factors are expressed in the form of
$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	−0.0098	0.0000	−0.0202	0.00625	0.01030	0.08550	−0.00245	0.00310	−0.01084

Atom	x/a	y/b	z/c	B (Å^2)
N(1)	0.3374	0.3668	0.2678	3.24
O(2)	0.5302	0.4771	0.3647	2.56
O(3)	0.5487	0.7302	0.2846	3.78
O(4)	0.6089	0.5240	0.0517	3.10
O(5)	0.4070	0.4218	−0.0386	2.90
C(1)	0.3600	0.4683	0.1415	2.49
C(2)	0.4398	0.5512	0.2831	2.43
C(3)	0.4733	0.6609	0.1494	3.33
C(4)	0.5224	0.5994	−0.0351	2.91
C(5)	0.4392	0.5216	−0.1735	2.95
C(6)	0.1021	0.1159	0.0729	5.04
C(7)	0.1563	0.1041	0.2777	5.02
C(8)	0.2361	0.1905	0.3307	4.17
C(9)	0.2565	0.2828	0.1969	2.94
C(10)	0.1990	0.2887	−0.0162	4.45
C(11)	0.1181	0.2048	−0.0776	4.28
C(12)	0.6979	0.3729	0.3241	3.02
C(13)	0.7057	0.3122	0.5250	3.82
C(14)	0.7861	0.2289	0.5888	4.93
C(15)	0.8571	0.1985	0.4516	5.35
C(16)	0.8530	0.2594	0.2535	5.82
C(17)	0.7722	0.3430	0.1901	4.07
B	0.6094	0.4595	0.2424	2.65

To give a model with an actual absolute configuration, these positional parameters should be based on a left-handed coordinate system.

---

[4] D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

TABLE 2. ESTIMATED STANDARD DEVIATIONS
($\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Br	0.0016	0.0037	0.0029	0.00009	0.00014	0.00094	0.00031	0.00046	0.00084

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
N(1)	0.0102	0.0110	0.0105	0.19
O(2)	0.0066	0.0077	0.0072	0.13
O(3)	0.0083	0.0103	0.0085	0.17
O(4)	0.0073	0.0086	0.0078	0.15
O(5)	0.0077	0.0085	0.0081	0.14
C(1)	0.0104	0.0108	0.0110	0.19
C(2)	0.0107	0.0115	0.0111	0.18
C(3)	0.0124	0.0138	0.0129	0.23
C(4)	0.0114	0.0126	0.0122	0.21
C(5)	0.0105	0.0127	0.0114	0.21
C(6)	0.0161	0.0173	0.0166	0.33
C(7)	0.0160	0.0178	0.0165	0.33
C(8)	0.0143	0.0149	0.0146	0.27
C(9)	0.0118	0.0121	0.0118	0.21
C(10)	0.0149	0.0152	0.0148	0.30
C(11)	0.0142	0.0148	0.0145	0.28
C(12)	0.0120	0.0131	0.0124	0.21
C(13)	0.0136	0.0143	0.0137	0.26
C(14)	0.0150	0.0186	0.0150	0.31
C(15)	0.0166	0.0174	0.0168	0.35
C(16)	0.0169	0.0223	0.0168	0.37
C(17)	0.0143	0.0150	0.0142	0.27
B	0.0128	0.0134	0.0134	0.22

Further refinement of the parameters was made by the block-diagonal matrix least-squares method. Anisotropic temperature factors in the form of $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$ were applied for the bromine atom, while the light atoms were treated as undergoing isotropic thermal motions. After nine cycles of refinement, the R factor was reduced to 0.100 for the observed reflections. The atomic scattering factors used in the calculations were taken from the International Tables for X-ray Crystallography (1962). The final atomic coordinates and temperature factors are given in Table 1, and their standard deviations in Table 2. The observed and calculated structure factors are listed in Table 3. The final three-dimensional electron density distribution calculated with phases based on these parameters is shown in Fig. 1.

The computations were done on a HITAC 5020E computer in the University of Tokyo with programs written by Dr. T. Ashida.

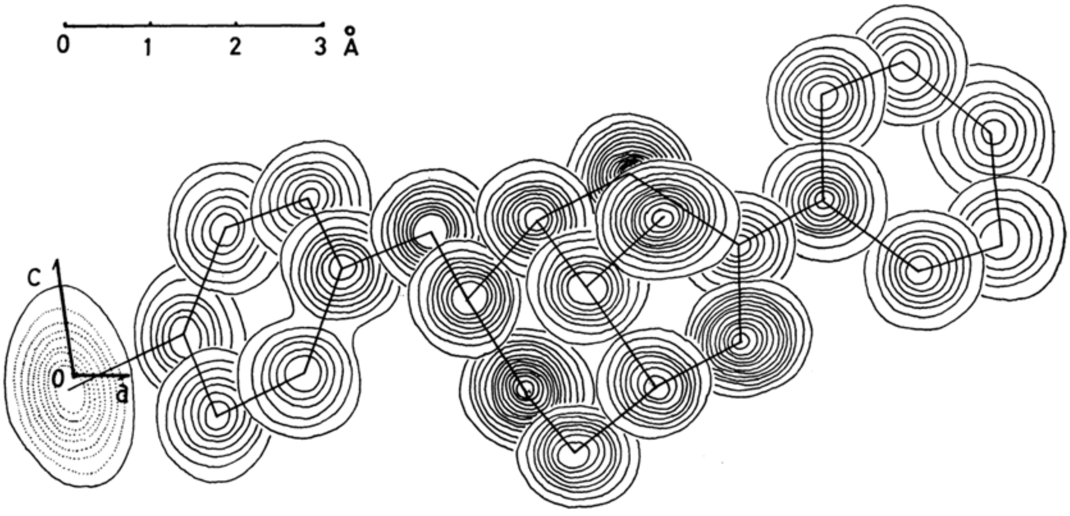


Fig. 1. Composite electron density diagram of sections parallel to (010). The contours of light atoms are at intervals of 1.0e.Å^{-3} starting with 1.0e.Å^{-3}, and those of the bromine atom are at intervals of 5.0e.Å^{-3} from 5.0e.Å^{-3} shown by dotted lines, the lowest being at 1.0e.Å^{-3}.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

K	FO	FC
H,L=	0	0
2	36	47
4	71	70
6	35	36
8	28	26
10	16	15
12	5	3
H,L=	1	0
1	12	14
2	17	16
3	19	19
4	29	31
5	7	6
6	26	28
7	10	8
8	21	20
9	7	5
10	19	18
11	6	5
12	7	8
13	3	3
H,L=	2	0
0	47	56
1	23	16
2	105	123
3	19	18
4	58	58
5	31	30
6	29	28
7	6	5
8	25	23
9	5	5
10	10	11
11	4	2
12	11	10
H,L=	3	0
0	6	8
1	26	25
2	90	98
3	13	12
4	27	27
5	11	7
6	38	38
7	17	16
8	20	21
9	13	10
10	9	8
11	7	6
12	3	4
H,L=	4	0
0	39	42
1	8	10
2	23	21
3	24	20
4	36	39
5	8	8
6	35	34
7	16	16
8	18	18
9	13	12
10	13	13
11	0	1
12	10	9
H,L=	5	0
0	48	49
1	14	13
2	56	58
3	41	39
4	52	53
5	5	5
6	21	20
7	14	15
8	12	13
9	13	12
10	9	9
11	4	3
12	6	7
13	2	3
H,L=	6	0
0	28	30
1	23	22
2	34	31
3	11	11
4	20	19
5	11	8
6	23	25
7	13	14
8	23	23
9	15	15
10	12	12
11	2	3
12	6	5
H,L=	7	0
0	41	41
1	22	21
2	31	29
3	11	12
4	31	29
5	19	19
6	18	14
7	18	18
8	11	12
9	4	2
10	10	10
11	4	4
12	4	4
H,L=	8	0
0	35	32
1	18	17
2	28	26
3	14	15
4	28	26
5	9	8
6	22	21
7	2	3
8	10	10
9	7	6
10	9	9
11	8	8
12	3	4
H,L=	9	0
0	33	31
1	11	9
2	14	12
3	8	6
4	18	18
5	10	11
6	16	18
7	12	13
8	12	12
9	4	3
10	5	4
11	1	2
12	0	2
H,L=	10	0
0	18	15
1	22	23
2	23	22
3	20	21
4	11	8
5	8	8
6	12	11
7	7	6
8	8	6
9	7	7
10	6	7
11	0	2
H,L=	11	0
0	14	13
1	5	6
2	19	17
3	7	4
4	15	17
5	5	6
6	12	11
7	4	4
8	8	8
9	5	4
10	3	4
H,L=	12	0
0	7	4
1	21	23
2	12	11
3	14	17
4	4	3
5	11	12
6	5	4
7	6	7
8	5	5
9	4	4
H,L=	13	0
0	15	15
1	7	6
2	11	9
3	3	3
4	8	8
5	5	4
6	7	7
7	6	5
8	6	6
H,L=	14	0
0	4	3
1	6	7
2	4	4
3	13	15
4	5	5
5	6	6
6	3	3
7	2	4
H,L=	15	0
0	6	6
1	7	8
2	5	4
3	7	8
4	7	6
5	5	6
H,L=	16	0
0	0	1
1	5	5
2	2	2
H,L=	-16	1
0	3	1
1	3	3
2	3	3
3	2	3
H,L=	-15	1
0	8	10
1	5	5
2	5	4
3	6	6
4	3	3
5	3	3
H,L=	-14	1
0	0	0
1	6	8
2	12	11
3	6	5
4	9	8
5	6	7
6	5	5
7	3	4
H,L=	-13	1
0	6	7
1	5	4
2	7	5
3	4	4
4	2	5
5	5	4
6	4	7
7	4	4
H,L=	-12	1
0	21	21
1	13	15
2	18	20
3	9	11
4	11	11
5	10	10
6	6	7
7	3	4
H,L=	-11	1
0	6	4
1	13	14
2	10	10
3	2	3
4	13	13
5	6	5
6	8	11
7	8	9
8	6	7
9	0	0
H,L=	-10	1
0	27	28
1	11	11
2	25	25
3	13	11
4	19	19
5	0	3
6	8	8
7	2	2
8	7	7
9	3	5
10	5	5
11	0	1
H,L=	-9	1
0	24	24
1	8	7
2	17	16
3	25	25
4	6	7
5	18	19
6	18	18
7	12	12
8	8	8
9	4	2
10	6	8
11	0	2
H,L=	-8	1
0	31	30
1	12	10
2	32	28
3	9	8
4	25	27
5	17	17
6	17	16
7	0	1
8	13	13
9	6	5
10	8	9
11	4	4
12	3	4
H,L=	-7	1
0	19	22
1	29	29
2	45	43
3	12	13
4	19	17
5	17	20
6	18	18
7	18	18
8	7	11
9	5	4
10	5	5
11	0	1
12	5	6
H,L=	-6	1
0	31	34
1	12	10
2	19	18
3	14	12
4	44	44
5	4	4
6	23	21
7	14	12
8	23	23
9	5	4
10	11	11
11	5	2
12	4	5
H,L=	-5	1
0	53	53
1	18	19
2	43	42
3	16	14
4	49	45
5	19	18
6	27	25
7	14	14
8	20	19
9	7	6
10	8	10
11	0	3
12	5	5
13	2	2
H,L=	-4	1
0	44	43
1	3	2
2	36	29
3	13	11
4	38	40
5	15	12
6	29	28
7	7	5
8	25	23
9	9	6
10	11	10
11	0	1
12	6	8
13	2	4
H,L=	-3	1
0	19	22
1	24	17
2	84	80
3	37	34
4	26	26
5	14	13
6	31	32
7	7	5
8	19	20
9	9	7
10	5	5
11	0	3
12	6	7
13	9	9
H,L=	-2	1
0	81	92
1	70	66
2	71	72
3	40	36
4	34	31
5	21	20
6	24	24
7	16	13
8	20	21
9	3	4
10	19	20
11	0	3
12	8	9
13	4	5
H,L=	-1	1
0	42	46
1	50	46
2	34	34
3	17	14
4	38	39
5	13	13
6	35	33
7	14	13
8	21	21
9	5	5
10	17	16
11	11	13
12	3	4
13	0	2
H,L=	0	1
0	78	95
1	57	57
2	80	83
3	28	23
4	38	36
5	26	24
6	28	26
7	6	5
8	23	22
9	8	7
10	13	14
11	13	13
12	8	10
13	0	1
H,L=	1	1
0	32	32
1	70	66
2	50	46
3	20	19
4	51	51
5	14	11
6	33	35
7	9	7
8	25	25
9	11	9
10	9	8
11	5	9
12	0	7
H,L=	2	1
0	71	74
1	34	31
2	25	27
3	46	43
4	24	22
5	17	17
6	32	30
7	10	9
8	14	14
9	4	4
10	10	11
11	4	3
12	6	8
13	3	0
H,L=	3	1
0	72	73
1	33	29
2	50	48
3	36	33
4	87	90
5	11	12
6	26	24
7	13	13
8	19	18
9	0	3
10	13	12
11	3	2
12	6	5
13	0	3
H,L=	4	1
0	1	1
1	16	14
2	34	33
3	11	9
4	17	13
5	21	20
6	19	19
7	10	9
8	14	11
9	9	8
10	11	12
11	4	3
12	5	6
13	4	3
H,L=	5	1
0	65	63
1	25	24
2	76	75
3	21	19
4	36	34
5	26	24
6	32	29
7	7	5
8	21	21
9	7	6
10	6	9
11	4	4
12	5	5
13	2	1
H,L=	6	1
0	5	5
1	13	16
2	35	32
3	8	8
4	17	16
5	10	9
6	22	22
7	11	10
8	7	6
9	7	8
10	6	6
11	5	6
12	4	5
H,L=	7	1
0	20	20
1	19	18
2	23	21
3	19	17
4	38	36
5	23	23
6	12	11
7	12	11
8	15	15
9	7	8
10	8	9
11	3	0
12	4	5
H,L=	8	1
0	39	39
1	22	21
2	24	23
3	12	12
4	15	14
5	8	7
6	14	14
7	6	5
8	11	10
9	8	8
10	4	4
11	6	7
H,L=	9	1
0	13	9
1	18	17
2	13	11
3	13	13
4	15	17
5	11	13
6	13	12
7	10	11
8	9	10
9	5	4
10	4	5
11	0	2
H,L=	10	1
0	22	21
1	12	12
2	14	12
3	14	16
4	10	9
5	4	4
6	9	7
7	10	10
8	4	5
9	5	6
10	5	6
H,L=	11	1
0	21	20
1	12	11
2	11	12
3	9	10
4	8	9
5	10	12
6	6	9
7	3	3
8	6	7
9	3	2
H,L=	12	1
0	5	4
1	8	8
2	5	4
3	9	12
4	6	6
5	9	9
6	3	4
7	5	6
8	3	3
H,L=	13	1
0	0	0
1	7	9
2	13	14
3	9	10
4	7	6
5	6	7
6	4	4
7	4	5
H,L=	14	1
0	0	4
1	4	5
2	8	7
3	5	5
4	3	3
5	4	5
6	2	4
H,L=	15	1
0	3	3
1	7	8
2	4	1
3	4	6
4	2	2
H,L=	-16	2
0	1	0
1	1	3
H,L=	-15	2
0	9	9
1	6	5
2	8	10
3	5	5
4	5	5
5	4	4
H,L=	-14	2
0	5	4
1	4	4
2	5	5
3	1	2
4	6	6
5	4	5
6	2	2
7	3	4
H,L=	-13	2
0	6	7
1	5	6
2	8	10
3	9	11
4	7	9
5	4	4
6	6	7
7	3	1
H,L=	-12	2
0	7	7
1	1	2
2	13	12
3	8	5
4	8	10
5	0	2
6	3	3
7	3	4
H,L=	-11	2
0	12	12
1	8	9
2	15	16
3	6	6
4	0	2
5	8	8
6	12	13
7	4	4
8	9	9
H,L=	-10	2
0	21	22
1	9	8
2	11	10
3	5	4
4	16	17
5	4	6
6	3	3
7	2	2
8	8	9
9	5	3
10	6	7
H,L=	-9	2
0	21	20
1	12	12
2	19	20
3	16	13
4	25	24
5	12	13
6	20	20
7	6	5
8	8	7
9	4	3
10	5	7
H,L=	-8	2
0	17	17
1	3	4
2	13	14
3	6	4
4	15	15
5	22	21
6	25	25
7	5	5
8	9	11
9	4	3
10	6	6
11	3	3
H,L=	-7	2
0	40	39
1	9	7
2	33	30
3	10	9
4	28	26
5	12	11
6	29	28
7	6	6
8	6	7
9	6	5
10	5	7
11	0	2
H,L=	-6	2
0	8	1
1	18	17
2	26	25
3	11	10
4	35	34
5	9	8
6	20	18
7	4	4
8	0	2
9	0	2
10	7	7
11	3	1
H,L=	-5	2
0	38	38
1	16	17
2	36	31
3	35	34
4	30	29
5	10	8
6	15	14
7	3	3
8	21	22
9	5	3
10	7	8
11	0	0
12	5	6
H,L=	-4	2
0	37	36
1	22	19
2	46	44
3	47	41
4	27	24
5	11	7
6	12	13
7	10	8
8	17	18
9	5	5
10	6	6
11	0	2
12	2	2
13	2	4
H,L=	-3	2
0	47	48
1	31	29
2	29	29
3	42	37
4	41	38
5	21	18
6	28	26
7	13	10
8	16	15
9	4	2
10	7	7
11	0	1
12	9	10
13	2	2
H,L=	-2	2
0	38	40
1	41	34
2	56	56
3	36	31
4	16	13
5	21	16
6	17	19
7	0	1
8	19	19
9	5	5
10	12	12
11	0	0
12	10	11
13	2	3
H,L=	-1	2
0	42	45
1	25	21
2	36	34
3	23	21
4	41	38
5	22	20
6	27	26
7	6	6
8	20	20
9	6	6
10	10	10
11	0	2
12	6	5
13	0	0
H,L=	0	2
0	23	22
1	6	5
2	44	42
3	13	12
4	28	28
5	25	22
6	24	22
7	11	9
8	9	8
9	5	3
10	20	20
11	3	4
12	8	8
13	0	1
H,L=	1	2
0	68	65
1	29	27
2	20	19
3	23	22
4	43	41
5	9	8
6	33	33
7	6	4
8	13	11
9	9	8
10	4	5
11	5	5
12	4	3
H,L=	2	2
0	44	43
1	9	8
2	29	29
3	28	25
4	18	15
5	18	18
6	21	20
7	23	21
8	21	21
9	8	6
10	12	14
11	0	1
12	4	4
H,L=	3	2
0	28	25
1	21	21
2	48	44
3	35	35
4	43	40
5	19	19
6	14	15
7	14	14
8	19	16
9	8	8
10	8	9
11	0	2
12	5	6
H,L=	4	2
0	7	7
1	0	0
2	24	23
3	28	26
4	17	19
5	5	4
6	21	22
7	22	21
8	17	17
9	8	7
10	9	9
11	5	5
12	5	6
H,L=	5	2
0	25	26
1	20	21
2	34	31
3	24	22
4	23	23
5	15	15
6	14	16
7	17	19
8	9	12
9	7	7
10	5	5
11	0	2
12	4	4
H,L=	6	2
0	38	36
1	24	22
2	11	11
3	13	13
4	25	23
5	8	7
6	16	16
7	4	2
8	8	9
9	7	7
10	6	7
11	4	4
12	2	3
H,L=	7	2
0	1	1
1	10	9
2	17	16
3	13	12
4	8	5
5	16	17
6	12	14
7	4	3
8	5	4
9	12	14
10	4	5
11	3	3
H,L=	8	2
0	24	28
1	29	31
2	32	32
3	9	9
4	12	13
5	6	5
6	8	9
7	8	8
8	10	10
9	5	6
10	2	3
11	1	2
H,L=	9	2
0	5	9
1	5	4
2	6	4
3	8	7
4	4	3
5	9	10
6	4	5
7	7	7
8	6	7
9	0	1
10	6	5
H,L=	10	2
0	34	38
1	9	10
2	6	7
3	12	12
4	11	13
5	11	11
6	6	6
7	5	6
8	4	3
9	5	5
10	0	3
H,L=	11	2
0	0	0
1	12	13
2	2	3
3	10	11
4	5	6
5	5	5
6	4	5
7	4	5
8	3	3
9	1	2
H,L=	12	2
0	0	3
1	3	4
2	9	9
3	7	8
4	5	6
5	7	7
6	2	2
7	4	5
8	1	3
H,L=	13	2
0	0	1
1	5	7
2	6	6
3	8	8
4	2	2
5	3	4
6	2	2
H,L=	14	2
0	0	4
1	5	6
2	0	0
3	3	3
4	3	4
H,L=	15	2
0	0	2
1	0	4
H,L=	-16	3
0	1	0
1	3	3
H,L=	-15	3
0	8	7
1	5	3
2	5	6
3	2	2
4	3	7
H,L=	-14	3
0	4	4
1	0	1
2	3	3
3	4	6
4	2	2
5	4	4
H,L=	-13	3
0	5	5
1	0	0
2	9	11
3	8	9
4	4	4
5	0	1
6	1	3
H,L=	-12	3
0	5	6
1	7	7
2	11	11
3	1	0
4	5	5
5	3	2
6	5	6
7	4	4
H,L=	-11	3
0	10	10
1	2	4
2	6	4
3	5	4
4	3	5
5	6	7
6	4	3
7	3	4
8	5	5
H,L=	-10	3
0	12	13
1	13	13
2	13	14
3	6	5
4	12	13
5	10	10
6	6	8
7	10	9
8	7	9
H,L=	-9	3
0	11	12
1	2	4
2	6	5
3	5	5
4	12	11
5	18	18
6	3	3
7	11	12
8	0	2
H,L=	-8	3
0	0	0
1	6	5
2	18	19
3	6	4
4	13	14
5	16	16
6	11	16
7	9	7

TABLE 3. (Continued)

K	FO	FC
8	5	5
9	0	2
10	0	4
11	4	3
H,L=	-7	3
0	18	20
1	4	4
2	14	13
3	6	4
4	15	15
5	13	12
6	9	8
7	9	9
8	6	7
9	0	2
10	0	4
11	3	2
12	1	4
H,L=	-6	3
0	19	18
1	6	3
2	19	20
3	11	11
4	19	17
5	6	5
6	14	14
7	7	6
8	12	12
9	6	7
10	0	7
11	7	0
12	0	0
H,L=	-5	3
0	32	34
1	15	13
2	8	7
3	14	11
4	13	12
5	12	9
6	13	13
7	4	5
8	7	6
9	10	10
10	0	11
11	10	1
12	0	5
H,L=	-4	3
0	21	22
1	23	19
2	45	42
3	12	10
4	22	22
5	17	13
6	14	15
7	3	3
8	7	6
9	5	3
10	8	9
11	2	3
H,L=	-3	3
0	4	3
1	17	13
2	8	10
3	26	20
4	5	6
5	21	17
6	15	14
7	5	6
8	15	15
9	6	5
10	3	3
11	2	4
12	2	4
H,L=	-2	3
0	36	41
1	20	19
2	40	40
3	11	7
4	29	27
5	6	5
6	7	8
7	9	7
8	10	12
9	4	1
10	6	4
11	4	4
12	3	5
H,L=	-1	3
0	2	3
1	29	30
2	10	9
3	14	11
4	21	20
5	9	7
6	24	22
7	5	5
8	10	10
9	7	7
10	0	2
11	3	1
12	4	5
H,L=	0	3
0	39	42
1	20	18
2	30	29
3	27	24
4	17	16
5	15	15
6	5	5
7	12	11
8	13	13
9	6	4
10	9	8
11	4	4
H,L=	1	3
0	10	13
1	10	10
2	20	19
3	9	8
4	9	11
5	15	14
6	22	20
7	8	6
8	14	10
9	8	6
10	6	7
11	3	3
12	3	3
H,L=	2	3
0	26	23
1	28	25
2	13	13
3	17	17
4	25	25
5	22	22
6	15	16
7	21	18
8	17	15
9	5	5
10	7	8
11	2	1
12	4	4
H,L=	3	3
0	14	17
1	3	0
2	24	22
3	14	11
4	6	6
5	0	2
6	25	26
7	14	11
8	12	9
9	3	4
10	4	4
11	4	3
12	4	4
H,L=	4	3
0	13	12
1	18	18
2	4	4
3	14	12
4	23	23
5	14	12
6	4	8
7	11	10
8	18	17
9	4	3
10	5	6
11	4	3
12	1	2
H,L=	5	3
0	10	10
1	8	8
2	17	16
3	11	13
4	20	20
5	13	11
6	12	13
7	7	8
8	12	10
9	3	5
10	0	3
11	4	4
H,L=	6	3
0	10	11
1	21	22
2	9	7
3	8	6
4	12	14
5	7	6
6	7	7
7	6	4
8	11	12
9	7	6
10	4	5
H,L=	7	3
0	7	7
1	4	4
2	19	19
3	12	11
4	4	4
5	7	8
6	7	7
7	6	7
8	9	10
9	5	5
10	5	6
11	3	3
H,L=	8	3
0	6	8
1	18	19
2	13	15
3	10	12
4	5	5
5	8	10
6	3	3
7	4	3
8	2	3
9	0	2
10	6	8
H,L=	9	3
0	9	6
1	1	3
2	1	1
3	9	9
4	6	7
5	4	3
6	4	5
7	6	6
8	4	4
9	2	2
H,L=	10	3
0	11	12
1	9	11
2	5	7
3	6	5
4	2	3
5	7	9
6	2	2
7	4	5
H,L=	11	3
0	0	2
1	6	7
2	1	1
3	4	5
4	5	7
5	6	7
6	2	4
H,L=	12	3
0	2	2
1	4	6
2	0	1
3	4	5
4	1	1
5	3	3
H,L=	13	3
0	3	6
1	4	5
2	4	4
3	5	7
4	3	5
H,L=	14	3
0	2	4
1	2	2
H,L=	-15	4
0	5	5
1	1	2
H,L=	-14	4
0	5	5
1	3	3
2	0	2
3	2	2
4	3	2
H,L=	-13	4
0	1	2
1	0	1
2	0	1
3	4	3
4	0	2
5	0	2
6	0	1
7	0	2
H,L=	-12	4
0	8	8
1	5	4
2	11	12
3	5	5
4	3	2
5	0	1
6	2	4
H,L=	-11	4
0	6	7
1	3	3
2	4	3
3	5	4
4	4	3
5	2	4
6	2	3
H,L=	-10	4
0	11	12
1	7	8
2	12	13
3	3	3
4	9	9
5	4	3
6	10	12
7	2	2
H,L=	-9	4
0	2	6
1	0	3
2	5	5
3	4	1
4	5	3
5	7	5
6	7	7
7	4	5
H,L=	-8	4
0	6	3
1	5	4
2	8	7
3	5	5
4	11	12
5	4	3
6	5	4
7	2	2
8	4	5
H,L=	-7	4
0	22	22
1	13	14
2	15	15
3	13	12
4	14	15
5	7	7
6	3	1
7	4	4
8	3	2
9	0	3
10	3	3
H,L=	-6	4
0	7	7
1	11	9
2	14	11
3	16	13
4	1	0
5	5	4
6	6	8
7	2	1
8	8	8
9	5	5
10	3	4
H,L=	-5	4
0	17	17
1	15	14
2	26	26
3	15	11
4	11	10
5	10	9
6	10	10
7	7	7
8	0	2
9	7	7
10	0	0
11	0	3
H,L=	-4	4
0	3	1
1	11	11
2	3	2
3	17	16
4	11	11
5	8	8
6	4	4
7	6	5
8	0	5
9	4	4
10	4	5
11	2	3
H,L=	-3	4
0	8	10
1	7	8
2	12	13
3	11	11
4	8	8
5	0	2
6	14	12
7	9	7
8	8	7
9	4	3
10	4	4
11	2	0
H,L=	-2	4
0	19	20
1	6	7
2	14	13
3	4	5
4	9	8
5	12	11
6	5	4
7	7	6
8	4	5
9	3	3
10	5	5
11	2	2
H,L=	-1	4
0	0	1
1	2	2
2	17	17
3	2	3
4	6	5
5	14	12
6	19	18
7	6	5
8	6	7
9	3	1
10	4	5
11	4	4
H,L=	0	4
0	22	23
1	11	9
2	7	6
3	15	15
4	10	11
5	21	21
6	5	3
7	13	12
8	0	3
9	0	3
10	3	3
11	0	1
H,L=	1	4
0	17	14
1	5	3
2	11	11
3	7	8
4	17	20
5	7	7
6	13	13
7	7	5
8	8	8
9	0	2
10	4	6
11	4	4
H,L=	2	4
0	8	8
1	12	13
2	7	7
3	11	9
4	8	8
5	25	24
6	7	7
7	3	2
8	3	4
9	5	3
10	0	0
11	0	1
H,L=	3	4
0	12	11
1	11	11
2	15	14
3	6	4
4	15	16
5	8	7
6	13	14
7	8	6
8	0	2
9	3	3
10	0	1
11	3	3
H,L=	4	4
0	4	0
1	3	3
2	5	6
3	9	8
4	11	11
5	7	7
6	6	6
7	9	7
8	0	2
9	3	3
10	3	4
11	1	0
H,L=	5	4
0	10	12
1	8	10
2	5	5
3	25	26
4	11	10
5	7	7
6	6	7
7	4	5
8	3	3
9	0	1
10	2	3
11	0	1
H,L=	6	4
0	2	4
1	6	6
2	7	10
3	10	10
4	7	7
5	0	1
6	2	0
7	3	3
8	3	4
9	5	5
10	3	4
H,L=	7	4
0	6	7
1	14	14
2	0	1
3	6	8
4	7	8
5	11	12
6	4	5
7	5	5
8	4	5
9	3	3
10	0	2
H,L=	8	4
0	2	4
1	7	7
2	7	8
3	4	5
4	3	3
5	0	1
6	0	1
7	0	2
8	2	3
9	3	3
H,L=	9	4
0	0	2
1	4	4
2	0	1
3	6	6
4	0	4
5	5	5
6	2	2
7	0	1
H,L=	10	4
0	0	0
1	4	6
2	3	4
3	3	2
4	3	4
5	2	3
6	4	6
7	2	3
H,L=	11	4
0	3	4
1	2	3
2	2	1
3	4	5
4	0	2
5	2	3
H,L=	12	4
0	0	1
1	0	1
2	0	1
3	3	4
4	2	3
H,L=	-13	5
0	2	0
H,L=	-12	5
0	7	6
1	0	1
2	0	1
3	0	1
4	3	3
5	0	1
6	1	3
H,L=	-11	5
0	2	1
1	0	1
2	0	0
3	0	1
4	0	1
5	2	2
6	2	3
H,L=	-10	5
0	5	5
1	1	1
2	3	3
3	0	3
4	3	3
5	2	2
6	2	3
H,L=	-9	5
0	0	1
1	5	5
2	8	9
3	5	5
4	3	3
5	4	4
6	2	4
7	0	0
H,L=	-8	5
0	0	0
1	8	6
2	6	4
3	1	2
4	1	3
5	2	3
6	3	2
7	2	3
H,L=	-7	5
0	12	10
1	7	5
2	19	17
3	10	9
4	7	7
5	4	5
6	3	4
7	0	0
H,L=	-6	5
0	14	11
1	10	9
2	14	13
3	11	8
4	4	4
5	4	5
6	2	5
7	0	1
H,L=	-5	5
0	19	18
1	10	11
2	12	8
3	11	10
4	11	10
5	3	1
6	3	4
7	6	6
H,L=	-4	5
0	15	19
1	9	9
2	9	7
3	9	7
4	1	0
5	0	0
6	0	2
7	6	4
H,L=	-3	5
0	8	7
1	8	9
2	12	13
3	8	7
4	6	4
5	4	3
6	2	0
7	3	1
H,L=	-2	5
0	7	4
1	5	7
2	20	22
3	0	3
4	8	7
5	11	9
6	7	7
7	3	3
H,L=	-1	5
0	0	0
1	4	3
2	5	5
3	6	7
4	8	10
5	10	8
6	6	5
7	4	6
H,L=	0	5
0	1	1
1	4	3
2	7	7
3	7	7
4	6	7
5	14	12
6	8	7
7	9	8
H,L=	1	5
0	8	7
1	5	6
2	1	0
3	6	5
4	11	13
5	10	9
6	0	1
7	3	4
H,L=	2	5
0	0	0
1	1	3
2	1	2
3	7	6
4	3	2
5	8	6
6	7	7
7	0	0
H,L=	3	5
0	4	5
1	7	9
2	0	1
3	1	2
4	9	8
5	0	1
6	0	1
7	5	6
H,L=	4	5
0	0	4
1	0	0
2	7	8
3	2	1
4	8	7
5	0	1
6	2	4
7	0	0
H,L=	5	5
0	1	3
1	8	8
2	9	9
3	1	2
4	5	6
5	7	8
6	0	2
7	2	3
H,L=	6	5
0	7	7
1	4	5
2	10	12
3	0	2
4	4	4
5	3	3
6	2	3
7	0	2
H,L=	7	5
0	10	12
1	3	2
2	3	3
3	5	6
4	2	1
5	3	3
6	2	2
7	2	3
H,L=	8	5
0	6	8
1	5	7
2	5	6
3	0	0
4	0	1
5	1	1
6	0	2
7	1	2
H,L=	9	5
0	0	0
1	2	2
2	0	2
3	0	1
4	0	0
5	2	2
H,L=	10	5
0	0	0
1	3	4
2	0	1
3	4	6
H,L=	-12	6
0	0	0
1	1	2
2	0	0
3	2	2
H,L=	-11	6
0	0	0
1	4	4
2	0	3
3	0	1
H,L=	-10	6
0	0	0
1	3	3
2	0	2
3	0	1
4	0	0
5	4	4
H,L=	-9	6
0	0	3
1	2	3
2	0	1
3	0	1
4	2	3
5	3	3
6	3	1
7	1	1
H,L=	-8	6
0	0	1
1	0	1
2	0	1
3	0	2
4	0	2
5	3	3
6	4	4
7	2	3
H,L=	-7	6
0	0	1
1	4	4
2	4	4
3	0	0
4	3	0
5	0	2
6	4	5
7	3	3
H,L=	-6	6
0	4	2
1	7	8
2	5	5
3	2	1
4	0	1
5	0	1
6	4	4
7	3	3
H,L=	-5	6
0	0	0
1	4	5
2	4	4
3	3	2
4	0	1
5	0	1
6	2	2
7	1	2
H,L=	-4	6
0	14	16
1	12	12
2	6	6
3	4	2
4	0	0
5	2	2
6	4	3
7	1	2
H,L=	-3	6
0	8	5
1	6	7
2	9	9
3	9	9
4	0	1
5	2	2
6	2	1
7	1	3
H,L=	-2	6
0	9	8
1	0	0
2	12	11
3	12	13
4	6	6
5	6	5
6	2	2
7	4	4
H,L=	-1	6
0	9	9
1	5	5
2	5	4
3	10	9
4	3	1
5	7	8
6	3	2
7	4	2
H,L=	0	6
0	2	3
1	4	2
2	1	3
3	5	3
4	0	1
5	6	7
6	5	5
7	4	2
H,L=	1	6
0	1	2
1	5	6
2	7	8
3	2	3
4	0	1
5	3	3
6	0	1
7	4	4
H,L=	2	6
0	7	8
1	4	4
2	6	5
3	0	0
4	0	0
5	3	1
6	0	1
7	3	4
H,L=	3	6
0	4	6
1	6	6
2	5	5
3	2	2
4	4	4
5	4	4
6	2	1
7	0	1
H,L=	4	6
0	3	5
1	1	2
2	5	5
3	4	3
4	1	1
5	2	3
6	0	1
7	2	3
H,L=	5	6
0	0	2
1	2	1
2	0	1
3	2	2
4	0	0
5	3	4
6	1	2
7	3	5
H,L=	6	6
0	2	3
1	3	3
2	0	1
3	4	5
4	2	2
5	1	1
6	1	2
7	0	1
H,L=	7	6
0	0	0
1	1	2
2	0	1
3	0	3
4	0	2
5	1	2
H,L=	8	6
0	0	1
1	0	4
H,L=	9	6
0	0	0
1	1	1
H,L=	-10	7
0	8	7
1	1	1
2	3	2
H,L=	-9	7
0	10	8
1	4	3
2	2	2
3	3	2
H,L=	-8	7
0	6	5
1	5	4
2	4	3
3	0	2
H,L=	-7	7
0	0	0
1	3	4
2	5	5
3	0	1
4	0	1
5	1	2
H,L=	-6	7
0	0	1
1	2	3
2	0	0
3	2	2
4	3	2
5	2	1
H,L=	-5	7
0	0	4
1	2	2
2	0	2
3	0	1
4	0	0
5	2	3
6	1	2
H,L=	-4	7
0	1	0
1	5	4
2	2	3
3	0	1
4	2	2
5	2	2
6	2	2
H,L=	-3	7
0	4	2
1	2	3
2	3	4
3	0	2
4	2	2
5	1	2
6	2	2
H,L=	-2	7
0	6	4
1	0	1
2	0	0
3	0	2
4	2	1
5	2	2
6	4	5
H,L=	-1	7
0	5	4
1	1	1
2	1	0
3	0	2
4	2	3
5	3	3
6	4	6
H,L=	0	7
0	3	1
1	4	4
2	2	1
3	0	1
4	0	0
5	0	2
6	0	2
H,L=	1	7
0	0	0
1	9	8
2	6	5
3	1	2
4	0	0
5	0	0
6	0	1
H,L=	2	7
0	0	0
1	7	7
2	6	5
3	5	4
4	0	1
5	0	1
H,L=	3	7
0	0	1
1	6	5
2	5	4
3	6	4
4	2	2
5	0	2
H,L=	4	7
0	0	1
1	2	3
2	4	2
3	6	4
4	3	3
5	0	2
H,L=	-4	8
0	0	0
1	4	4
H,L=	-3	8
0	0	1
1	4	4
H,L=	-2	8
0	0	1
1	1	1

Determination of Absolute Configuration

After the errors due to neglecting the correction for absorption were taken into account, it was observed that for seven sets of Bijvoet pair in the upper layer photographs around the *c* axis, intensities in each pair were significantly different. For the Bijvoet pairs, $|F(hkl)|$ and $|F(\bar{h}\bar{k}\bar{l})|$ were calculated using $\Delta f'$ and $\Delta f''$ for the bromine atom on the basis of the model in a right-handed coordinate system. As shown in Table 4, inequality relation observed in each pair is opposite to that of the calculated values, so that the model used in the calculations is the mirror image of the actual molecule. Therefore, the absolute configuration of ribose has been established as indicated in Fig. 2.

TABLE 4. THE DETERMINATION OF THE ABSOLUTE CONFIGURATION

h k l	Calculated $\lvert F(hkl)\rvert$		Calculated $\lvert F(\bar{h}\bar{k}\bar{l})\rvert$	Observed $\lvert I(hkl)\rvert$		Observed $\lvert I(\bar{h}\bar{k}\bar{l})\rvert$
12 1 1	7.8	$<$	8.7		$>$	
10 4 1	9.1	$<$	9.4		$>$	
12 4 1	5.9	$<$	6.3		$>$	
7 1 2	9.8	$>$	8.1		$<$	
7 1 3	3.4	$<$	4.6		$>$	
11 1 3	7.1	$<$	7.9		$>$	
7 4 3	4.0	$<$	5.1		$>$	

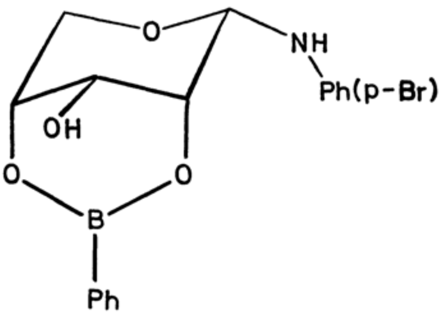


Fig. 2. Absolute configuration and conformation.

Results and Discussion

Conformation. As shown in Fig. 2 three surprising features are found in the molecular conformation. The first is that the sugar residue is pyranoid; the ribose residue so far reported is in the furanose form in crystal.[5-7] The second is that it is the α-D anomer; the free sugar customarily crystallizes as a β-D anomer. The third is that it is in a chair 1C conformation (1*e*2*a*3*e*4*a*); in free ribopyranose this is a very unstable form owing to strong 1,3-diaxial O(2)···O(4) interaction. These features are interrelated to each other as will be discussed below.

The conformations about the six single bonds in the pyranose ring are shown in Fig. 3[8] and the

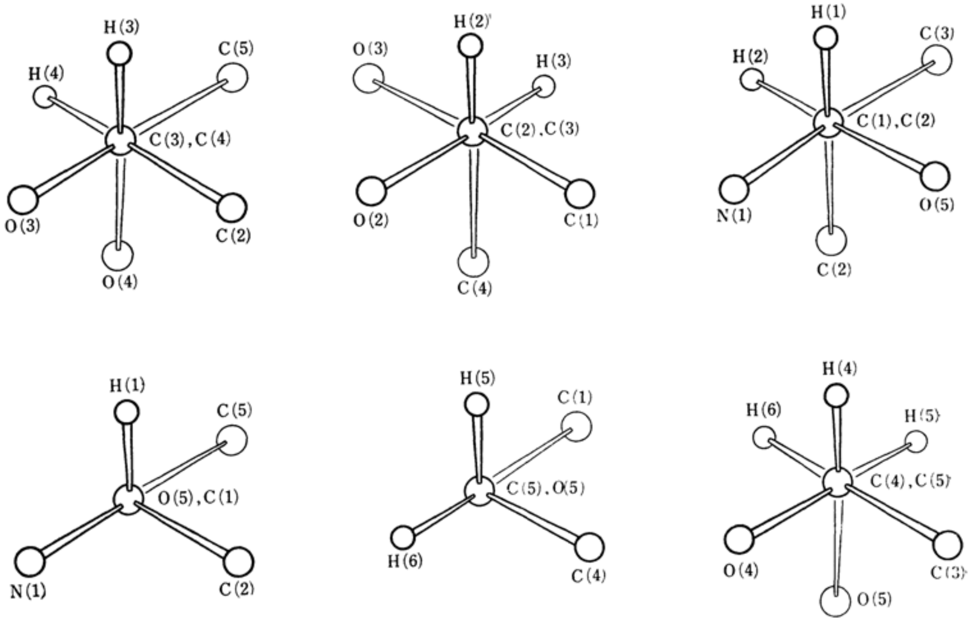


Fig. 3. Conformations about the six single bonds of the pyranose ring.

---

5) E. Alver and S. Furberg, *Acta Chem. Scand.*, **13**, 910 (1959).

6) S. Furberg and A. Mostad, *ibid.*, **16**, 1627 (1962).

7) J. Kraut and L. H. Jensen, *Acta Cryst.*, **16**, 79 (1963).

8) In the preparation of this figure, the positions of the hydrogen atoms were assumed.

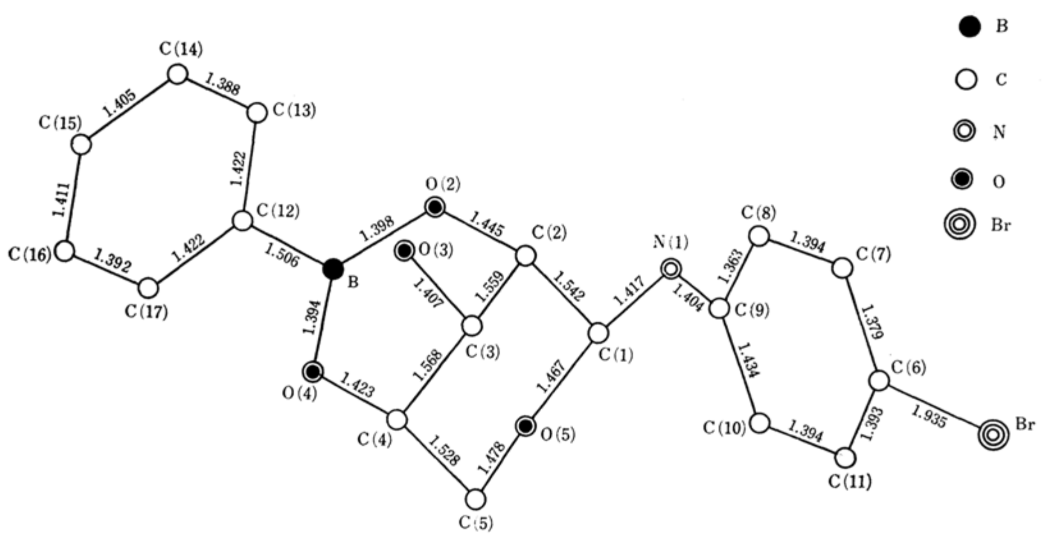


Fig. 4. Bond lengths (Å).

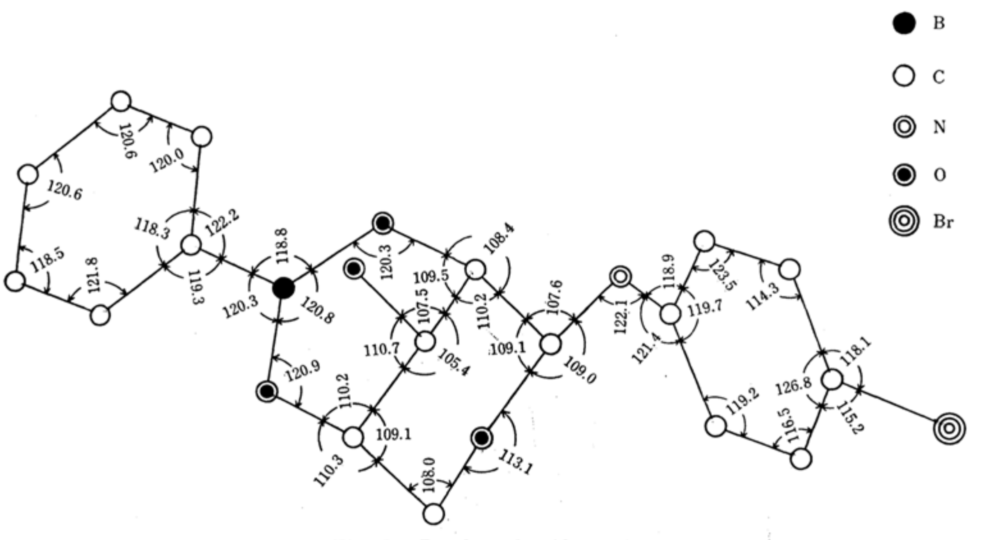


Fig. 5. Bond angles (degrees).

conformation angles range from 56.0 to 62.5°, as compared with 55.8—61.7° for an ideal pyranose ring,[9] 51.3—62.2° for glucose,[10] 54.8—56.0° for sucrose[11] and 56.2—60.5° for β-methyl maltoside.[12] The range in the present molecule is very close to that in an ideal pyranose ring indicating no evidence of strain in the ring. This suggests that the pyranose 1C conformation is most favorable to form a borate complex with ribose. In this ring conformation the present equatorial α-D anomer is more stable than the axial β-D one. It follows that the energy of the present three-dimensional structure is undoubtedly lower than any other isomer and only one isomer is predominantly formed and crystallizes as a pure form. Thus, it is reasonably interpreted that the formation of a stable borate complex is characteristic of D-ribose.[13]

Molecular Geometry. The intramolecular bond lengths and angles are shown in Figs. 4 and

---

[9] H. M. Berman and S. H. Kim, *Acta Cryst.*, **B24**, 897 (1968).

[10] G. M. Brown and H. A. Levy, *Science*, **147**, 1038 (1965).

[11] G. M. Brown and H. A. Levy, *ibid.*, **141**, 920 (1963).

[12] S. S. C. Chu and G. A. Jeffrey, *Acta Cryst.*, **23**, 1038 (1967).

[13] T. Fujita, D. Sc. thesis submitted to Tokyo Institute of Technology in 1960 (under supervision of Professor T. Sato).

5, respectively. The mean estimated standard deviations in bond lengths of C–Br, C–O, C–N C–C, O–B and C–B, are 0.018, 0.015, 0.016, 0.021, 0.016 and 0.019 Å, respectively, and that in bond angle is about 1.2°. The C–C single bond lengths range from 1.528 to 1.568 Å and none of them differ significantly from the mean value of 1.549 Å. The C–O bond lengths range from 1.407 to 1.478 Å with the mean value of 1.444 Å. The distance of C(1)–N(1) is 1.417 Å, which is significantly shorter than the normal $C(sp^3)$–N$<$ length, *i. e.* 1.463 Å in *N,N'*-dinitroethylenediamine.[14] There is no significant inequality of the ring C(1)–O(5) and C(5)–O(5) bonds. Similar shortening of the equatorial C(1)–O(1) bond, which corresponds to the present C(1)–N(1), and equality of the ring C–O bonds have been observed in pyranose sugars.[15] These phenomena have been connected with a property of the equatorial C(1)–O(1) bond,[12,15] and by the present observation this interpretation may be extended to the equatorial C(1)–X bond where X is an atom with lone pair.

The valence angles on O(2) and O(4) atoms are somewhat larger than the usual. This tendency is consistent in that the C(2)–O(2) and C(4)–O(4) distances are shorter than C(1)–O(5) and C(5)–O(5).

The two B–O bond lengths are essentially equal to the mean value of 1.396 Å. The π-bond order of these B–O bonds was found to be about 0.35 using B–O π-bond order *versus* bond length curve given by Coulson.[16] Armstrong and Perkins have predicted that in some substituted phenylboronic acids a migration of charge from the oxygen to the boron atom results in a π-bond order in the range 0.3 to 0.5.[17] The present π-bond order agrees well with their prediction. The three bond angles around the boron atom are very close to 120°. The equation for the least-squares plane of the four atoms, O(2), O(4), B and C(12) is:

$$-0.438x' - 0.751y' - 0.494z' + 7.841 = 0$$

where $x' = x + z\cos\beta$, $y' = y$ and $z' = z\sin\beta$. The deviations from this plane are shown in Fig. 6. It is apparent that the boron atom is trigonally hybridized and the C(2) and C(4) atoms also lie nearly within the plane. This seems to satisfy the most favorable condition for forming B–O π-bond. The dihedral angle between this plane and the benzene ring, C(12)–C(17), plane is only

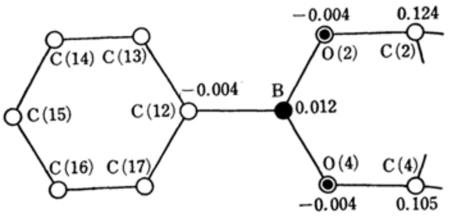


Fig. 6. The deviations (Å) of the atoms from the least-squares plane through atoms, O(2), O(4), B and C(12).

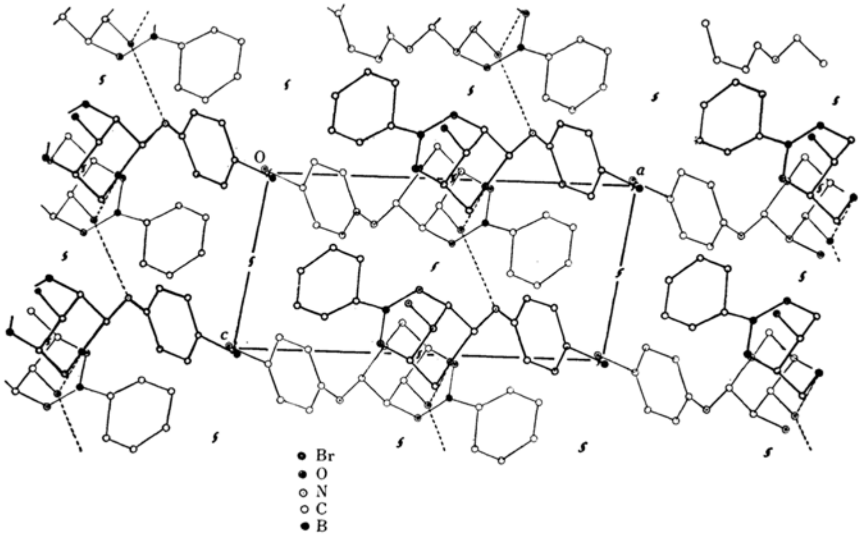


Fig. 7. The crystal structure projected along the *b* axis. The dashed lines indicate the presumed hydrogen bonds. Concerning the absolute configuration, this figure is the mirror image of the actual crystal.

---

[14] J. W. Turley, *Acta Cryst.*, **B24**, 942 (1968).

[15] S. S. C. Chu and G. A. Jeffrey, *ibid.*, **B24**, 830 (1968).

[16] C. A. Coulson and T. W. Dingle, *ibid.*, **B24**, 153 (1968).

[17] D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.*, (*A*), **1967**, 123.

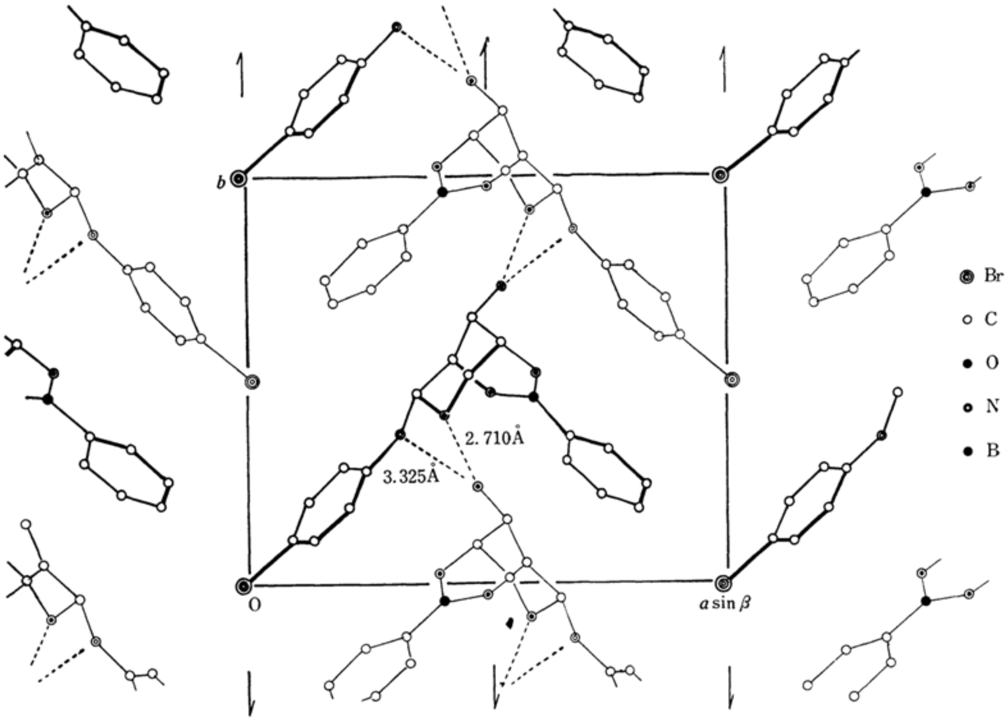


Fig. 8. The crystal structure projected along the *c* axis. The dashed lines indicate the presumed hydrogen bonds. Concerning the absolute configuration, this figure is the mirror image of the actual crystal.

TABLE 5. HYDROGEN-BOND DISTANCES AND ANGLES

Bonds		Acceptor at
O(3)···O(5)	2.710 Å	$1-x,\ \frac{1}{2}+y,\ \bar{z}$
N(1)···O(3)	3.325 Å	$1-x,\ \frac{1}{2}+y,\ 1-z$

Angles	
C(3)—O(3)···O(5)	104.3°
C(9)—N(1)···O(3)	101.1°
C(1)—N(1)···O(3)	136.2°

6.8°, suggesting some π interaction between the phenyl group and the boron atom. The C(12)–B distance is 1.506 Å.

Crystal Structure. The packing arrangements of the crystal viewed along the *b* and *c* axes are shown in Figs. 7 and 8, respectively. The presumed hydrogen bonds are indicated by dashed lines. As shown in Table 5, a strong hydrogen-bond clearly exists between O(3) and O(5) atoms forming a helical chain along the b axis. Although the N(1)···O(3) distance is rather long, the angles lie within possible range to form a hydrogen-bond. There may be weak interaction between them along the *c* axis. These are compatible with the predominant shape of the crystal. There is no unusual short approach in the crystal.

The authors are indebted to Professor Tetsuo Sato for suggesting the problem and continued interest and Mr. Yoshikuni Sato for a gift of the sample.