Acta Cryst. (1965). **19**, 125

The Crystal Structure of a Hydrogen Bonded Complex of Deoxyguanosine and 5-Bromodeoxycytidine

By A. E. V. Haschemeyer* and Henry M. Sobell*

Department of Biology, Massachusetts Institute of Technology, Cambridge 39, *Massachusetts, U.S.A.*

(*Received* 20 *August* 1964 *and in revised form* 9 *November* 1964)

The crystal structure of a 1:1 complex of deoxyguanosine and 5-bromodeoxycytidine has been determined by heavy-atom and trial-and-error methods, and has been refined by the full-matrix least-squares method to a final residual of 13·5 % for 1052 measureable reflections. The space group is orthorhombic, $P22_12_1$, with $a=5{\cdot}14$, $b=19{\cdot}11$, and $c=23{\cdot}66$ Å. The bromocytosine and guanine rings form a planar complex joined by three hydrogen bonds of length 2·78, 2·92, and 2·83 Å. Both deoxyribose sugars are puckered with *C*2′ lying out of the plane formed by the other four ring atoms. The orientation of the sugars with respect to the bases is *anti* in the case of bromodeoxycytidine but *syn* for deoxyguanosine. Refinement indicated considerable disorder in the region of the bromodeoxycytidine sugar residue, and two positions for O(5′) were found, each with approximately half the electron density of an oxygen atom.

Introduction

One of the more remarkable properties of the purines and pyrimidines is their ability to form hydrogen bonded complexes in the crystalline state. In the past few years structures have been solved for a number of complexes containing free bases alkylated at the glycosidic nitrogen (Hoogsteen, 1959, 1963; O'Brien, 1963; Sobell, Tomita & Rich, 1963; Mathews & Rich, 1964) and for a complex of adenosine and 5-bromouridine (Haschemeyer & Sobell, 1963, 1965). We have now solved the structure of a 1:1 complex of deoxyguanosine and 5-bromodeoxycytidine, as reported in a preliminary communication (Haschemeyer & Sobell, 1964). This paper describes the refinement of the structure and discusses several features of particular interest.

Experimental

The crystals appeared as clusters of very small needles upon evaporation of aqueous solutions of the two nucleosides. Details of the preparation are given in the preliminary communication. Only a few crystals of sufficient size for X-ray analysis were found, and repeated attempts to prepare larger crystals were unsuccessful. Two very small crystals were used to collect about half of the theoretically available data. Oscillation and Weissenberg photographs were taken about the *a* axis with copper radiation. Systematic absences were observed at 0*k*0 for *k* odd and 00*l* for *l* odd with the exception of faint reflections at 070 and 009. The space group $P22_12_1$ appeared to be valid for the entire structure except for a disordered region involving several atoms of the bromodeoxycytidine sugar residue. The crystal data are as follows:

$$a=5{\cdot}14\pm0{\cdot}02\,,\quad b=19{\cdot}11\pm0{\cdot}02\,,\quad c=23{\cdot}66\pm0{\cdot}03\ \text{Å};$$
$$Z=4;\quad D_c=1{\cdot}638\,,\quad D_m=1{\cdot}63\pm0{\cdot}01\ \text{g.cm}^{-3}\,.$$

Refinement of the structure

The determination of the structure was discussed in the preliminary paper. Refinement was carried out on an IBM 7094 computer using the full-matrix least-squares program of Busing, Martin & Levy (1962). The atomic scattering factors used were as follows: carbon, nitrogen and oxygen from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); bromine from Thomas & Umeda (1957). The quantity minimized in the least-squares refinement was $\Sigma w(|F_o|^2-|sF_c|^2)^2$ where w is a weighting factor, F_o is the observed structure factor (on an arbitrary scale), F_c is the calculated structure factor, and s is a scale factor, varied independently for each h level of data. The data were weighted by a slightly modified version (Haschemeyer & Sobell, 1965) of the method of Hughes (1941).

Refinement based on the measurable reflections, using individual atomic isotropic temperature factors, was carried out until no significant changes in coordinates and temperature factors occurred. Disorder in the region of the bromodeoxycytidine sugar residue was observed early in the structure determination, and particular attention was given to this region. Throughout the analysis, Fourier maps showed two very broad peaks for O(5′), each with about half the electron density of an oxygen atom. Refinement on atom multipliers (a factor by which the values in the scattering factor table are multiplied) gave weights of about 0·6 and 0·4 for the two peaks.

In order to test the validity of the space group assignment for the questionable atoms of the bromodeoxycytidine sugar, a (100) electron density projection without symmetry (*i.e.*, *p*1) was calculated. The

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* Helen Hay Whitney Postdoctoral Fellow.

data were phased on the structure in *pgg* (corresponding to the projection of $P22_12_1$) with C(4′), C(5′) and O(5′) omitted. For this calculation the complete $0kl$ data were used ($\pm l$), although no significant intensity differences were found between $+l$ and $-l$ reflections. The resultant Fourier map showed the same appearance in the disordered region for all four molecules in the unit cell, and was the same as that observed in the *pgg* electron density projection. There remained the possibility that O(5′) occupied alternate sites along the *a* axis, corresponding to a periodicity of 10·28 Å. However, no reflections were observed at this spacing.

Additional three-dimensional refinement was then carried out (in $P22_12_1$) to determine whether there were two distinct orientations of the sugar ring. Each atom of the sugar residue was divided into two fractional parts with positions based upon the previous Fourier maps. In every case a single position resulted after refinement except for the two parts of C(4′), C(5′) and O(5′), which continued to show large movements and erratic changes in temperature factor. The bond lengths between various pairs of fractional atoms were unsatisfactory, and the difference Fourier maps were not improved by these calculations. Therefore, the refinement was concluded with two cycles on the complete structure with only one set of fractional atoms, O(5′)–1 and O(5′)–2. These two positions are approximate only, as evidenced by the large standard deviations of coordinates and high temperature factors for these atoms.

Difference Fourier maps were examined for hydrogen atoms, but conclusive positions could not be determined. The final coordinates and temperature factors for the structure and their estimated standard deviations are given in Table 1. The observed and calculated structure factors, including unobserved reflections at their threshold value, are listed in Table 2. The residual based on F for the measureable reflections was 0·135.

Results and discussion

Covalent and hydrogen bonding distances and angles for the structure are given in Fig. 1. Standard deviations were determined from the standard error of atomic

Table 1. *Final coordinates (given in fractions of the unit cell axes* $\times 10^4$*), isotropic temperature factors, and approximate standard deviations calculated from the diagonal elements of the inverse matrix*

	x/a	$\sigma(x)$(Å)	y/b	$\sigma(y)$(Å)	z/c	$\sigma(z)$(Å)	B	$\sigma(B)$
5-Bromodeoxycytidine								
Br	20443	0·004	1227	0·004	1683	0·004	5·01	0·12
N(1)	16850	0·027	2178	0·023	334	0·022	2·70	0·52
C(2)	15063	0·051	2598	0·033	597	0·035	5·28	0·81
O(2)	13450	0·023	2963	0·021	258	0·020	4·01	0·52
N(3)	15001	0·032	2672	0·020	1156	0·022	3·07	0·48
C(4)	16494	0·036	2278	0·031	1503	0·031	3·62	0·75
N(4)	16277	0·028	2399	0·022	2039	0·024	2·97	0·54
C(5)	18302	0·040	1798	0·032	1220	0·034	4·48	0·83
C(6)	18534	0·038	1726	0·032	657	0·033	3·97	0·73
C(1′)	16860	0·039	2117	0·033	−300	0·033	4·38	0·79
C(2′)	19531	0·041	2217	0·028	−534	0·029	4·03	0·70
C(3′)	19418	0·039	1774	0·027	−1087	0·028	3·37	0·64
C(4′)	17571	0·048	1173	0·043	−958	0·039	6·60	0·99
C(5′)	19169	0·068	465	0·048	−776	0·049	8·84	1·30
O(1′)	16149	0·023	1407	0·020	−425	0·020	3·81	0·48
O(3′)	18245	0·024	2204	0·020	−1507	0·019	3·83	0·49
O(5′)–1	20617	0·063	585	0·047	−298	0·048	7·81	1·25
O(5′)–2	16809	0·105	110	0·083	−767	0·084	9·79	2·52
Deoxyguanosine								
N(1)	10853	0·028	3603	0·021	1531	0·022	3·07	0·54
C(2)	9350	0·041	4010	0·029	1161	0·033	4·23	0·77
N(2)	9555	0·030	3881	0·022	601	0·025	4·06	0·58
N(3)	7376	0·027	4442	0·022	1351	0·023	2·55	0·50
C(4)	7349	0·034	4446	0·027	1921	0·027	2·42	0·60
C(5)	8633	0·038	4106	0·031	2319	0·034	3·88	0·78
C(6)	10794	0·037	3645	0·029	2109	0·030	3·99	0·73
O(6)	12125	0·025	3250	0·021	2412	0·021	3·92	0·49
N(7)	7909	0·030	4253	0·025	2851	0·025	3·51	0·57
C(8)	6135	0·036	4725	0·029	2805	0·031	3·53	0·69
N(9)	5476	0·030	4864	0·021	2230	0·022	3·21	0·51
C(1′)	3989	0·032	5463	0·024	2059	0·025	1·88	0·54
C(2′)	5425	0·034	6085	0·024	1936	0·025	2·74	0·59
C(3′)	3797	0·041	6467	0·032	1528	0·034	5·11	0·91
C(4′)	2324	0·036	5882	0·029	1190	0·029	3·22	0·65
C(5′)	3579	0·049	5660	0·036	611	0·038	5·11	0·91
O(1′)	2522	0·022	5277	0·017	1574	0·018	2·85	0·41
O(3′)	1818	0·027	6828	0·022	1882	0·021	4·60	0·55
O(5′)	6345	0·028	5584	0·022	630	0·023	4·35	0·53

Table 2. *Observed and calculated structure factors*

Within each group, the numbers, reading from left to right, are h, k, l, F_o, F_c, A_c, and B_c. A 'less than' sign indicates the estimated minimum observable F_o for reflections too weak to be measured.

H	K	L	FOBS	FCALC	ACALC	BCALC
0	0	4	89	87	-87	0
0	0	6	75	83	83	0
0	0	8	127	121	-121	0
0	0	9	19	0	0	0
0	0	10	123	100	-100	0
0	0	12	41	26	-26	0
0	0	14	18	11	-11	0
0	0	16	36	31	-31	0
0	0	18	55	48	48	0
0	0	22	42	41	-41	0
0	0	24	<9	4	4	0
0	0	28	<7	4	-4	0
0	1	3	72	58	58	0
0	1	4	71	73	73	0
0	1	5	<4	9	-9	0
0	1	6	<4	1	-1	0
0	1	7	27	26	26	0
0	1	8	36	40	-40	0
0	1	9	46	47	-47	0
0	1	10	<6	1	-1	0
0	1	11	68	60	60	0
0	1	12	20	11	11	0
0	1	13	<7	5	5	0
0	1	14	37	35	-35	0
0	1	15	73	70	-70	0
0	1	16	31	25	25	0
0	1	17	<8	0	0	0
0	1	18	26	26	-26	0
0	1	19	<9	6	6	0
0	1	20	28	23	-23	0
0	1	21	28	25	-25	0
0	1	22	27	22	22	0
0	1	23	36	34	34	0
0	1	24	<9	9	9	0
0	2	0	32	43	-43	0
0	2	1	22	22	-22	0
0	2	2	75	93	-93	0
0	2	3	14	11	11	0
0	2	4	15	13	13	0
0	2	5	164	188	188	0
0	2	6	55	53	-53	0
0	2	7	125	133	-133	0
0	2	8	30	29	-29	0
0	2	9	68	70	70	0
0	2	10	40	32	32	0
0	2	11	91	83	83	0
0	2	12	26	17	17	0
0	2	13	59	52	-52	0
0	2	14	57	53	53	0
0	2	15	28	24	24	0
0	2	16	<8	0	0	0
0	2	17	<8	4	4	0
0	2	18	25	20	20	0
0	2	19	46	39	-39	0
0	2	20	21	15	-15	0
0	2	21	<9	1	-1	0
0	2	22	21	14	14	0
0	2	23	26	21	21	0
0	2	24	<9	4	4	0
0	3	1	95	106	-106	0
0	3	2	25	18	18	0
0	3	3	57	65	65	0
0	3	4	115	136	136	0
0	3	5	16	12	12	0
0	3	6	73	75	75	0
0	3	7	42	44	-44	0
0	3	8	88	79	-79	0
0	3	9	83	82	82	0
0	3	10	70	68	68	0
0	3	11	<6	3	3	0
0	3	12	19	13	13	0
0	3	13	<7	2	-2	0
0	3	14	47	44	-44	0
0	3	15	35	35	35	0
0	3	16	48	42	42	0
0	3	17	19	16	-16	0
0	3	18	18	19	-19	0
0	3	19	26	24	-24	0
0	3	20	<9	5	5	0
0	3	21	25	19	19	0
0	3	22	<9	4	4	0
0	3	23	23	14	-14	0
0	4	0	82	89	-89	0
0	4	1	25	27	27	0
0	4	2	76	71	71	0
0	4	3	58	50	-50	0
0	4	4	84	75	75	0
0	4	5	37	29	-29	0
0	4	6	67	69	-69	0
0	4	7	12	14	-14	0
0	4	8	36	45	45	0
0	4	9	46	41	-41	0
0	4	10	23	21	21	0
0	4	11	44	35	35	0
0	4	12	85	74	-74	0
0	4	13	30	22	-22	0
0	4	14	57	55	55	0
0	4	15	<8	11	11	0
0	4	16	<8	8	-8	0
0	4	17	19	17	17	0
0	4	18	40	39	-39	0
0	4	19	<9	1	-1	0
0	4	20	<9	13	13	0
0	4	21	39	30	-30	0
0	4	22	<9	0	0	0
0	4	23	18	12	12	0
0	4	24	27	18	-18	0
0	4	25	<8	2	-2	0
0	5	1	66	57	57	0
0	5	2	86	76	76	0
0	5	3	55	58	58	0
0	5	4	23	29	-29	0
0	5	5	95	96	-96	0
0	5	6	43	46	46	0
0	5	7	32	31	-31	0
0	5	8	34	36	36	0
0	5	9	34	37	37	0
0	5	10	75	49	-49	0
0	5	11	74	46	-46	0
0	5	12	68	41	-41	0
0	5	13	33	27	-27	0
0	5	14	43	52	52	0
0	5	15	73	63	63	0
0	5	16	21	17	-17	0
0	5	17	<9	10	-10	0
0	5	18	<9	4	4	0
0	5	19	<9	0	0	0
0	5	20	51	46	46	0
0	5	21	21	16	16	0
0	5	22	25	18	-18	0
0	5	23	29	22	-22	0
0	5	24	<9	2	2	0
0	6	0	70	63	-63	0
0	6	1	85	88	88	0
0	6	2	41	31	-31	0
0	6	3	28	25	-25	0
0	6	4	19	23	23	0
0	6	5	86	81	-81	0
0	6	6	<6	2	2	0
0	6	7	38	42	42	0
0	6	8	24	24	24	0
0	6	9	27	24	24	0
0	6	10	<7	12	-12	0
0	6	11	27	21	-21	0
0	6	12	35	38	38	0
0	6	13	77	68	68	0
0	6	14	20	12	-12	0
0	6	15	<8	1	-1	0
0	6	16	17	17	-17	0
0	6	17	22	10	-10	0
0	6	18	<9	4	-4	0
0	6	19	36	32	32	0
0	6	20	<9	1	-1	0
0	6	21	21	21	-21	0
0	6	22	16	7	7	0
0	7	0	19	0	0	0
0	7	1	43	40	40	0
0	7	2	125	125	125	0
0	7	3	<4	8	-8	0
0	7	4	69	66	-66	0
0	7	5	57	35	-35	0
0	7	6	36	38	38	0
0	7	7	12	12	-12	0
0	7	8	41	40	40	0
0	7	9	39	29	-29	0
0	7	10	57	65	-65	0
0	7	12	<8	4	-4	0
0	7	14	16	23	23	0
0	7	15	<8	3	-3	0
0	7	16	36	30	-30	0
0	7	17	70	56	56	0
0	7	18	16	14	-14	0
0	7	19	16	15	-15	0
0	7	20	53	43	43	0
0	7	21	<9	12	-12	0
0	7	22	<9	14	-14	0
0	7	23	<9	9	9	0
0	8	0	46	45	45	0
0	8	1	<6	1	1	0
0	8	2	61	55	-55	0
0	8	3	51	46	-46	0
0	8	4	63	56	-56	0
0	8	5	<6	9	9	0
0	8	6	86	84	84	0
0	8	7	<7	5	-5	0
0	8	8	48	46	-46	0
0	8	9	<7	12	-12	0
0	8	10	35	30	-30	0
0	8	11	<8	17	17	0
0	8	12	56	55	55	0
0	8	13	<8	6	6	0
0	8	14	19	14	-14	0
0	8	15	<9	5	-5	0
0	8	16	49	42	-42	0
0	8	17	<9	1	1	0
0	8	18	62	46	46	0
0	8	19	<9	12	-12	0
0	8	20	<9	0	0	0
0	9	1	46	49	49	0
0	9	2	58	52	-52	0
0	9	3	92	87	-87	0
0	9	4	71	72	72	0
0	9	5	73	64	64	0
0	9	6	<7	6	-6	0
0	9	7	44	36	36	0
0	9	8	<7	2	2	0
0	9	9	86	91	-91	0
0	9	10	45	37	37	0
0	9	11	18	14	14	0
0	9	12	<8	11	-11	0
0	9	13	33	27	27	0
0	9	14	<9	6	8	0
0	9	15	20	22	-22	0
0	9	16	<9	9	9	0
0	9	17	21	13	-13	0
0	9	18	<9	3	-3	0
0	9	19	<9	3	3	0
0	9	20	26	22	-22	0
0	9	21	<9	6	6	0
0	10	0	13	18	-18	0
0	10	1	45	47	-47	0
0	10	2	<7	6	6	0
0	10	3	79	73	73	0
0	10	4	14	14	14	0
0	10	5	82	80	80	0
0	10	6	<7	0	0	0
0	10	7	47	43	-43	0
0	10	8	27	27	27	0
0	10	9	<8	11	-11	0
0	10	10	<8	13	13	0
0	10	11	37	31	31	0
0	10	12	<8	12	12	0
0	10	13	73	65	-65	0
0	10	14	35	35	-35	0
0	10	15	<9	8	-8	0
0	10	16	<9	4	-4	0
0	10	17	23	20	20	0
0	10	18	<9	4	4	0
0	10	19	<9	1	1	0
0	10	20	29	22	-22	0
0	10	21	<9	3	3	0
0	10	22	<9	4	4	0
0	10	24	24	5	-5	0
0	11	1	28	28	-28	0
0	11	2	26	23	-23	0
0	11	3	13	11	11	0
0	11	4	<7	5	-5	0
0	11	5	44	48	-48	0
0	11	6	30	27	-27	0
0	11	7	<8	7	-7	0
0	11	8	38	38	-38	0
0	11	9	29	33	33	0
0	11	10	17	18	18	0
0	11	11	<9	0	0	0
0	11	12	<9	2	-2	0
0	11	13	<9	3	-3	0
0	11	14	18	22	-22	0
0	11	15	41	46	46	0
0	11	16	23	30	30	0
0	11	17	16	10	-10	0
0	11	18	<9	9	-9	0
0	11	19	<9	11	11	0
0	11	20	25	20	-20	0
0	11	21	<9	4	-4	0
0	11	22	23	21	21	0
0	12	0	72	76	-76	0
0	12	1	28	26	-26	0
0	12	2	<8	7	-7	0
0	12	3	15	12	-12	0
0	12	4	16	20	20	0
0	12	5	53	54	54	0
0	12	6	88	89	-89	0
0	12	7	34	36	-36	0
0	12	8	43	47	47	0
0	12	9	<9	4	-4	0
0	12	10	31	32	32	0
0	12	11	<9	3	-3	0
0	12	12	33	29	-29	0
0	12	13	<9	2	-2	0
0	12	14	19	16	16	0
0	12	15	<9	11	11	0
0	12	16	45	32	32	0
0	12	17	<9	5	-5	0
0	12	18	<9	2	-2	0
0	13	1	14	3	-3	0
0	13	2	16	20	20	0
0	13	3	32	31	31	0
0	13	4	69	64	-64	0
0	13	5	28	25	25	0
0	13	6	15	27	-27	0
0	13	7	15	23	-23	0
0	13	8	36	33	33	0
0	13	9	<9	8	8	0
0	13	10	16	19	-19	0
0	13	11	<9	20	-20	0
0	13	12	36	33	33	0
0	13	13	19	17	-17	0
0	13	14	<9	17	17	0
0	13	15	27	30	30	0
0	13	16	<9	0	0	0
0	13	17	18	32	-32	0
0	13	18	16	6	-6	0
0	13	19	<9	1	-1	0
0	14	0	<8	7	-7	0
0	14	1	35	39	39	0
0	14	2	35	35	35	0
0	14	3	15	18	-18	0
0	14	4	15	17	17	0
0	14	5	<9	9	-9	0
0	14	6	<9	14	14	0
0	14	7	<9	11	11	0
0	14	8	<9	5	5	0
0	14	9	<9	15	-15	0
0	14	10	13	28	-28	0
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3	12	10	16	14	13	-4
3	12	11	<7	6	6	-2
3	12	12	<7	4	-3	2
3	12	13	<6	11	-11	0
3	12	14	15	11	11	0
3	13	0	24	32	0	-32
3	13	1	32	29	6	28
3	13	2	<7	18	14	11
3	13	3	22	22	22	-5
3	13	4	20	14	-10	9
3	13	5	19	16	-14	7
3	13	6	<7	20	-4	-19
3	13	7	<7	12	-5	10
3	13	8	13	18	6	16
3	13	9	15	15	15	3
3	13	10	<7	14	5	12
3	13	11	16	17	-15	-8
3	13	12	13	14	-5	-13

coordinates calculated from the diagonal elements of the inverse of the full normal matrix. They ranged from 0·04 to 0·05 Å for bond lengths and 2° to 3° for bond angles. Most bond lengths have reasonable values, although a few such as C(2)–O(2) of the cytosine ring and C(5)–C(6) of the guanine ring are poor. The bond lengths and angles in the sugar ring in bromodeoxycytidine are uncertain because of the disorder in that region of the lattice, and the position of C(5′) is certainly in error. The two positions obtained in the refinement for O(5′) are shown, and the angles and distances for the contacts across the twofold axis are indicated.

Conformation of 5-*bromodeoxycytidine*

The results of least-squares planes calculations are given in Table 3. For the cytosine ring the fit to the least-squares plane for the ring atoms is satisfactory, considering the large standard error in atomic positions in this structure. The substituents N(4) and O(2) show rather large deviations, which may be significant, although the atomic positions are fairly unreliable. The back contacts between substituents on the ring are 2·73 Å for C(1′) · · · O(2) and 3·21 Å for Br · · · N(4). The distances of the three hydrogen bonding atoms of the guanine residue to the plane of cytosine are similar, indicating that the two bases are not twisted with respect to one another.

The deoxyribose ring is puckered with C(2′) lying 0·54 Å above the plane formed by the other four atoms of the ring [*i.e.* on the same side as C(5′)]. Distances of the other sugar atoms to the plane are given in Table 3. The dihedral angle between the cytosine and sugar planes is 77°. The orientation of the sugar is *anti* with a torsion angle φ_{CN} (as defined by Donohue & Trueblood, 1960) of −61°.

Conformation of deoxyguanosine

Least-squares plane data are given in Table 3. The guanine ring atoms form a satisfactory plane, though

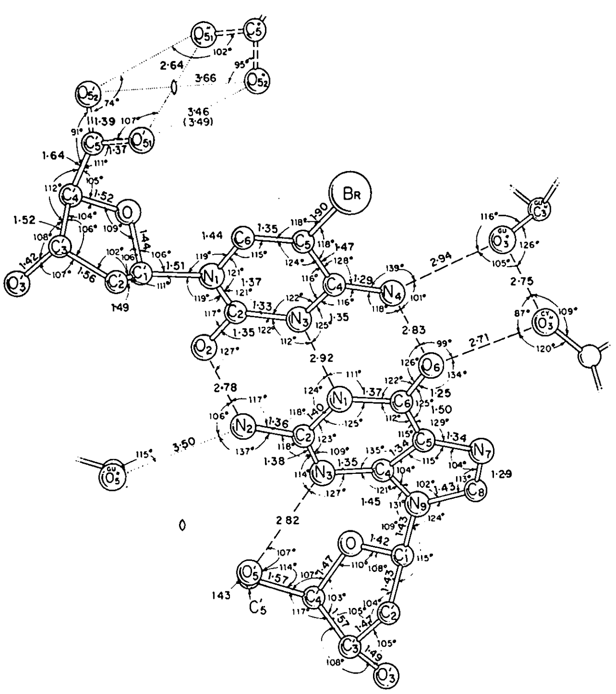

Fig. 1. Covalent bond and hydrogen bond distances and angles of the deoxyguanosine-5-bromodeoxycytidine pair. The view is down the short *a* axis of the unit cell. Atoms belonging to neighboring molecules are labeled GU for deoxyguanosine and CY for bromodeoxycytidine. Probable hydrogen bonds are shown with dashed lines. Dotted lines indicate the contact between N(2) of guanine and a neighboring O(5′) of deoxyguanosine [labeled GU O(5″)] and the various contacts for the two positions of bromodeoxycytidine O(5′) across the twofold axis. The *syn* conformation of deoxyguanosine as compared with the *anti* conformation of bromodeoxycytidine is apparent in this projection.

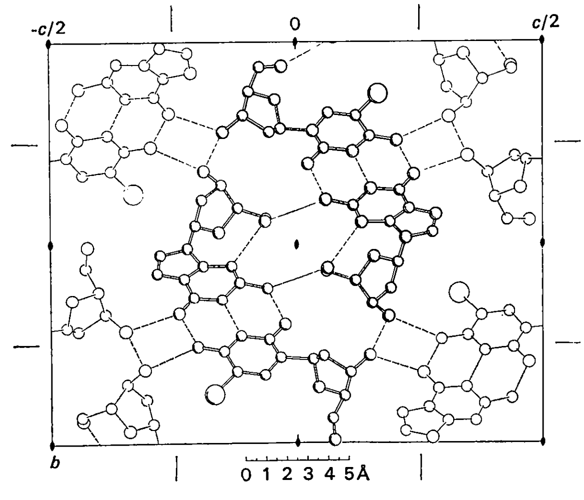

Fig. 2. Packing diagram of the deoxyguanosine-5-bromodeoxycytidine crystal structure viewed down the *a* axis. The atoms are identified in Fig. 1. Dashed lines indicate probable hydrogen bond contacts. Dotted lines show other contacts of interest. The O(5′) atoms of bromodeoxycytidine are arbitrarily shown in either position 1 or position 2, and do not obey the twofold symmetry.

the substituent atoms show deviations from the plane. The values of 0·12 Å for N(2) and 0·33 Å for C(1′) are large enough to be significant. Large deviations of C(1′) have also been found in other purine nucleosides: 0·21 Å in adenosine-5′-phosphate (Kraut & Jensen, 1963) and 0·22 Å in deoxyadenosine (Watson, Sutor & Tollin, 1965).

The 0·33 Å deviation of C(1′) from the guanine plane may be related to the unusual orientation of the sugar with respect to the base. In contrast to every previous case of a β-linked nucleoside the sugar in this structure assumes the *syn* orientation with $\varphi_{CN} = +138°$. Calculations based on this structure and others (Haschemeyer & Rich, 1965) show that there is little restriction on rotation about the glycosidic bond in purine nucleosides, in agreement with earlier predictions (Donohue & Trueblood, 1960). In this case the *syn* conformation is stabilized by a possible intramolecular hydrogen bond between N(3) of guanine and O(5′) of the sugar. The distance (2·82 Å) and C(5′)–O(5′) · · · N(3) angle (107°) are reasonable, although the distance of O(5′) from the guanine plane indicates the bond would lie out of that plane by 27°.

The puckering of the deoxyribose ring in deoxyguanosine is similar to that in bromodeoxycytidine, as indicated in Table 3. The dihedral angle between the guanine and sugar planes is 69°, similar to the values found for nucleosides in the *anti* conformation.

Configuration of the base pair

The guanine and cytosine rings are approximately coplanar, as shown in Fig. 1. The dihedral angle between their least-squares planes is 3·4°. The observed hydrogen bond lengths 2·78, 2·92 and 2·83 Å may be compared to the values 2·82, 2·91 and 2·93 Å found in the complex of 9-ethylguanine and 1-methylcytosine (O'Brien, 1963) and 2·91, 2·95 and 2·86 Å found in the complex of 9-ethylguanine and 5-bromo-1-methylcytosine (Sobell, Tomita & Rich, 1963). The distance between the glycosidic carbon atoms [C(1′)] of the two nucleosides is 10·8 Å.

Overall hydrogen bonding and molecular packing

The packing of this structure and the probable hydrogen bonding are shown in Fig. 2. The latter is interesting in that the only hydrogen bonds stabilizing the structure, other than those within the base pair, are the bonds involving cytidine N(4) and guanine O(6) and the neighboring O(3′) atoms of both deoxyguanosine and bromodeoxycytidine. These bonds form a continuous spiral along the *a* axis. The distances and angles, as shown in Fig. 1, are reasonable.

None of the other possible hydrogen-bond donors or acceptors appear to contribute to the overall stabilization of the lattice. An available proton on N(2) of guanine does not participate in hydrogen bonding. The sugar residue of bromodeoxycytidine is disordered in the region of O(5′), and it seems doubtful that O(5′) is hydrogen bonded to its countpart across the twofold axis. Considering the equal weight between positions 1 and 2, it is possible that position 1 is occupied on one side of the axis and position 2 on the other side. The bromine atom does not participate in hydrogen bonding; its closest contacts are 3·73, 3·83, and 3·84 Å to C(4), N(3) and N(4) in the cytosine ring above, 3·77 Å to the neighboring O(3′) of deoxyguanosine shown in Fig. 1, and 3·83 Å to the closest O(5′)-2 position of bromodeoxycytidine.

We thank Professor Alexander Rich for providing facilities and support for this investigation. The work was done in part at the Computation Center at the Massachusetts Institute of Technology.

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Table 3. *Least-squares planes**

Coordinates are expressed in Å.

Bromocytosine ring

$0{\cdot}6927x+0{\cdot}7211y-0{\cdot}0143z-8{\cdot}9609=0$

Atoms comprising the plane	Displacements (Å)	Displacements (Å) of other atoms	
N(1)	0·029	Br	−0·048
C(2)	−0·038	O(2)	−0·098
N(3)	0·023	N(4)	0·071
C(4)	0·000	C(1′)	−0·030
C(5)	−0·008	Guanine N(1)	−0·184
C(6)	−0·006	Guanine N(2)	−0·231
		Guanine O(6)	−0·247

Deoxyribose sugar of bromodeoxycytidine

$0{\cdot}7068x-0{\cdot}3703y+0{\cdot}6027z-4{\cdot}2255=0$

Atoms comprising the plane	Displacements (Å)	Displacements (Å) of other atoms	
C(1′)	−0·026	C(2′)	0·540
O(1′)	0·040	C(5′)	1·303
C(3′)	0·024	O(3′)	−1·305
C(4′)	−0·038	O(5′)-1	2·426
		O(5′)-2	0·710

Guanine ring

$0{\cdot}6606x+0{\cdot}7504y+0{\cdot}0209z-8{\cdot}9574=0$

Atoms comprising the plane	Displacements (Å)	Displacements (Å) of other atoms	
N(1)	−0·029	N(2)	−0·117
C(2)	0·026	O(6)	−0·060
N(3)	−0·016	C(1′)	0·333
C(4)	0·009	O(5′)	1·236
C(5)	−0·024		
C(6)	0·039		
N(7)	−0·033		
C(8)	0·040		
N(9)	−0·012		

Deoxyribose sugar of deoxyguanosine

$0{\cdot}8489x-0{\cdot}2642y-0{\cdot}4578z+3{\cdot}2559=0$

Atoms comprising the plane	Displacements (Å)	Displacements (Å) of other atoms	
C(1′)	0·008	C(2′)	0·454
O(1′)	−0·013	C(5′)	1·298
C(3′)	−0·007	O(3′)	−1·436
C(4′)	0·012	O(5′)	2·523

* Planes were calculated with a program based on the method of Blow (1960).