BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3325—3331 (1970)

The Crystal and Molecular Structure of Bromoanhydrotetrodoic Lactone Hydrobromide

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(Received February 26, 1970)

The absolute configuration of bromoanhydrotetrodoic lactone, $C_{11}H_{14}O_7N_3Br$, has been determined on the basis of an X-ray study of its hydrobromide. The crystals are orthorhombic, with four chemical units in a unit cell of these dimensions: $a=10.88\pm0.04$, $b=15.95\pm0.05$, and $c=8.55\pm0.03$ Å; the space group is $P2_12_12_1$. The observations for Bijvoet inequalities were made on equi-inclination integrating Weissenberg photographs taken with Cu$K\alpha$ radiation around the a axis. On the other hand, the calculations were carried out with the parameters at the stage of the R factor of 11.9% and with anomalous dispersion correction of -0.9 for $\Delta f'_{Br}$ and 1.5 for $\Delta f''_{Br}$. The observed and calculated inequalities for ten pairs of reflections were all in agreement with each other, so the absolute configuration was determined without any uncertainty. In addition to the X-ray determination of the absolute configuration mentioned above, the present paper will describe the details of the crystal and molecular structure.

Tetrodotoxin is well-known as a highly poisonous principle of the puffer fish, but, to say nothing of its molecular structure, even its chemical formula remained uncertain till quite recently. In 1964, through independent investigations, Tsuda *et al.*, Hirata *et al.*, and Woodward *et al.* arrived at the same molecular structure for this poison.[1-3] All their results were based on X-ray structure analyses of halogen-containing derivatives of tetrodotoxin.[3-6] In cooperation with the organic chemical investigation by Hirata *et al.*, the structure of one of the derivatives, bromoanhydrotetrodoic lactone hydrobromide, was studied in our laboratory by means of X-ray methods, an outline of the results having already been published at the stage when the R factor was 15.4%.[6] Although very delayed in publication due partly to the unexpected death of one of the authors, Yujiro Tomiie, the present account will describe the X-ray determination of the absolute structure, which had been already reported at the Third International Symposium on the Chemistry of Natural Products held in Kyoto in 1964, and will discuss in detail the molecular and crystal structure thus obtained.

Structure Determination

The crystal data obtained from the oscillation and Weissenberg photographs taken with Cu$K\alpha$ radiation are summarized in Table 1. The crystal structure was elucidated by means of the minimum-function and Fourier methods, using the 1860 structure factors which were obtained from equi-inclination integrating Weissenberg photographs taken around the a and c axes. The approximate atomic coordinates thus obtained were refined at first by the diagonal-matrix least-squares method, assuming isotropic thermal motions for all the atoms, and then by the block-diagonal-matrix least-squares method, assuming anisotropic thermal motions only for the bromine atoms. The latter

TABLE 1. CRYSTAL DATA

Formula	$C_{11}H_{14}O_7N_3Br\cdot HBr$
Orthorhombic	$a=10.88\pm0.04$Å
	$b=15.95\pm0.05$
	$c=8.55\pm0.03$
Space Group	$P2_12_12_1$
Z	4
D_m	2.03 g/cm³
D_x	2.06 g/cm³

1) K. Tsuda, S. Ikuma, M. Kawamura, R. Tachikawa, K. Sakai, C. Tamura and O. Amakasu, *Chem. Pharm. Bull.*, **12**, 1357 (1964).

2) T. Goto, Y. Kishi, S. Takahashi and Y. Hirata, *Tetrahedron Lett.*, **1964**, 779.

3) R. B. Woodward, "Special Lectures presented at the Third International Symposium on the Chemistry of Natural Products," ed. by IUPAC (1964), p. 49.

4) K. Tsuda, C. Tamura, R. Tachikawa, K. Sakai, O. Amakasu, M. Kawamura and S. Ikuma, *Chem. Pharm. Bull.*, **11**, 1473 (1963); C. Tamura, O. Amakasu, Y. Sasada and K. Tsuda, *Acta Cryst.*, **21**, 219 (1966).

5) K. Tsuda, C. Tamura, R. Tachikawa, K. Sakai, O. Amakasu, M. Kawamura and S. Ikuma, *Chem. Pharm. Bull.*, **12**, 643 (1964); C. Tamura, O. Amakasu, Y. Sasada and K. Tsuda, *Acta Crystallogr.*, **21**, 226 (1966).

6) Y. Tomiie, A. Furusaki, K. Kasami, N. Yasuoka, K. Miyake, M. Haisa and I. Nitta, *Tetrahedron Lett.*, **1963**, 2102.

Table 2. The final atomic parameters

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Br(1)	0.2079	0.1744	0.2944	*	C(2)	−0.1126	0.1345	0.3222	2.29
Br(2)	−0.1065	−0.0752	−0.4579	*	C(4)	−0.0114	0.2161	0.1129	1.97
O(5)	0.2536	0.1175	−0.0839	3.65	C(4a)	0.0963	0.1509	0.1216	2.34
O(6)	−0.0510	0.2097	−0.0427	2.63	C(5)	0.1520	0.1651	−0.0321	2.15
O(7)	0.0675	0.0156	−0.2135	3.04	C(6)	0.0347	0.1588	−0.1323	2.47
O(8)	−0.0588	−0.0461	0.0207	2.95	C(7)	−0.0146	0.0720	−0.1419	2.71
O(9)	0.2305	−0.0112	0.1058	3.37	C(8)	−0.0563	0.0432	0.0153	2.32
O(10)	0.0598	−0.1542	0.0822	5.09	C(8a)	0.0344	0.0634	0.1565	1.84
O(11)	0.1230	0.2674	−0.2987	3.26	C(9)	0.1147	−0.0172	0.1670	2.94
N(1)	−0.0425	0.0720	0.2955	2.99	C(10)	0.0383	−0.0790	0.0745	3.80
N(2)	−0.1944	0.1343	0.4329	3.03	C(11)	0.0461	0.1989	−0.2910	2.67
N(3)	−0.1071	0.2023	0.2215	2.59					

*	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
Br(1)	0.00532	0.00490	0.00917	−0.00157	−0.00228	−0.00280
Br(2)	0.00661	0.00287	0.01098	−0.00069	−0.00113	0.00132

refinement was carried out using a program devised by Yoshiharu Okaya, IBM Thomas Watson Research Center.*1 Thus, the R factor reached a value of 11.9%. The final atomic parameters are given in Table 2. Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.*2

Determination of the Absolute Configuration

The absolute configuration of the present crystal structure was determined by using the anomalous dispersion effects of bromine atoms for Cu$K\alpha$ radiation. For the present point group 222, $|F(h\bar{k}l)|^2$ should be equal to $|F(\bar{h}\bar{k}\bar{l})|^2$ even if the anomalous dispersion effects are taken into account. Accordingly, the intensities of the hkl reflections were compared with those of $h\bar{k}l$ instead of with those of $\bar{h}\bar{k}\bar{l}$ on integrating Weissenberg photographs around the a axis. The observed signs of $\Delta|F(hkl)|^2$'s for ten reflections are listed in Table 3, together with the values calculated, using $\Delta f'_{Br}=-0.9$ and $\Delta f''_{Br}=1.5$, from the final atomic parameters in Table 2. Table 3 clearly shows that the atomic coordinates which have been so far used correspond exactly to the actual absolute configuration.

Table 3. Bijvoet inequalities

h	k	l	$\Delta\|F_o\|^2$	$\Delta\|F_c\|^2$	$\|F_c\|^2$	$\|\Delta\|F_c\|^2/\|F_c\|^2\|$
1	1	5	−	−93	819	0.114
1	2	3	−	−62	396	0.157
1	2	6	−	−76	386	0.197
1	5	5	−	−176	512	0.344
1	9	1	+	+210	1083	0.194
2	1	4	−	−323	1439	0.224
3	9	2	−	−66	231	0.286
3	11	1	−	−131	327	0.401
4	3	5	+	+81	546	0.148
5	3	5	+	+191	1601	0.119

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*2 The complete data of the F_o-F_c table are kept as Document No. 7006 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥500 for photoprints. Pay by check or money order, payable to: The Chemical Society of Japan.

Results and Discussion

Molecular Structure. The framework of the molecular ion of bromoanhydrotetrodoic

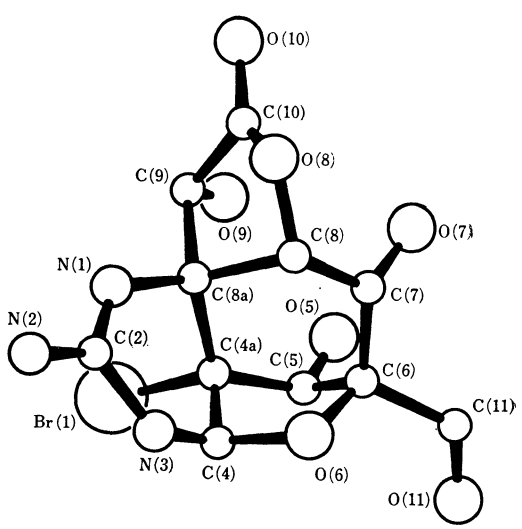

Fig. 1. The framework of the bromoanhydrotetrodoic lactone ion.

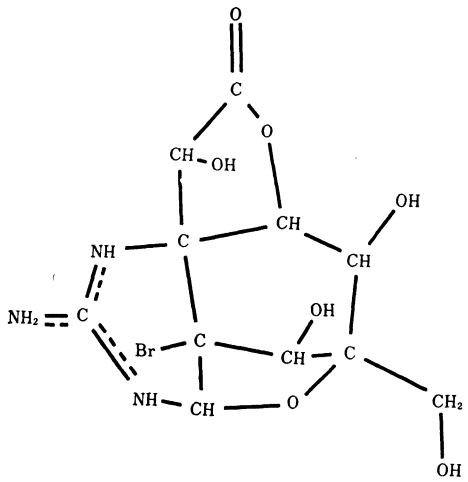

Fig. 2. The structural formula corresponding to Fig. 1.

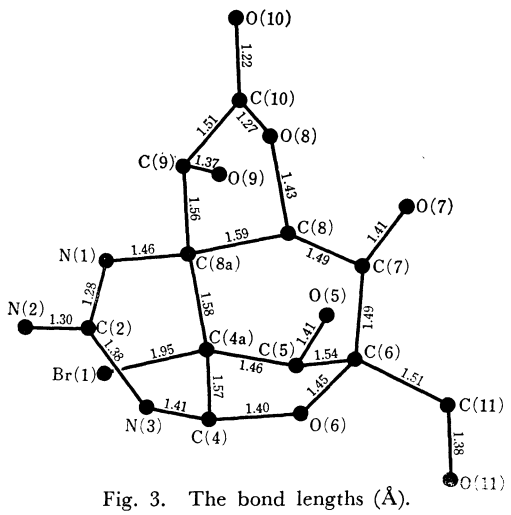

Fig. 3. The bond lengths (Å).

lactone and the corresponding structural formula are shown in Figs. 1 and 2 respectively. The bond lengths and angles calculated from the final atomic coordinates are given, respectively, in Fig. 3 and Table 4. The average standard deviations of the interatomic distances are 0.016 Å for C–Br, 0.021 Å for C–O, 0.022 Å for C–N, and 0.023 Å for C–C. Considering these standard deviations, the molecular dimensions calculated are all reasonable, except for the C(10)–C(8) bond distance (1.27 Å).

The skeleton of the present molecular ion is composed of two six-membered and two five-membered rings. One of the first two rings is heterocyclic, with two nitrogen atoms of a guanidinium group, while the other is homocyclic, with a somewhat distorted chair form. These two rings are joined to each other in the *cis* configuration. On the other hand, both of the five-membered rings are heterocyclic; one of them is a γ-lactone ring attached in the *cis* configuration to the second of the six-membered rings mentioned above, while the other contains an ethereal oxygen atom which bridges, additionally, the two fused six-membered rings. Since, moreover, a bromine atom, a hydroxymethyl group, and three hydroxyl groups are connected to the skeleton, the molecular ion assumes quite a complicated stereostructure and includes very close interatomic contacts. Such intramolecular contacts are listed in Table 5, together with the distances.

Table 4. The bond angles (°)

N(1)-C(2)-N(2)	122	C(6)-C(7)-O(7)	113
N(1)-C(2)-N(3)	118	C(8)-C(7)-O(7)	113
N(2)-C(2)-N(3)	119	C(7)-C(8)-C(8a)	116
N(3)-C(4)-C(4a)	115	C(7)-C(8)-O(8)	110
N(3)-C(4)-O(6)	113	C(8a)-C(8)-O(8)	101
C(4a)-C(4)-O(6)	103	C(8)-C(8a)-N(1)	106
C(4)-C(4a)-C(5)	99	C(8)-C(8a)-C(4a)	107
C(4)-C(4a)-C(8a)	106	C(8)-C(8a)-C(9)	103
C(4)-C(4a)-Br(1)	112	C(9)-C(8a)-N(1)	110
C(5)-C(4a)-C(8a)	119	C(9)-C(8a)-C(4a)	120
C(5)-C(4a)-Br(1)	113	C(4a)-C(8a)-N(1)	108
C(8a)-C(4a)-Br(1)	107	C(8a)-C(9)-C(10)	101
C(4a)-C(5)-C(6)	98	C(8a)-C(9)-O(9)	116
C(4a)-C(5)-O(5)	121	C(10)-C(9)-O(9)	111
C(6)-C(5)-O(5)	116	C(9)-C(10)-O(8)	112
C(5)-C(6)-C(7)	113	C(9)-C(10)-O(10)	120
C(5)-C(6)-C(11)	114	O(8)-C(10)-O(10)	126
C(5)-C(6)-O(6)	102	C(6)-C(11)-O(11)	115
C(7)-C(6)-C(11)	112	C(4)-O(6)-C(6)	110
C(7)-C(6)-O(6)	109	C(8)-O(8)-C(10)	114
C(11)-C(6)-O(6)	107	C(2)-N(1)-C(8a)	124
C(6)-C(7)-C(8)	110	C(2)-N(3)-C(4)	124

Table 5. Intramolecular non-bonded distances (Å)

Br(1)···O(5)	3.39	O(7)···C(11)	3.01
Br(1)···O(9)	3.38	O(8)···N(1)	3.02
Br(1)···N(1)	3.18	O(9)···C(5)	3.17
Br(1)···N(3)	3.50	O(11)···C(5)	2.82
Br(1)···C(9)	3.40	N(1)···C(4)	2.80
O(5)···O(7)	2.82	N(1)···C(10)	3.18
O(5)···O(9)	2.63*	N(3)···C(8a)	2.75
O(5)···C(8a)	3.26	C(2)···C(8)	3.06
O(5)···C(9)	3.39	C(2)···C(4a)	2.86
O(5)···C(11)	3.15	C(4)···C(8)	2.92
O(6)···O(11)	3.03	C(4a)···C(9)	2.72
O(6)···C(8a)	3.03	C(5)···C(8)	3.01
O(7)···O(8)	2.62	C(5)···C(9)	3.39
O(7)···O(9)	3.28	C(6)···C(8a)	2.90
O(7)···C(8a)	3.27	C(7)···C(9)	3.31
O(7)···C(9)	3.33	C(7)···C(10)	3.09
O(7)···C(10)	2.90		

* hydrogen-bonded

The guanidinium group is almost planar, and C(4) and C(8a) are apart from the mean plane of this group by about 0.23 and 0.22 Å respectively; C(4) is on the same side of the plane as the C(4a) atom, while C(8a) is on the opposite side.

The hydroxyl oxygen atoms, O(5) and O(7), are both attached in the axial orientation to the cyclohexane ring of the chair form; consequently, these atoms are very close to each other, their distance being about 2.82 Å. Though this distance may be taken numerically to correspond to the hydrogen bonding, it is not so, as will be described later. Further, O(5) and O(7) approach closely to the hydroxyl oxygen O(9) and the lactone oxygen O(8) respectively. The former contact occurs at a distance of 2.63 Å and corresponds to an intramolecular hydrogen bond. On the other hand, the latter contact, although the distance is also very small, 2.62 Å, and although the azimuthal angle between C(7)–O(7) and C(8)–O(8) around C(7)–C(8) is only about 31° which is small considering that O(7) and O(8) occupy roughly the axial and equatorial positions of the cyclohexane ring, is not due to hydrogen-bond formation, but to the distortion of the ring. This point will be explained later.

The lactone ring deviates considerably from a planar structure. The distances of the atoms from the mean plane through the four atoms, C(9), C(10), O(8), and O(10), are given in Fig. 4. From this figure, it is found that the lactone ring takes a conformation close to the half-chair form. In this molecule, such a ring conformation seems to favor to some degree the relaxation of the repulsions between Br(1) and O(9) and between O(7) and O(8).

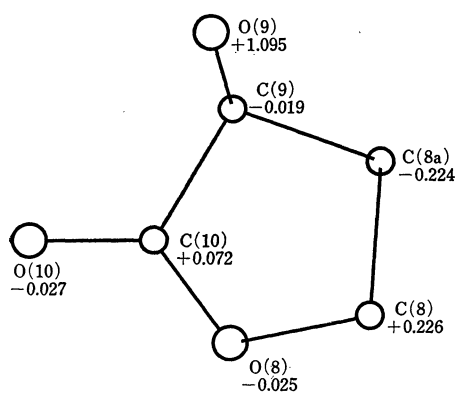

Fig. 4. The deviations from the mean plane through C(9), C(10), O(8) and O(10).

The five-membered ethereal ring takes a conformation of the envelope type; C(4), C(4a), C(6), and O(6) are nearly coplanar, and the remaining C(5) is considerably apart from the mean plane of the first four atoms. The deviations of the atoms from the plane are shown in Fig. 5.

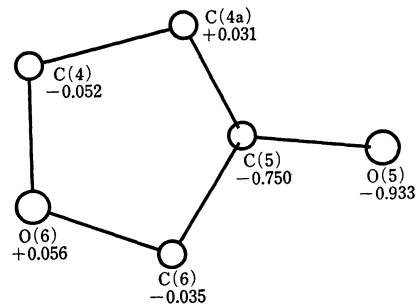

Fig. 5. The deviations from the mean plane through C(4), C(4a), C(6) and O(6).

The hydroxymethyl group is linked to the C(6) of the cyclohexane ring in the equatorial orientation. The C(11)–O(11) bond makes azimuthal angles of about 32° with C(5)–C(6) and 100° with C(6)–O(6) around C(6)–C(11). Consequently, O(11) is much closer to C(5) than to O(6), in spite of the larger van der Waals radius of the former, the O(11)—C(5) distance being only about 2.82 Å.

Crystal Structure. The projections of the present crystal structure along the *a* and *c* axes are shown in Figs. 6 and 7 respectively. The molecular and bromide ions are connected by several hydrogen bonds, forming a three-dimensional hydrogen-bonded structure. Each bromide ion makes three hydrogen bonds with its adjacent molecular ions; one is formed with O(7) at a distance of 3.17 Å; another, with O(11) at 3.34 Å, and the remaining one, with N(1) at 3.23 Å. Besides these, each molecular ion forms four additional hydrogen bonds; one of them is the O(5)–H···O(9) intramolecular bond, as has already been mentioned. The remaining three hydrogen bonds, N(2)–H···O(11′), N(3)–H···O(10″), and O(9)–H···O(7‴), connect molecular ions around screw axes along the *a*, *b*, and *c* axes respectively, their distances being 2.78, 2.88, and 2.69 Å respectively. As for the first two of these, if the protons of the nitrogen atoms are in the plane of the guanidinium group, it follows that they are considerably off the hydrogen bond directions.

It has been mentioned already, without any explanation, that neither of the intramolecular close approaches, O(7)···O(8) and O(5)···O(7), is due to hydrogen bonding. This may be explained as follows. As for the former approach, since O(7) donates its proton to the bromide ion to form the O(7)–H···Br(2) hydrogen bond, while O(8) has no proton, these two oxygen atoms can not make a hydrogen bond with each other. On the other hand, as for the latter approach, if O(5) forms a hydrogen bond with O(7), the proton donor in this bond should be the former oxygen for the same reason. Therefore, in this case, the O(5)···O(9) approach can not be accepted as a

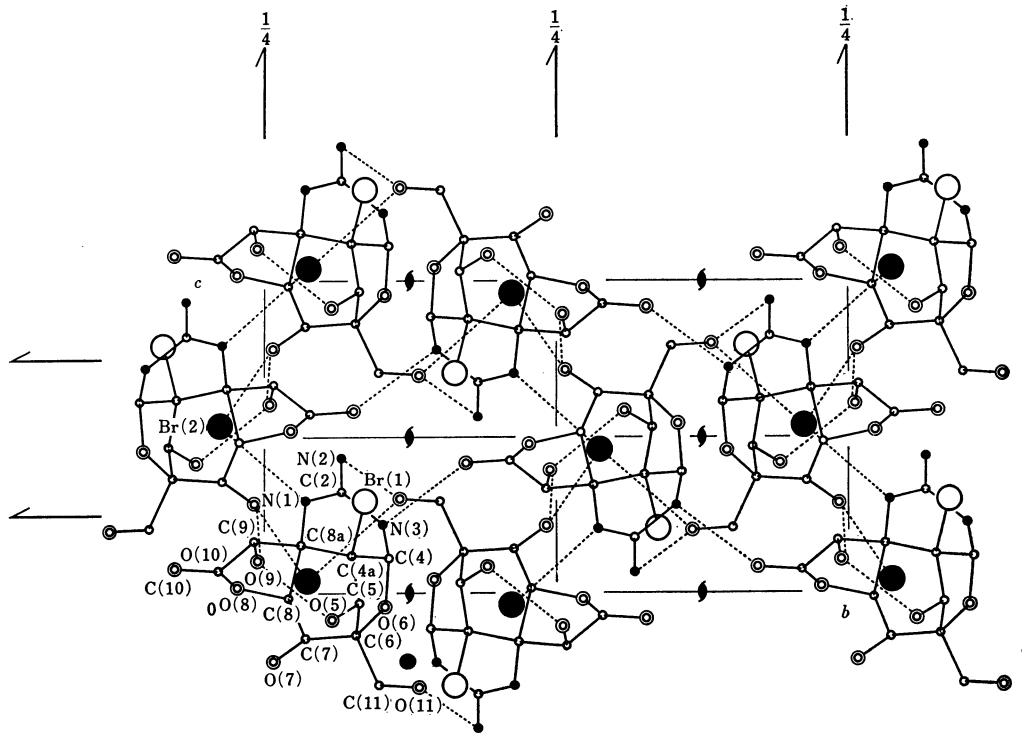

Fig. 6. The crystal structure viewed down along the *a* axis.

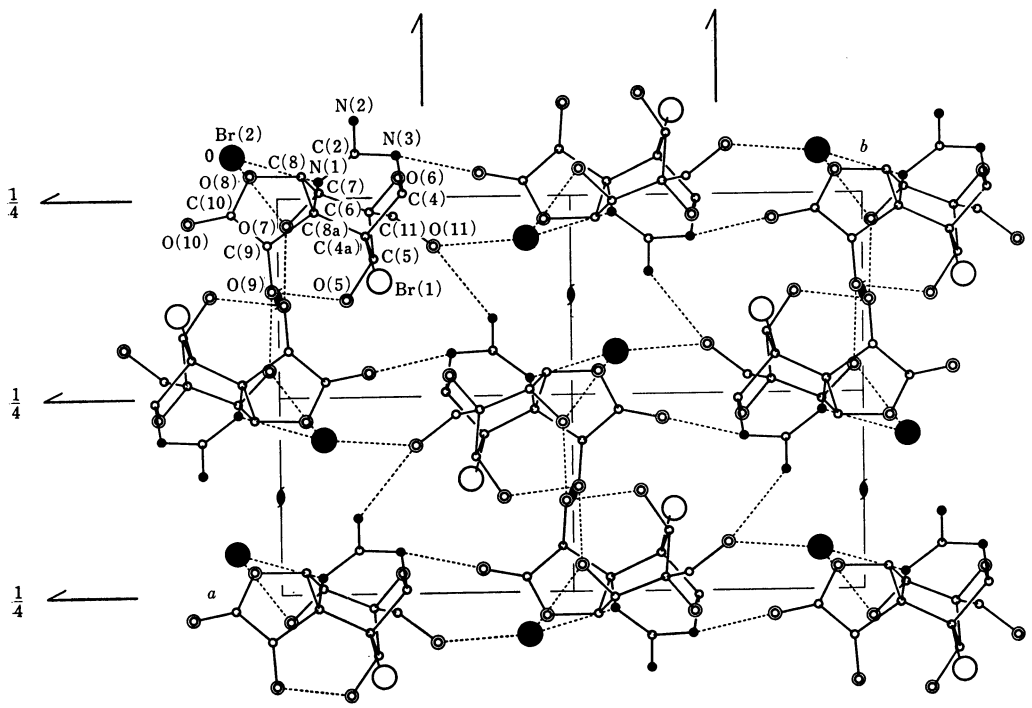

Fig. 7. The crystal structure viewed down along the *c* axis.

Table 6. Intermolecular distances (Å) smaller than 4.0 Å

Atom of I	Atom	Molecule	Distance	Atom of I	Atom	Molecule	Distance
Br(1)	O(6)	IV (0, 1, 0)**	3.86		C(11)	III (0, 0, −1)	3.61
	O(7)	II	3.89	O(11)	Br(1)	I (0, 0, −1)	3.89
	O(9)	II	3.78		Br(2)	III (0, 1, −1)	3.34*
	O(10)	II	3.54		O(8)	III (0, 1, −1)	3.60
	O(11)	I (0, 0, 1)	3.89		O(10)	III (0, 1, −1)	3.37
	N(2)	IV (0, 1, 1)	3.98		N(2)	IV (0, 1, 0)	2.78*
	C(10)	II	3.96		N(3)	IV (0, 1, 0)	3.05
	C(11)	I (0, 0, 1)	3.97		C(2)	IV (0, 1, 0)	3.28
Br(2)	O(6)	III (0, 0, −1)	3.83		C(10)	III (0, 1, −1)	3.83
	O(7)	I	3.17*	N(1)	Br(2)	I (0, 0, 1)	3.23*
	O(11)	III (0, 0, −1)	3.34*	N(2)	Br(1)	IV (−1, 1, 1)	3.98
	N(1)	I (0, 0, −1)	3.23*		Br(2)	I (0, 0, 1)	3.60
	N(2)	I (0, 0, −1)	3.60		O(8)	II (−1, 0, 0)	3.12
	C(2)	I (0, 0, −1)	3.84		O(10)	III (0, 1, 0)	3.68
	C(2)	II (−1, 0, −1)	3.99		O(11)	IV (−1, 1, 0)	2.78*
	C(4)	III (0, 0, −1)	3.80		C(8)	II (−1, 0, 0)	3.98
	C(7)	I	3.71		C(11)	I (0, 0, 1)	3.67
	C(8)	II (−1, 0, −1)	3.71	N(3)	O(5)	IV (−1, 1, 0)	3.45
O(5)	O(6)	IV (0, 1, 0)	3.64		O(10)	III (0, 1, 0)	2.88*
	O(9)	II (0, 0, −1)	3.15		O(11)	IV (−1, 1, 0)	3.05
	O(10)	II (0, 0, −1)	3.55		C(5)	IV (−1, 1, 0)	3.74
	N(3)	IV (0, 1, 0)	3.45		C(10)	III (0, 1, 0)	3.97
	C(4)	IV (0, 1, 0)	3.69	C(2)	Br(2)	I (0, 0, 1)	3.84
	C(9)	II (0, 0, −1)	3.02		Br(2)	II (−1, 0, 0)	3.99
	C(10)	II (0, 0, −1)	3.74		O(10)	III (0, 1, 0)	3.51
O(6)	Br(1)	IV (−1, 1, 0)	3.86		O(11)	IV (−1, 1, 0)	3.28
	Br(2)	III (0, 1, −1)	3.83		C(11)	I (0, 0, 1)	3.87
	O(5)	IV (−1, 1, 0)	3.64	C(4)	Br(2)	III (0, 1, −1)	3.80
	C(5)	IV (−1, 1, 0)	3.85		O(5)	IV (−1, 1, 0)	3.69
O(7)	Br(1)	II (0, 0, −1)	3.89		O(10)	III (0, 1, 0)	3.37
	Br(2)	I	3.17*	C(5)	O(6)	IV (0, 1, 0)	3.85
	O(9)	II (0, 0, −1)	2.69*		N(3)	IV (0, 1, 0)	3.74
	C(9)	II (0, 0, −1)	3.60	C(7)	Br(2)	I	3.71
O(8)	O(11)	III (0, 0, −1)	3.60		O(9)	II (0, 0, −1)	3.89
	N(2)	II (−1, 0, −1)	3.12	C(8)	Br(2)	II (−1, 0, 0)	3.71
O(9)	Br(1)	II (0, 0, −1)	3.78		N(2)	II (−1, 0, −1)	3.98
	O(5)	II	3.15	C(9)	O(5)	II	3.02
	O(7)	II	2.69*		O(7)	II	3.60
	C(7)	II	3.89	C(10)	Br(1)	II (0, 0, −1)	3.96
	C(11)	II	3.95		O(5)	II	3.74
O(10)	Br(1)	II (0, 0, −1)	3.54		O(11)	III (0, 0, −1)	3.83
	O(5)	II	3.55		N(3)	III	3.97
	O(11)	III (0, 0, −1)	3.37	C(11)	Br(1)	I (0, 0, −1)	3.97
	N(2)	III	3.68		O(9)	II (0, 0, −1)	3.95
	N(3)	III	2.88*		O(10)	III (0, 1, −1)	3.61
	C(2)	III	3.51		N(2)	I (0, 0, −1)	3.67
	C(4)	III	3.37		C(2)	I (0, 0, −1)	3.87

I: x, y, z (given in Table 2)
II: $a/2-z, -y, c/2+z$
III: $-x, -b/2+y, c/2-z$
IV: $a/2+x, -b/2-y, -z$
* These are corresponding to a hydrogen-bonded approach.
** (l, m, n) shows a translational transformation, $(la+x, mb+y, nc+z)$, to be further applied to I, II, III or IV.

hydrogen bond, because, if it is so assumed, O(9) would donate a proton to O(5) and, consequently, could not form the O(9)···O(7‴) intermolecular hydrogen bond. If, on the contrary, O(5) forms a hydrogen bond with O(9), it follows that O(5) does not form one with O(7). Thus, it is the key to the present problem which of the two hydroxyl oxygens, O(7) and O(9), forms a hydrogen bond with O(5). Considering the facts that the distance between O(5) and O(9) is much smaller than that between O(5) and O(7), and that the C(5)–O(5)··· O(9) angle, 99°, is closer to the H–O–H angle, 104.5°, of a water molecule in the gas phase than to that of C(5)–O(5)···O(7), 83°, the latter possibility, *i.e.*, O(5)–H···O(9), seems to be more probable, though the evidence is not quite conclusive.

Intermolecular distances smaller than 4.0 Å in the present crystal are listed in Table 6. These values are all reasonable except for the distance of 3.02 Å between C(9) of the I molecule and O(5) of II. This approach may be called a kind of hydrogen bonding, since C(9) is expected to carry a considerable amount of positive charge because of the existence of two more electronegative groups, a hydroxyl and a lactone group. This view is also supported by the fact that the estimated position of the hydrogen atom at C(9) is not far off the C(9)···O(5) line; the C(9)–H bond and the C(9)···O(5) line make an angle of only about 28°, and hence the atomic distance between H and O(5) is no more than 2.12 Å.*3 As may be seen from Table 6, each bromide ion Br(2) is surrounded by four molecular ions. Of these four, three approach the anion by hydrogen bonds, as has already been mentioned. As for the remaining one, the smallest interatomic distance, 3.71 Å, is found between Br(2) and C(8). This value is somewhat smaller than the sum of the van der Waals radii, 3.95 Å.

In conclusion, the authors would like to express their hearty thanks to Professor Yoshimasa Hirata, Nagoya University, for providing them with the samples. The authors also wish to express their thanks to Professor Yoshiharu Okaya, State University of New York at Stony Brook, for his kind help in the structure refinement.

*3 In the estimation of the position of the H atom, it was assumed that the four unit vectors from C(9) to C(8a), C(10), O(9), and H are in tetrahedral directions and that the atomic distance between C(9) and H is 1.09 Å.