The bromine ion on one plane is situated directly above the pyrimidine ring of uracil on the plane below. The distances are as follows: Br–N(1) 3·45 Å, Br–C(6) 3·65 Å, Br–C(5) 3·82 Å, Br–C(4) 3·78 Å, Br–N(3) 3·59 Å, Br–C(2) 3·43 Å. If one considers the half thickness of the aromatic molecule to be 1·7 Å, and the ionic radius of bromine to be 1·95 Å, it is evident that the observed distance of 3·43 Å must reflect a shortening of the carbon van der Waals radius in the direction of the center of the pyrimidine ring. The Br–N(1) distance of 3·45 Å is considerably shorter than the other bromine–light atom distances. This may be due to electrostatic interaction between the bromine ion and the positively charged nitrogen N(1) atom associated with resonant form (I).

The O(2) oxygen of an adjacent molecule is roughly equidistant from C(6) and C(5), the O(2) · · · C(6) distance being 3·12 Å and the O(2) · · · C(5) distance 3·05 Å. The angle subtended by atoms

C(4)–O(4) · · · Br(1)

is 115·3°, which is in good agreement with the C–O · · · O angle of 114° found in formic acid (Jones & Templeton, 1958).

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The Crystal Structures of Salts of Methylated Purines and Pyrimidines.
IV. 9-Methylguanine Hydrobromide

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Crystals of 9-methylguanine hydrobromide are monoclinic, with $a = 4·54$, $b = 17·46$, and $c = 10·68$ Å, $\gamma = 90°$. The space group is $P2_1/b$ with four molecules per unit cell. The molecular structure has been determined by the heavy atom method and refined isotropically and anisotropically by the least-squares method using partial three-dimensional data. Bond lengths and angles are given; the estimated standard deviations for bond lengths and angles involving light atoms are 0·03 Å and 2° respectively. The acidic proton has been identified as being attached directly to the purine ring at N(7). The crystal structure is quite interesting in that the bromide ions are stacked one on another to form neighboring pairs of infinite columns through the crystal. Each pair of bromide columns is surrounded in turn by six columns consisting of guanine molecules stacked 3·37 Å apart in a tilted arrangement. Each guanine molecule participates in two hydrogen bonds of the N–H · · · Br involving the ring nitrogen N(7) and the amino nitrogen N(10), forming a continuous zigzag hydrogen bonded network along the *c* axis. There are no inter-purine hydrogen bonds formed.

Introduction

This is the fourth in a series of articles describing the crystal structures of salts of the methylated purines and pyrimidines. The purpose of these studies was to investigate the nature of hydrogen bonding in crystal structures of nucleic acid derivatives and to relate this to hydrogen bonding in polynucleotide fibers drawn in acidic solution. It was of particular interest to ascertain the first site of protonation on the guanine molecule and to determine the predominant resonant

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forms of the molecule. With this in mind, the crystal and molecular structure of 9-methylguanine hydrobromide was determined by three-dimensional X-ray diffraction methods and the results are described below.

Experimental

Crystals of 9-methylguanine hydrobromide were prepared by adding an excess of concentrated hydrobromic acid to a powder preparation of 9-methylguanine[*] and allowing the solution to evaporate to dryness at room temperature. A crystal suitable for X-ray analysis, approximately 0·10 mm × 0·15 mm × 0·4 mm, was mounted on a thin glass needle and used subsequently to collect all the data for this crystal determination. The unit-cell dimensions and space group were determined by 30° precession photographs with Cu $K\alpha$ radiation. Intensity data were collected at room temperature on an equi-inclination Weissenberg camera for the zero, first, and second layers around the a axis, the multiple film technique being used. Intensities were then estimated visually with a calibrated standard scale obtained by recording different time exposures of a selected single reflection. Lorentz polarization corrections were applied but no absorption correction was made. 181 ($0kl$), 312 ($1kl$), and 290 ($2kl$) non-zero reflections were recorded from the theoretical number of 246 ($0kl$), 476 ($1kl$), and 374 ($2kl$) reflections available.

Crystal data

9-Methylguanine hydrobromide, $C_6H_7N_5O.HBr$, mol.wt. 245·9.

Monoclinic

$a=4{\cdot}54\pm0{\cdot}01$, $b=17{\cdot}46\pm0{\cdot}01$, $c=10{\cdot}68\pm0{\cdot}08$ Å; $\gamma=90°$.

Volume of unit cell: 846·6 Å^3, $D_m=1{\cdot}933$ g.cm^{-3}, $Z=4$, $D_x=1{\cdot}940$ g.cm^{-3}. $F(000)=488$, Space group $P2_1/b$.

Structure determination

The structure was solved by the heavy atom method first in two dimensions, and then in three dimensions. The y and z coordinates for the bromide ion were obtained by locating the Br–Br peaks on the ($0kl$) Patterson function and found to be $y=0{\cdot}1375$ and $z=0{\cdot}1077$. The phases calculated from the bromide position were then used for the first (100) Fourier synthesis (Fig. 1). All the light atom peaks could be

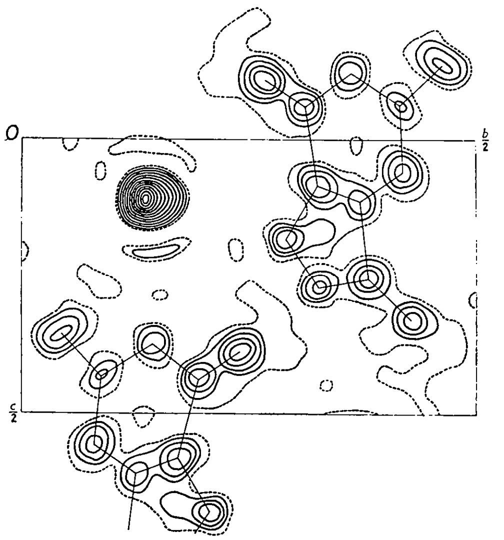

Fig. 1. First Fourier (100) synthesis using bromine phases only, showing the position of the bromide ion and light atoms. Contours are drawn at equal but arbitrary levels of electron density.

Table 1. *Final atomic coordinates expressed as fraction coordinates after anisotropic least-squares refinement*

Atom	x/a	y/b	z/c
N1	0·9838	0·1447	0·3786
C2	0·7982	0·0879	0·4308
N3	0·2119	0·4243	0·0533
C4	0·0123	0·3781	0·1178
C5	0·8593	0·3212	0·0746
C6	0·1671	0·1940	0·4437
N7	0·7080	0·2896	0·1748
C8	0·8010	0·3265	0·2776
N9	0·9799	0·3802	0·2474
C9	0·1402	0·4323	0·3345
O6	0·3101	0·2397	0·3894
N10	0·6337	0·0467	0·3526
Br	0·3118	0·1366	0·1072

Table 2. *Final anisotropic thermal parameters after least-squares refinement*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N1	0·0560	0·0012	0·0038	−0·0015	−0·0022	−0·0010
C2	0·0229	0·0020	0·0034	−0·0042	0·0027	0·0004
N3	0·0528	0·0014	0·0037	−0·0036	0·0005	0·0000
C4	0·0657	0·0010	0·0051	−0·0019	−0·0027	0·0002
C5	0·0835	0·0018	0·0035	−0·0043	0·0012	0·0004
C6	0·1130	0·0010	0·0036	0·0036	−0·0020	0·0003
N7	0·0617	0·0014	0·0039	−0·0006	0·0018	0·0003
C8	0·1156	0·0011	0·0036	0·0052	0·0055	0·0001
N9	0·0812	0·0009	0·0029	−0·0015	0·0013	−0·0003
C9	0·0423	0·0021	0·0031	−0·0069	−0·0032	−0·0006
O6	0·0740	0·0024	0·0061	−0·0083	0·0009	0·0003
N10	0·1492	0·0014	0·0039	−0·0025	−0·0105	−0·0002
Br	0·1082	0·0021	0·0027	−0·0043	−0·0012	0·0003

[†] Obtained from the Cyclo Chemical Corporation, Los Angeles, California.

Table 3. *Observed and calculated structure factors*

0	k	l	F_o	F_c
0	0	2	15.1	21.5
	0	4	118.3	-147.4
	0	6	76.6	-79.7
	0	8	42.8	41.8
	0	10	35.7	31.0
	1	1	20.4	18.7
	1	2	55.3	-61.6
	1	3	33.4	-29.0
	1	4	28.4	-25.9
	1	5	29.1	-28.1
	1	6	36.3	38.8
	1	8	32.1	32.9
	1	9	44.4	45.6
	1	11	25.0	22.7
	1	12	35.5	-36.2
	1	13	15.9	-18.2
	2	0	54.1	-58.8
	2	1	29.3	-27.9
	2	2	3.4	-1.7
	2	3	97.6	-141.5
	2	4	25.0	21.6
	2	5	41.9	43.3
	2	6	25.0	22.6
	2	7	73.2	75.5
	2	8	6.7	-7.4
	2	9	14.8	14.9
	2	10	21.0	-18.7
	2	11	51.5	-49.6
	2	13	14.0	-14.3
	3	1	26.9	-22.5
	3	2	49.7	-50.9
	3	3	32.0	29.8
	3	4	69.1	-66.1
	3	5	51.1	48.9
	3	6	35.0	32.7
	3	8	45.3	43.9
	3	9	53.7	-55.9
	3	10	30.5	-28.2
	3	11	4.3	-10.7
	3	12	27.7	-25.5
	3	13	15.7	19.2
	4	0	141.4	-161.1
	4	2	20.0	-15.6
	4	3	52.4	47.9
	4	4	64.4	68.5
	4	6	76.4	73.3
	4	7	18.8	-18.1
	4	8	47.7	-49.2
	4	10	41.9	-38.4
	4	11	16.3	16.6
	4	12	3.6	9.5
	5	1	47.7	-41.4
	5	2	109.4	130.2
	5	3	32.8	33.2
	5	4	36.4	34.5
	5	5	31.9	27.7
	5	6	77.6	-77.9
	5	8	43.7	-41.7
	5	9	6.5	-8.1
	5	10	13.5	13.6
	5	11	19.7	-19.0
	5	12	35.1	35.9
	5	13	2.8	9.7
	6	0	16.5	17.7
	6	1	61.6	48.3
	6	2	5.5	5.4
	6	3	77.9	77.8
	6	4	22.9	-19.7
	6	5	29.2	-26.3
	6	6	24.7	-22.8
	6	7	40.3	-41.6
	6	8	22.8	22.3
	6	9	29.1	-27.3
	6	10	25.9	24.6
	6	11	35.9	36.9
	6	13	19.5	22.0
	7	1	94.4	100.0
	7	2	34.3	29.9
	7	3	26.8	-25.1
	7	4	16.2	10.0
	7	5	64.0	-65.8
	7	6	11.4	-9.5
	7	7	17.5	-17.7
	7	9	34.1	32.5
	7	10	17.1	15.9
	7	11	12.7	14.5
	8	0	56.0	52.6
	8	1	56.6	-50.2
	8	3	41.3	-39.2
	8	4	67.0	-66.2
	8	5	35.5	35.2
	8	6	46.7	-48.6
	8	7	26.5	26.0
	8	8	60.4	63.7
	8	10	51.3	47.1
	8	11	20.6	-20.0
	8	12	8.8	-10.2
	9	1	4.2	5.5
	9	2	61.2	-56.5
	9	3	20.1	-16.3
	9	4	33.0	-31.9
	9	5	17.6	-19.1
	9	6	37.1	35.6
	9	8	44.1	41.8
	9	10	13.4	-14.7
	9	12	25.3	-27.6
	10	1	42.2	-40.6
	10	3	69.0	-63.7
	10	4	65.8	66.1
	10	5	11.4	9.6
	10	6	13.7	14.5
	10	7	35.1	33.8
	10	8	43.5	-41.3
	10	9	12.7	12.5
	10	10	28.2	-28.4
	10	11	23.6	-25.2
	10	12	10.2	11.3
	11	1	56.6	-53.7
	11	2	28.8	-25.9
	11	3	8.9	5.2
	11	4	24.8	-23.6
	11	5	52.2	58.0
	11	6	14.2	14.5
	11	7	21.8	21.8
	11	9	22.8	-22.9
	11	11	19.1	-19.4
0	k	l	F_o	F_c
0	12	0	41.1	-45.4
	12	1	46.3	44.2
	12	2	3.6	-9.1
	12	3	41.4	42.6
	12	4	37.0	36.6
	12	5	16.9	-17.6
	12	7	57.2	-57.7
	12	8	29.0	-27.9
	12	10	17.5	-16.2
	12	11	29.0	31.1
	13	2	52.8	57.7
	13	3	12.8	-13.2
	13	4	19.5	19.2
	13	6	28.5	-28.5
	13	8	38.4	-38.3
	13	10	15.6	15.8
	14	0	42.5	45.2
	14	2	13.4	13.6
	14	3	21.2	23.4
	14	4	42.6	-44.5
	14	8	5.7	13.8
	14	9	3.9	-5.5
	14	10	17.6	20.9
	15	1	32.3	31.3
	15	2	12.9	-15.2
	15	3	19.2	-21.8
	15	5	41.6	-42.7
	15	9	24.3	27.1
	16	0	34.6	34.1
	16	1	24.9	-27.2
	16	3	29.5	-30.1
	16	4	10.8	-11.8
	16	6	18.6	-19.2
	16	7	41.7	42.4
	16	8	11.6	9.4
	17	2	31.4	-33.4
	17	4	15.6	-15.9
	17	5	22.9	24.0
	17	6	20.9	22.2
	17	8	19.2	20.1
	18	0	39.5	-37.1
	18	2	24.1	-23.0
	18	4	28.8	32.9
	18	6	21.6	21.8
	19	3	18.7	19.5
	19	4	5.3	8.2
	19	5	6.7	11.4
	20	0	9.4	-11.1
	20	1	33.0	33.7
	20	3	26.0	29.1
	21	2	18.6	21.0
	21	4	15.2	15.1
	22	0	17.7	21.1
	22	1	18.0	17.8
	22	2	6.7	8.4
1	0	0	36.7	-40.3
	0	1	43.3	-40.1
	0	2	13.8	-12.9
	0	3	87.8	-112.3
	0	4	37.9	32.4
	0	5	9.3	11.8
	0	6	7.5	5.4
	0	7	58.3	63.7
	0	10	25.7	-23.2
	0	11	45.4	-43.1
	0	12	13.5	2.4
	0	13	15.8	-17.7
	1	1	59.6	-73.3
	1	2	59.8	-57.9
	1	3	11.0	-8.7
	1	4	4.1	-5.5
	1	5	76.4	84.4
	1	6	37.1	36.3
	1	7	14.6	12.8
	1	8	17.9	14.3
	1	9	59.3	-63.6
	1	12	13.5	-11.7
	1	13	23.9	26.7
	2	0	86.2	-92.0
	2	1	56.7	61.5
	2	2	7.3	-3.9
	2	3	52.2	55.9
	2	4	56.3	58.4
	2	6	49.6	48.3
	2	7	58.9	-58.8
	2	8	42.3	-38.6
	2	10	45.4	-42.0
	2	11	12.7	16.6
	2	12	10.8	11.4
	2	13	11.2	12.2
	3	1	39.2	-42.9
	3	2	79.4	96.3
	3	3	7.5	3.4
	3	4	52.1	45.0
	3	5	15.5	13.7
	3	6	57.8	-60.6
	3	7	16.8	16.1
	3	8	49.2	-48.1
	3	12	35.5	43.7
	4	0	87.7	102.9
	4	1	75.9	63.3
	4	2	36.6	36.5
	4	3	58.0	55.7
	4	4	42.8	-41.8
	4	5	42.9	-40.7
	4	6	17.8	-17.9
	4	7	27.0	-28.7
	4	8	17.6	16.7
	4	10	15.1	16.8
	4	11	24.9	24.0
	4	13	16.0	17.7
	5	1	79.1	79.4
	5	2	14.4	10.6
	5	3	73.1	-74.3
	5	4	9.3	7.7
	5	5	90.9	-76.7
	5	6	9.9	-8.4
	5	7	34.5	-8.9
	5	8	6.6	-8.3
	5	9	72.4	72.6
	5	11	24.4	20.0
	5	13	27.9	-32.8
1	k	l	F_o	F_c
1	6	0	69.8	59.4
	6	1	17.7	-19.2
	6	2	13.2	13.7
	6	3	27.3	-27.6
	6	4	54.5	-59.7
	6	6	30.4	-29.0
	6	7	45.5	47.7
	6	8	40.2	35.6
	6	10	30.3	28.7
	6	11	22.2	-21.7
	6	13	12.5	-18.6
	7	1	21.2	-18.0
	7	2	65.8	-67.3
	7	3	59.4	56.1
	7	4	62.1	-64.4
	7	5	15.7	14.4
	7	6	47.7	47.4
	7	7	29.4	28.5
	7	8	46.5	43.2
	7	9	30.6	-27.8
	7	10	22.5	-22.0
	7	12	26.7	-29.2
	8	0	63.7	-58.9
	8	1	57.6	-48.0
	8	2	54.4	-46.2
	8	3	45.1	-45.1
	8	4	39.2	38.5
	8	5	22.2	20.5
	8	6	49.3	45.0
	8	7	63.7	55.7
	8	10	33.5	-30.3
	8	11	30.9	-28.5
	9	1	58.8	-52.8
	9	2	26.2	21.6
	9	3	52.3	52.4
	9	4	13.0	13.8
	9	5	48.0	45.8
	9	6	30.7	-29.2
	9	7	15.2	14.4
	9	9	39.5	-36.6
	9	11	13.6	-15.2
	10	0	41.9	-44.6
	10	1	59.8	57.5
	10	2	13.7	-10.9
	10	3	52.2	55.0
	10	4	38.8	38.0
	10	5	11.1	-9.8
	10	7	61.6	-61.6
	10	10	20.1	-16.3
	10	11	30.1	30.1
	11	1	24.7	21.5
	11	2	53.3	50.6
	11	3	13.7	-9.3
	11	4	20.2	16.7
	11	5	13.3	-13.4
	11	6	26.5	-23.4
	11	8	26.0	-23.0
	11	9	20.7	18.4
	11	10	13.3	13.3
	11	11	27.0	1.7
	12	0	40.8	41.8
	12	2	17.8	16.4
	12	3	9.1	12.4
	12	4	51.5	-56.3
	12	5	15.2	-14.6
	12	6	16.9	-19.0
	12	7	36.1	-30.8
	12	8	22.2	22.2
	12	10	34.3	35.3
	12	11	12.1	11.9
	13	1	48.2	41.7
	13	2	29.4	-28.1
	13	3	17.7	-14.5
	13	4	9.5	-9.3
	13	5	57.7	-55.3
	13	6	22.3	18.8
	13	8	16.5	14.9
	13	9	36.5	34.6
	14	0	15.0	14.7
	14	1	47.6	-49.4
	14	2	13.6	14.5
	14	3	46.0	-43.8
	14	7	46.0	42.8
	15	1	43.5	-41.5
	15	2	19.4	-20.0
	15	5	42.5	44.0
	15	6	17.1	17.4
	15	8	20.5	21.7
	15	9	19.3	-22.9
	16	0	16.9	-17.5
	16	1	25.7	-23.6
	16	3	18.0	-16.2
	16	4	42.2	38.3
	16	8	18.1	-18.3
	17	2	42.2	37.2
	17	5	22.4	21.5
	17	6	21.3	-22.1
	17	8	13.8	-16.5
	18	1	45.1	42.6
	18	3	38.6	37.6
	18	7	28.2	-32.3
	19	1	26.3	27.4
	19	3	15.6	-16.7
	19	5	25.5	-26.7
	20	0	17.7	16.3
	20	2	15.1	13.1
	20	4	20.1	-24.9
	21	1	12.8	14.0
	21	2	15.8	-15.8
	21	4	9.1	-10.8
2	0	0	75.4	-74.9
	0	1	27.2	24.7
	0	2	25.8	-25.9
	0	3	41.8	43.2
	0	4	35.6	36.1
	0	5	9.7	-8.9
	0	6	21.1	19.4
	0	7	46.3	-52.1
	0	9	15.8	-14.2
	0	10	21.5	-18.2
	0	11	26.0	24.4
	1	1	10.2	10.0
2	k	l	F_o	F_c
2	1	2	48.6	59.1
	1	3	25.7	-22.8
	1	4	19.1	16.4
	1	6	38.7	-37.9
	1	7	13.4	-13.3
	1	8	23.7	-21.4
	1	9	22.4	20.6
	1	10	15.1	16.8
	1	12	26.5	27.3
	2	0	74.3	73.7
	2	1	8.0	8.8
	2	2	5.9	4.4
	2	3	20.5	18.4
	2	4	47.8	-55.8
	2	5	8.9	-8.7
	2	6	20.6	-17.8
	2	7	30.2	-32.8
	2	8	22.1	21.2
	2	10	29.6	28.6
	2	11	10.9	12.0
	3	1	49.1	58.9
	3	2	6.8	-6.9
	3	3	57.9	-62.3
	3	4	14.2	-16.4
	3	5	45.3	-55.1
	3	7	16.5	-18.8
	3	9	48.2	49.5
	3	11	9.3	9.8
	3	12	6.0	-7.5
	4	0	17.6	18.9
	4	1	23.7	-26.3
	4	2	35.2	34.2
	4	3	51.1	-50.8
	4	6	24.2	-21.2
	4	7	30.8	32.5
	4	8	15.7	19.4
	4	11	18.3	-20.3
	5	1	21.2	-22.7
	5	2	58.4	-63.1
	5	3	24.2	23.7
	5	4	31.0	-34.4
	5	5	25.8	29.2
	5	6	48.9	55.2
	5	7	22.5	21.6
	5	8	38.2	38.0
	5	10	19.7	-16.7
	5	12	25.8	-30.8
	6	0	14.6	-34.4
	6	1	23.3	-22.8
	6	2	8.7	-6.0
	6	3	13.3	-11.7
	6	4	36.2	33.7
	6	6	31.7	29.3
	6	7	22.8	22.7
	6	8	28.9	-27.6
	6	10	26.7	-27.0
	6	11	6.9	-8.9
	7	1	49.2	-49.9
	7	2	42.0	46.4
	7	3	29.6	28.5
	7	4	18.7	14.8
	7	5	34.2	39.8
	7	6	33.6	-31.9
	7	8	20.4	-21.0
	7	9	34.1	-34.6
	7	11	6.5	-7.2
	7	12	15.5	15.7
	8	1	46.2	43.7
	8	2	11.2	-8.8
	8	3	44.4	44.5
	8	4	22.6	22.4
	8	5	25.3	-23.6
	8	7	24.1	-20.7
	8	10	10.7	-10.3
	8	11	18.6	18.9
	9	1	23.3	22.2
	9	2	38.0	39.3
	9	3	21.7	-18.2
	9	4	20.4	16.0
	9	5	16.8	-17.4
	9	6	27.1	-26.4
	9	8	24.5	-23.4
	9	9	19.8	18.4
	10	0	42.8	45.7
	10	1	20.0	17.0
	10	2	10.2	9.1
	10	4	38.7	-41.6
	10	6	35.9	-34.2
	10	8	30.9	29.3
	10	10	31.7	35.2
	11	1	43.3	43.4
	11	2	39.7	-40.2
	11	4	25.2	-26.1
	11	5	43.2	-46.0
	11	6	25.9	23.9
	11	7	6.3	-10.8
	11	8	16.8	15.0
	11	9	24.9	24.6
	12	0	43.3	-47.2
	12	1	17.0	-11.5
	12	2	8.7	-6.2
	12	3	28.3	-23.7
	12	5	12.9	9.5
	12	6	20.2	21.0
	12	7	35.7	33.7
	13	1	25.4	-21.2
	13	2	45.3	-48.4
	13	3	23.2	22.4
	13	5	28.6	21.7
	13	6	23.2	21.7
	13	8	14.0	13.5
	13	9	21.7	-20.6
	14	0	28.8	-30.2
	14	3	6.4	8.6
	14	4	24.8	22.4
	14	5	11.8	-7.4
	14	6	14.6	11.8
	14	8	11.7	-9.3
	15	1	28.8	-26.9
	15	2	47.6	48.5
	15	3	6.3	11.8
	15	4	24.0	21.8
	15	5	26.7	24.9
	15	6	24.2	-24.0
	15	8	20.5	-21.3
	16	0	34.5	30.8
2	k	l	F_o	F_c
2	16	1	11.9	8.3
	16	3	22.8	19.4
	16	4	14.4	-10.6
	16	7	26.0	-28.5
	17	1	23.8	19.8
	17	5	30.0	-26.4
	18	0	37.1	35.1
	18	2	10.6	9.0
	18	3	17.0	-13.7
	18	4	26.3	-24.6
	18	6	13.2	-13.5
	19	2	21.0	-20.3
	19	3	6.3	-9.3
	20	0	11.5	-12.6
	20	1	13.3	-14.9
	20	3	18.1	-19.4
	20	4	10.6	11.3
	21	1	11.3	-15.5
1	-1	1	6.6	10.6
	-1	2	76.0	-115.2
	-1	3	17.5	-11.5
	-1	4	7.1	-8.0
	-1	5	9.4	-8.6
	-1	6	55.6	57.5
	-1	8	32.4	31.1
	-1	9	21.6	24.0
	-2	0	89.0	95.9
	-2	1	58.6	-59.4
	-2	3	19.7	-20.6
	-2	4	59.4	-63.4
	-2	5	10.7	9.4
	-2	6	42.0	-45.7
	-2	7	10.3	7.7
	-2	8	38.6	38.8
	-2	10	50.8	49.3
	-2	13	13.3	-14.2
	-3	1	120.0	168.2
	-3	2	43.7	51.8
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	-3	6	30.1	-32.4
	-3	8	20.7	-21.4
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	-3	12	21.4	23.3
	-3	13	20.8	-21.9
	-4	0	146.7	174.0
	-4	1	26.9	29.4
	-4	2	13.7	11.3
	-4	3	53.8	56.8
	-4	4	24.7	-20.3
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	-4	6	15.3	-11.8
	-4	7	47.9	-51.3
	-4	9	18.7	-18.2
	-4	10	19.1	20.5
	-4	11	34.1	35.3
	-4	13	17.9	20.7
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	-5	3	37.1	35.5
	-5	4	36.6	33.9
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	-5	6	44.8	-44.7
	-5	8	45.0	-38.5
	-5	9	40.9	-37.8
	-5	10	26.0	25.8
	-5	11	19.2	-16.0
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	-5	13	14.5	17.8
	-6	0	47.5	-50.3
	-6	1	29.7	28.7
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	-6	3	12.5	13.5
	-6	4	48.8	53.1
	-6	5	23.1	-23.0
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	-7	1	58.1	-62.2
	-7	2	55.5	-56.8
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	-7	5	48.3	51.3
	-7	6	35.4	35.4
	-7	8	38.8	37.4
	-7	9	16.8	-17.0
	-7	10	31.1	-29.8
	-7	11	17.2	-15.5
	-7	12	24.8	-25.2
	-8	0	29.4	24.4
	-8	1	57.6	-55.2
	-8	3	54.2	-55.6
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	-8	7	52.0	52.6
	-8	8	21.7	21.5
	-8	9	13.6	17.4
	-8	11	30.0	-28.8
	-9	1	38.0	39.1
	-9	2	20.3	-19.1
	-9	3	24.6	-24.5
	-9	4	13.0	-12.4
	-9	5	41.1	-41.6
	-9	8	23.9	24.0
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	-9	11	15.4	17.8
	-9	12	12.4	-14.0
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	-10	1	15.4	14.2
	-10	2	21.7	22.5
	-10	3	21.8	22.4
	-10	4	47.4	-49.9
	-10	6	26.9	-27.4
	-10	8	13.7	15.6
	-10	9	11.6	-13.6
	-10	10	16.5	18.7
	-11	2	53.3	60.0
	-11	3	17.0	-14.3
	-11	5	23.0	-25.6
	-11	6	33.5	-33.9
	-11	8	20.1	-22.3
1	k	l	F_o	F_c
1	-11	9	28.0	28.6
	-11	10	22.5	23.0
	-11	11	8.5	10.6
	-12	0	13.7	-11.7
	-12	1	15.1	14.7
	-12	3	35.3	35.5
	-12	4	21.0	20.6
	-12	6	15.4	16.8
	-12	7	30.5	-29.7
	-12	8	29.2	-29.2
	-12	9	11.8	-13.7
	-12	10	19.3	-17.7
	-12	11	13.9	17.2
	-13	1	32.4	-31.6
	-13	2	18.5	18.1
	-13	3	13.3	13.3
	-13	5	48.8	49.3
	-13	9	30.1	-30.6
	-14	0	36.8	-34.4
	-14	1	11.6	-10.2
	-14	2	15.2	-14.1
	-14	3	21.6	-21.9
	-14	4	11.9	11.5
	-14	6	30.1	28.6
	-14	7	6.3	9.2
	-14	10	11.2	-13.7
	-15	2	51.2	-52.4
	-15	3	13.8	13.7
	-15	6	37.6	38.2
	-15	8	20.5	24.3
	-15	9	8.6	-9.0
	-15	10	3.3	-16.4
	-16	0	25.8	27.2
	-16	3	25.4	-23.4
	-16	4	18.8	-21.2
	-16	8	12.5	12.8
	-17	1	22.3	21.8
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	-18	6	18.6	-18.6
	-18	7	5.6	-8.2
	-19	2	20.7	21.2
	-19	4	17.6	18.4
	-19	6	15.1	-20.3
	-20	0	17.4	-25.1
	-20	3	9.0	11.6
	-20	4	12.9	15.1
2	-1	1	44.9	-40.2
	-1	3	30.5	32.3
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	-1	9	42.4	-41.9
	-1	10	8.7	7.2
	-1	11	11.0	-10.5
	-2	0	28.3	-28.0
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	-2	2	24.3	-23.0
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	-2	5	13.1	9.4
	-2	6	14.6	13.1
	-2	7	46.7	49.3
	-2	8	13.0	-7.7
	-2	10	19.0	-14.6
	-2	11	19.7	-16.3
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	-3	2	52.7	-53.1
	-3	3	10.6	-12.6
	-3	4	28.4	-27.4
	-3	5	19.5	-21.3
	-3	6	28.0	28.4
	-3	8	30.7	28.5
	-3	9	23.2	17.7
	-3	10	20.5	-20.4
	-3	12	23.1	-23.5
	-4	0	11.1	2.3
	-4	1	37.7	-38.3
	-4	2	11.7	12.1
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	-4	7	21.3	19.5
	-4	8	23.1	18.4
	-4	10	27.1	26.1
	-5	1	50.2	49.3
	-5	2	31.2	35.3
	-5	3	17.1	-22.5
	-5	5	45.0	-50.5
	-5	6	18.5	-19.3
	-5	9	32.5	30.0
	-5	11	18.5	16.5
	-6	0	40.3	40.8
	-6	1	55.4	55.3
	-6	2	27.5	28.8
	-6	3	29.8	26.4
	-6	4	29.4	-30.5
	-6	5	7.8	-7.0
	-6	6	16.3	-16.9
	-6	7	34.7	-30.2
	-6	11	15.5	14.9
	-7	1	62.3	-66.6
	-7	2	27.3	26.3
	-7	3	25.0	21.7
	-7	4	10.7	8.3
	-7	5	34.7	38.9
	-7	6	21.3	-17.7
	-7	8	25.0	-22.5
	-7	10	11.2	7.4
	-8	0	10.6	-8.9
	-8	1	24.3	23.5
	-8	2	15.9	-16.2
	-8	3	20.5	20.3
	-8	4	33.3	33.2
	-8	6	13.5	13.9
	-8	7	18.3	-14.2
	-8	8	23.1	-21.6
	-8	10	30.7	-30.1
	-8	12	10.0	7.1
	-9	1	20.2	-19.2
	-9	2	24.0	-23.2
	-9	3	7.9	5.2
2	k	l	F_o	F_c
2	-9	4	13.1	-11.4
	-9	5	23.8	25.9
	-9	6	18.1	17.3
	-9	8	18.3	17.1
	-9	9	18.7	-17.3
	-9	10	17.0	-15.6
	-10	0	17.5	-15.6
	-10	1	35.2	-35.9
	-10	3	33.3	-31.2
	-10	7	39.2	36.0
	-10	11	18.8	-20.7
	-11	1	26.3	25.7
	-11	2	24.7	-21.9
	-11	3	13.7	-14.5
	-11	5	27.2	-27.3
	-11	6	15.8	14.6
	-11	8	14.1	11.2
	-11	9	15.0	10.7
	-12	0	28.7	28.0
	-12	1	10.6	-5.1
	-12	4	32.1	-28.7
	-12	10	17.0	16.7
	-13	1	20.1	18.5
	-13	2	24.8	21.8
	-13	5	14.3	-14.2
	-13	6	10.7	-10.6
	-13	8	18.3	-16.7
	-13	9	13.3	11.7
	-14	0	14.4	-15.0
	-14	1	14.4	14.5
	-14	3	21.0	18.5
	-14	7	27.9	-25.8
	-15	1	9.1	-7.5
	-15	3	10.9	10.0
	-15	4	15.1	16.1
	-15	5	22.3	21.2
	-15	9	16.9	-22.7
	-16	0	25.2	-23.1
	-16	4	20.3	16.8
	-17	2	17.6	-16.5
	-17	4	9.3	-8.2
	-17	7	8.6	9.4
	-18	1	13.4	-12.6
	-18	3	13.6	-13.8
	-18	5	12.9	13.7
	-18	6	10.0	-10.7
	-19	5	8.0	-6.6

identified unambigously, and it was then decided to solve the structure in three dimensions using zero, first, and second level intensity data. The three-dimensional Patterson function revealed the bromide position to be $x=0{\cdot}3200$, $y=0{\cdot}1417$ and $z=0{\cdot}1067$. A three-dimensional Fourier synthesis calculated with the bromine phases revealed all the light atom coordinates. The structure was then refined by the Busing–Levy least-squares program on the IBM 7090 with individual isotropic, and later anisotropic, temperature factors for all atoms.

The least-squares refinement based on F's began with a residual of 0·292. After two cycles of isotropic refinement in which the atomic coordinates and the individual temperature factors were varied, the individual layer line scale factors set at a common value and held constant, the residual dropped to 0·13. Three cycles of individual light atom and bromine anisotropic refinement left a residual of 0·082. Finally, the scale factors and atomic coordinates were varied holding the temperature factors fixed, yielding a final residual of 0·077 unweighted, and 0·102 using an arbitrary weighting scheme (Hughes, 1941). This refinement procedure was found to give the best residual and smallest standard deviations in coordinates. The final atomic coordinates given in fractional coordinates are presented in Table 1. The anisotropic thermal parameters are presented in Table 2. Final F_o and F_c values are presented in Table 3.

The atomic scattering factors for carbon, nitrogen, and oxygen were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and for the bromide ion, from Thomas & Umeda (1957). The following anisotropic temperature factors, $\exp(-\beta)$ were used:

$$\beta = \beta_{11}h_1^2 + \beta_{22}h_2^2 + \beta_{33}h_3^2 + 2\beta_{12}h_1h_2 + 2\beta_{13}h_1h_3 + 2\beta_{23}h_2h_3$$

where β_{ij} are the six anisotropic temperature components, and h_i the Miller indices.

Description of structure and discussion

The bond lengths and angles of 9-methylguanine hydrobromide obtained from the present analysis are shown in Fig. 2. The estimated standard deviation for bond lengths involving light atoms, based on diagonal elements of the inverse matrix, is 0·03 Å and for bond angles 2°. The molecule is planar; the best least-squares plane calculated by the method of Blow (1960) is:

$$0{\cdot}7430x - 0{\cdot}6629y - 0{\cdot}0924z + 1{\cdot}2514 = 0\ .$$

Individual atomic distances from this plane are given in Table 4. The maximum deviation from this plane is 0·06 Å and is not considered large enough to be significant. The bromine ion closest to N(7) is not in the plane of the molecule, being approximately 0·2 Å from the least-squares plane. The distance between molecular planes is 3·37 Å.

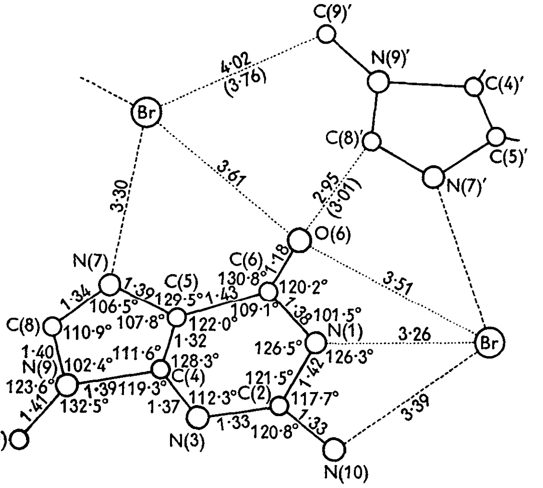


Fig. 2. Schematic diagram showing the bond lengths and angles of 9-methylguanine hydrobromide. Hydrogen bonds are indicated by broken lines. Other interatomic distances are shown by dotted lines.

Table 4. *Individual atomic distances from the molecular least-squares plane*

Atom	Perpendicular distance from plane
N1	0·018 Å
C2	−0·002
N3	−0·015
C4	0·030
C5	−0·040
C6	0·002
N7	0·005
C8	0·018
N9	−0·069
C9	0·043
O6	0·010
N10	−0·002

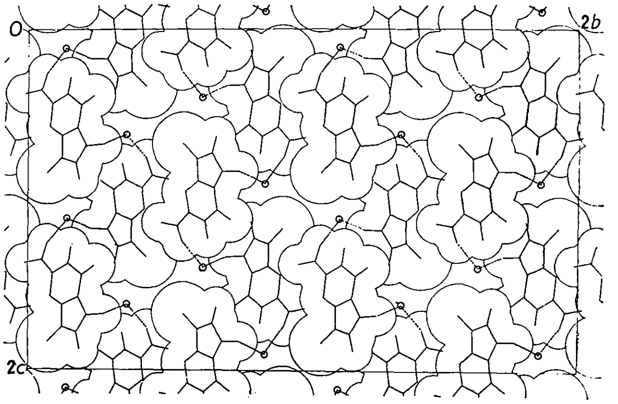


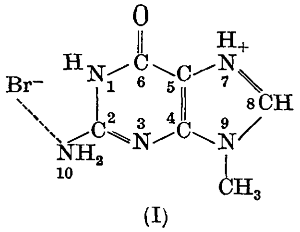
Fig. 3. Three-dimensional packing diagram of 9-methylguanine hydrobromide as viewed down the *a* axis. Hydrogen bonds are shown by the broken lines. Small circles indicate bromine position.

Fig. 3 shows a three-dimensional packing diagram viewed down the *a* axis. Conventional van der Waals radii have been inscribed, *i.e.* C = 1·4 Å, N = 1·5 Å, O = 1·4 Å, H = 1 Å, and Br = 1·95 Å. It is quite interesting to note that this crystal structure contains bromide ions stacked one on another 4·54 Å apart to form neighboring pairs of infinite columns along the *a* axis of the crystal. The 9-methylguanine molecules are also stacked one on another in a tilted fashion to form six surrounding columns. There are no interpurine hydrogen bonds formed. Instead, each guanine molecule participates in two hydrogen bonds of the type N–H · · · Br involving N(7) and N(10) forming a continuous zigzag hydrogen bonded network along the *c* axis.

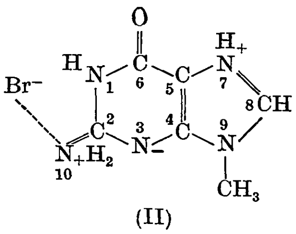
The Br · · · N(7) distance is 3·30 Å and the hydrogen bond formed deviates from linearity by approximately 8°. The Br · · · N(10) distance is 3·39 Å, the angle subtended by the atoms C(2)–N(10)–Br is 118·5°. The hydrogen bond distance of 3·39 Å is in good agreement with the N–H · · · Br hydrogen bond distances of 3·40 Å and 3·39 Å found in 3-methylcytosine hydrobromide (Bryan & Tomita, 1962*a*), and 3·30 and 3·44 Å found in 11-aminoundecanoic acid $HBr.\frac{1}{2}H_2O$ (Sim, 1955); however, it is longer than the hydrogen bond distance of 3·21 Å found in 9-methyladenine dihydrobromide (Bryan & Tomita, 1962*b*). In view of the inaccuracy of this latter determination (estimated standard deviations of 0·1 Å and 6°) no significance was attached to these hydrogen bond length differences.

More interesting, however, is the shortness of the Br · · · N(1) approach of 3·26 Å. The N(1) ring nitrogen is normally covalently linked to a hydrogen atom lying in the plane of the molecule. Although the distance 3·26 Å corresponds to a hydrogen bond distance, such a hydrogen bond would have to deviate from linearity by more than 36°. In view of this, significant hydrogen bonding appears to be highly unlikely, and one must look elsewhere to explain this short contact.

In examining the bond distances obtained from this determination certain salient features arise placing important limitations on the choice of tautomers and the types of resonance possible. The C(6)–O bond is 1·18 Å, indicating that the bond is predominantly double bond in character and that the molecule exists in the keto form. The distance of 1·34 Å between N(7) and C(8) appears to be significantly shorter than the other bond distances C(8)–N(9), N(9)–C(4), C(5)–N(7) which are 1·40 Å, 1·39 Å, and 1·39 Å respectively, indicating that this bond has a large amount of double bond character. Since protonation occurs at N(7), this means that the nitrogen atom has a positive electrostatic charge associated with it which contributes a large amount of electrostatic interaction energy to the N(7)–Br hydrogen bond. The C(4)–C(5), C(2)–N(3), and C(2)–N(10) bonds are 1·32 Å. 1·33 Å, and 1·33 Å respectively and are all significantly shorter than the other ring bond lengths. In particular, the C(2)–N(10) bond of 1·33 Å is a great deal shorter than the normal single bond distance of 1·42 Å, and must be predominantly double bond in character. There is similar shortening of the C(2)–N(3) bond indicating partial double bond character. This suggests that the molecule exists as the following tautomer with the two resonant forms (I) and (II):



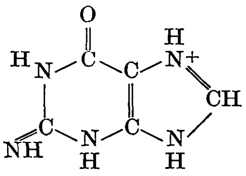
(I)



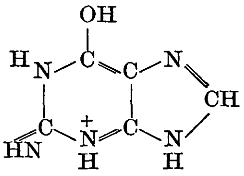
(II)

Resonant form (I) allows greater freedom of rotation around the C(2)–N(10) bond, and permits hydrogen bond formation to occur at the observed angle of 118·5°. Resonant form (II) provides a large electrostatic bond energy contribution to the hydrogen bond and may act to pull the molecule closer to the bromide ion and thus cause the close contact observed between Br · · · N(1). The two resonant forms appear to exist in roughly equal proportions as judged by the bond distances.

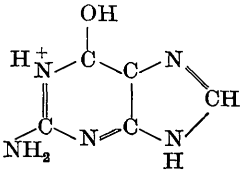
The crystal structure of guanine hydrochloride monohydrate has been studied previously (Broomhead, 1951) in an attempt to ascertain the site at which protonation occurs on the molecule. Unfortunately, Broomhead's analysis was not accurate enough to decide conclusively which tautomer existed in the crystal structure, and she had to consider the possibility of four possible tautomeric structures, (*a*), (*b*), (*c*), and (*d*):



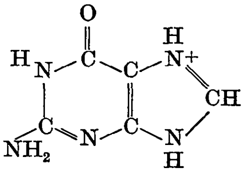
(*a*)



(*b*)



(*c*)



(*d*)

Although the crystal structure of 9-methylguanine hydrobromide bears little resemblance to that of guanine hydrochloride monohydrate, it seems reasonable to assume that the acidic proton attaches to the same position on the guanine molecule in both crystal structures, *i.e.* N(7). If this assumption is made, then one can eliminate the tautomers (*b*) and (*c*) immediately from consideration in the chloride structure since they lack hydrogen atoms at N(7). One is then left with tautomers (*a*) and (*d*), and it is not possible to choose between them with any certainty. It is interesting to note, however, that the resonant form (I) associated with tautomer (*d*) would give extra electrostatic energy to the interpurine hydrogen bonding observed to occur in the chloride crystal structure between N(7) and O(6) of adjacent guanine molecules. Similarly, resonant form (II) would contribute extra electrostatic energy to the N(10)–N(3) interpurine hydrogen bond in the chloride structure. It therefore seems possible that the same tautomer and predominant resonant forms exist in the bromide and chloride crystal structures in spite of the remarkable differences between them. However, this suggestion is speculative and must await a more accurate determination of these compounds.

We wish to express thanks to the M.I.T. Computation Center for allowing us generous computing time on the IBM 7090. Our thanks are due to Dr David P. Shoemaker for allowing us to use his MIFR1 Fourier program and to Dr Henri Levy and Dr William Busing for their full-matrix anisotropic least-squares program. Finally, we wish to express deep appreciation to Dr Alexander Rich for his interesting discussions about this work and to Dr Scott Mathews for his help in computer programing.

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The Crystal Structure of Phenylcyclobutenedione[*]

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The crystal structure of phenylcyclobutenedione, $C_{10}H_6O_2$, has been determined by three-dimensional analysis of X-ray diffraction data. The crystals are monoclinic, space group $P2_1/c$, with

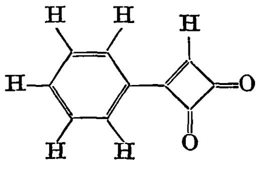
$$a=6{\cdot}998\pm0{\cdot}005,\ b=9{\cdot}287\pm0{\cdot}020,\ c=12{\cdot}338\pm0{\cdot}005\ \text{Å};\ \beta=103{\cdot}31\pm0{\cdot}30^\circ.$$

The unit cell contains four molecules. The three-dimensional Patterson function led to a trial structure which was refined by difference maps and least-squares calculations.

The molecule is very nearly planar and lies close to the $(20\bar{1})$ plane. The bond distances suggest a considerable degree of conjugation between the benzene ring and the cyclobutenedione group, which is no doubt responsible for the stability of the compound.

Introduction

Phenylcyclobutenedione, $C_{10}H_6O_2$ (I) was synthesized in these laboratories by Smutny & Roberts (1955). In view of the bond-angle strain associated with a four-membered ring, the phenylcyclobutenedione molecule is surprisingly stable; whereas cyclobutene itself decomposes at room temperature, phenylcyclobutenedione is stable up to 150 °C. This surprising stability and our general interest in the geometry of small-ring compounds have prompted this investigation.



(I)

Experimental

Phenylcyclobutenedione crystallizes from acetone solution in the form of yellow monoclinic needles with the needle axis parallel to *a*. Rotation and multiple-film equi-inclination Weissenberg photographs were prepared for layer lines 0 through 6 about *a* and 0 through 8 about *b*, copper X-radiation being used. For the *a*-axis photographs, a needle-shaped crystal about 0·2 mm in diameter was selected; for the *b*-axis photographs a larger crystal was cleaved and shaped into roughly cylindrical form by means of acetone-soaked filter paper, the resulting specimen again being about 0·2 mm in diameter. The diffraction spots on the *b*-axis photographs were streaked, suggesting that the crystal had been damaged when cleaved. However, a careful comparison of intensities of equivalent reflections measured about the two axes showed no serious dis-

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