The Crystal Structure of 1-Ethyl-5-bromouracil. I. The Crystal Structure of the Form I Crystal of 1-Ethyl-5-bromouracil

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1-Ethyl-5-bromouracil, $C_6H_7N_2O_2Br$, is crystallized in two forms. Crystals of the form I are monoclinic with four molecules in a unit cell of dimensions; $a=7.89$, $b=12.01$, $c=9.71$ Å, $\beta=121.0°$, space group $P2_1/c$. Three-dimensional intensity data were collected by diffractometer with Mo-$K\alpha$ radiation. The structure was determined by heavy atom method and refined by the block-diagonal least-squares method. The final R-value was 0.052 for all observed reflections. The molecules are joined together in pairs around a center of symmetry with two N–H···O hydrogen bonds connecting N(3) to carbonyl oxygen O(4), and stacked with the base plane tilted each other.

5-Bromouracil, one of base analogue mutagens, can be incorporated into DNA in place of the normal thymine base. Such an incorporation probably reflects the structural similarity of 5-bromouracil and thymine; the van der Waals radius of bromine atom (1.95 Å) is close to that of methyl group (2.01 Å). In fact, the crystal structure of 1-methyl-5-bromouracil has been found to be isomorphous with that of 1-methylthymine[1] by X-ray study in this laboratory.[2] Once incorporated into DNA, however, the substituted bromine atom may cause to perturb an electron distribution on the pyrimidine ring, since bromine atom has the greater electronegativity than the methyl group. Therefore, this substitution of DNA affects on important biological properties; the increase of the sensitivity to ultraviolet irradiation[3] and the significantly higher melting temperature as compared with that of normal DNA.[4]

The structure analysis of 1-ethyl-5-bromouracil is of great interest in order to examine the influence of bromine atom on the molecular arrangement and the hydrogen bonding. In an earlier report, we described our finding of two forms of 1-ethyl-5-bromouracil, in which the main structural difference between two forms is on the mode of hydrogen bond.[5] In this paper, we describe the precise crystal structure analysis of the form I of 1-ethyl-5-bromouracil.

Experimental

1-Ethyl-5-bromouracil was kindly supplied by Professor A. Rich, M.I.T., U.S.A. and colorless plate-like crystal were obtained by slow evaporation of dimethyl sulfoxide solution. Rotation and Weissenberg photographs around the elongated axis showed the crystals to be monoclinic. The systematic absences for $h0l$ with $l=2n+1$ and for $0k0$ with

TABLE 1. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS
(Estimated standard deviations are shown in parentheses ($\times 10^4$). Thermal parameters are in the form of exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$).

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	1.2419(1)	0.2499(1)	0.9325(1)	0.0167(1)	0.0073(0)	0.0013(1)	−0.0029(2)	−0.0038(1)	0.0037(0)
C(2)	0.7281(8)	0.2801(8)	0.3950(5)	0.0125(13)	0.0040(5)	0.0062(6)	−0.0004(12)	0.0013(10)	0.0009(3)
C(4)	1.0155(8)	0.3653(6)	0.6369(7)	0.0135(14)	0.0043(5)	0.0051(4)	0.0003(13)	0.0017(10)	−0.0001(3)
C(5)	1.0340(7)	0.2619(6)	0.7172(6)	0.0125(12)	0.0043(5)	0.0054(5)	0.0017(14)	0.0016(9)	0.0017(3)
C(6)	0.9117(9)	0.1766(6)	0.6406(7)	0.0157(15)	0.0053(5)	0.0073(6)	−0.0007(14)	0.0049(10)	0.0021(3)
C(7)	0.6347(10)	0.0866(6)	0.3990(8)	0.0155(16)	0.0055(6)	0.0109(7)	−0.0045(15)	0.0036(13)	−0.0028(4)
C(8)	0.6985(13)	0.0287(8)	0.2949(11)	0.0311(28)	0.0084(8)	0.0238(12)	−0.0131(24)	0.0148(20)	−0.0121(7)
O(2)	0.6003(7)	0.2913(4)	0.2551(6)	0.0155(11)	0.0070(4)	0.0002(5)	−0.0010(11)	−0.0086(10)	0.0018(4)
O(4)	1.1202(6)	0.4480(4)	0.6943(5)	0.0176(11)	0.0042(4)	0.0035(5)	−0.0041(10)	−0.0019(8)	−0.0017(2)
N(1)	0.7610(7)	0.1849(4)	0.4814(6)	0.0136(12)	0.0039(4)	0.0078(5)	−0.0038(11)	0.0025(9)	−0.0013(3)
N(3)	0.8567(7)	0.3678(5)	0.4809(6)	0.0150(13)	0.0050(4)	0.0041(6)	0.0020(12)	0.0010(9)	0.0004(3)
H(1)	0.8715	0.4238	0.4195	3.42					
H(2)	0.9408	0.1006	0.7050	1.56					
H(3)	0.6619	0.0321	0.4984	3.18					
H(4)	0.4886	0.1178	0.3306	2.46	isotropic thermal parameters				
H(5)	0.8430	0.0035	0.3746	4.47					
H(6)	0.6730	0.0839	0.2062	2.82					
H(7)	0.6441	−0.0410	0.2451	3.58					

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2) K. Morita, unpublished result.
3) R. L. Erikson and W. Szybalski, *Biochem. Biophys. Res. Commur.*, **4**, 258 (1961).
4) S. Kit and T. C. Hsu, *ibid.*, **5**, 120 (1961).
5) H. Mizuno, N. Nakanishi, T. Fujiwara, K. Tomita, T. Tsukihara, T. Ashida, and M. Kakudo, *ibid.*, **41**, 1161 (1970).

TABLE 2. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

K	FO	FC
H,L=	0	0
2	290	321
4	206	216
6	152	-157
8	97	92
10	82	-83
12	37	33
14	30	-29
16	28	22
H,L=	0	1
2	38	-37
4	123	-124
5	33	-36
7	16	17
8	31	-31
9	19	20
11	44	-43
H,L=	0	2
0	91	87
1	176	171
2	158	-161
3	162	-167
4	34	39
5	142	145
6	56	-61
7	108	-112
8	76	79
9	49	48
10	35	-35
11	32	-30
12	35	37
13	34	31
14	20	-18
H,L=	0	3
1	13	-10
4	19	17
5	30	-30
6	22	17
7	40	41
8	15	13
10	16	14
11	22	18
H,L=	0	4
0	17	15
1	256	249
3	147	-144
5	152	153
6	21	17
7	104	-105
8	15	-17
9	72	75
11	61	-62
13	23	26
H,L=	0	5
1	24	23
2	17	17
3	15	15
4	13	9
5	40	-40
6	20	-20
9	17	-19
10	17	14
H,L=	0	6
0	107	-103
1	85	82
2	130	124
3	64	-61
4	122	-119
5	14	10
6	103	103
7	31	-28
8	57	-57
9	39	37
10	30	32
11	16	-14
12	28	-29
H,L=	0	7
2	13	-11
4	26	26
5	23	-26
6	48	-49
7	19	23
8	14	16
10	15	-12
H,L=	0	8
0	69	-61
1	21	-21
2	59	56
3	20	17
4	89	-88
5	18	-18
6	74	73
8	49	-46
10	47	44
H,L=	0	9
7	17	-10
H,L=	0	10
0	18	-18
1	50	-50
2	34	33
3	50	53
4	23	-18
5	44	-44
H,L=	1	0
0	121	114
1	89	-82
2	28	-26
3	191	199
4	25	-25
5	188	-198
7	141	143
8	22	24
9	126	-109
10	40	-38
11	80	80
13	33	-34
15	32	28
H,L=	1	1
1	60	58
2	53	-50
3	45	44
4	14	12
5	62	-63
6	66	-64
7	38	37
H,L=	1	2
0	83	80
1	166	-163
2	201	-191
3	118	117
4	98	97
5	113	-113
6	62	-64
7	72	72
8	81	81
9	57	-57
10	39	-40

K	FO	FC
11	31	32
12	33	32
13	26	-24
14	25	-22
H,L=	1	3
1	12	-13
2	68	62
3	28	-27
4	27	24
6	27	25
7	12	-10
10	11	12
11	19	22
H,L=	1	4
0	142	139
1	87	81
2	111	-106
3	21	-19
4	160	154
5	14	15
6	136	-135
8	90	91
9	22	29
10	73	-73
12	42	41
14	31	-28
H,L=	1	5
1	16	14
4	23	21
6	54	-54
9	24	-21
H,L=	1	6
0	72	75
1	106	102
2	71	-70
3	81	-79
4	48	47
5	25	26
6	52	-52
7	59	-59
8	38	35
9	49	49
11	29	-29
12	15	11
H,L=	1	7
10	18	18
H,L=	1	8
0	20	-20
1	106	107
2	25	22
3	76	-75
4	25	-25
5	76	76
6	16	17
7	51	-51
8	12	-8
9	34	35
H,L=	1	10
0	54	-54
1	15	15
2	47	51
H,L=	2	0
0	232	-237
1	69	-66
2	183	186
3	13	11
4	193	-199
5	117	-113
6	116	118
8	73	-75
10	55	53
11	13	3
12	44	-43
14	28	27
H,L=	2	1
1	57	-52
2	19	17
3	41	-41
4	33	29
5	37	36
6	18	-15
7	11	9
9	15	14
11	15	13
H,L=	2	2
0	170	-165
1	146	-141
2	145	141
3	151	149
4	100	-99
5	96	-95
6	74	73
7	94	94
8	56	-54
9	59	-60
10	48	50
11	45	43
13	34	-34
14	21	15
H,L=	2	3
1	15	-14
2	32	30
3	18	17
5	17	18
7	20	-15
8	13	14
H,L=	2	4
0	34	34
1	154	-151
2	27	-26
3	158	158
4	71	68
5	114	-114
6	68	-68
7	64	62
8	16	13
9	42	-40
11	38	39
13	20	-24
H,L=	2	5
1	13	13
3	28	-25
4	31	-29
5	52	50
7	32	-30
10	19	16
H,L=	2	6
0	63	59
1	20	-21
2	83	-83
3	44	42
4	81	79
5	54	-55
6	62	-63
7	22	24
8	52	57
9	27	-30

K	FO	FC
10	30	-32
11	25	21
H,L=	2	7
6	17	13
8	18	-13
H,L=	2	8
0	60	60
1	23	23
2	59	-62
3	20	-19
4	60	60
5	31	34
6	44	-44
H,L=	3	0
1	171	172
3	153	-154
5	93	96
7	116	-115
9	58	58
11	49	-47
13	34	35
H,L=	3	1
1	69	-66
2	17	-12
4	15	-16
5	12	-9
6	15	12
7	12	8
9	13	12
10	15	-9
13	14	7
H,L=	3	2
0	160	-160
1	49	50
2	120	118
3	30	-28
4	95	-95
5	105	105
6	98	99
7	51	-53
8	87	-88
9	46	45
10	57	58
11	30	-33
12	22	-25
13	17	17
H,L=	3	3
2	17	16
3	27	25
4	20	-21
5	22	20
6	22	21
7	45	-43
H,L=	3	4
0	114	-114
1	22	-24
2	92	97
3	12	5
4	58	-56
5	23	-21
6	67	69
8	71	-74
10	37	38
12	29	-30
H,L=	3	5
1	14	-13
2	19	16
3	13	8
4	23	-23
H,L=	3	6
0	69	-71
1	90	-91
2	46	46
3	80	80
4	40	-39
5	62	-65
6	35	35
7	46	50
8	22	-15
9	29	-27
H,L=	3	7
4	17	14
H,L=	3	8
0	39	38
1	50	-51
2	25	-25
3	39	40
4	20	21
H,L=	4	0
0	116	112
1	12	11
2	173	-174
3	12	-11
4	135	134
5	26	28
6	80	-82
7	13	-5
8	88	91
10	48	-47
12	41	37
H,L=	4	1
2	26	-23
3	11	14
4	38	39
7	13	-14
9	16	11
10	17	-12
H,L=	4	2
0	73	71
1	117	118
2	70	-70
3	131	-131
4	57	58
5	107	109
6	26	-25
7	51	-52
9	37	39
10	13	-13
11	30	-30
H,L=	4	3
1	14	-13
3	46	46
4	12	-13
5	20	-16
6	22	23
8	18	-17
H,L=	4	4
0	36	-37
1	67	68
2	36	37
3	90	-91
4	22	-19
5	62	63
6	13	22
7	62	-63
8	24	-22

K	FO	FC
9	45	45
H,L=	4	5
1	16	-18
6	15	-19
H,L=	4	6
0	60	-60
1	23	24
2	60	56
4	60	-62
5	17	22
6	42	47
7	17	-9
H,L=	5	0
0	22	28
1	107	-109
2	52	-54
3	83	83
5	74	-79
6	18	-24
7	91	94
8	23	26
9	64	-66
11	37	37
H,L=	5	1
2	20	-17
3	13	11
4	33	32
6	28	28
7	20	18
H,L=	5	2
0	80	80
1	34	-36
2	39	-40
3	23	22
4	59	57
5	27	-26
6	55	-56
7	39	39
8	26	29
9	36	-34
10	38	-38
H,L=	5	3
2	32	-35
6	18	-17
H,L=	5	4
0	80	80
1	20	20
2	83	-87
4	68	69
6	43	-48
7	18	-16
8	34	38
H,L=	5	5
3	15	-9
H,L=	5	6
1	45	52
H,L=	6	0
0	92	-94
1	33	-33
2	100	100
3	37	38
4	83	-86
5	16	-13
6	46	46
7	24	28
8	25	-24
9	27	-30
10	21	17
H,L=	6	1
2	31	-30
4	17	15
H,L=	6	2
0	26	-25
1	68	-70
2	32	31
3	55	57
5	45	-49
6	23	21
7	39	45
8	17	-16
9	34	-33
H,L=	6	3
5	17	9
H,L=	6	4
1	41	-45
2	31	-33
3	40	41
4	16	22
5	39	-42
H,L=	7	0
1	24	26
2	16	18
3	33	-32
4	14	-17
5	51	50
6	17	14
7	30	-31
9	32	33
H,L=	7	1
1	22	21
3	17	-16
H,L=	7	2
0	48	-50
1	24	25
2	44	47
3	36	-38
4	39	-42
5	16	16
H,L=	7	3
1	16	-7
H,L=	8	0
0	59	61
1	13	14
2	40	-40
3	13	-18
4	30	28
5	13	16
6	27	-31
H,L=	8	1
4	17	-8
H,L=	-1	0
0	119	114
1	90	82
2	29	-26
3	194	-199
4	23	-25
5	189	198
7	140	-143
8	23	24
9	106	109
10	38	-38
11	80	-80
13	39	34
15	31	-28
H,L=	-1	1
1	66	63

K	FO	FC
3	63	-63
4	17	19
5	20	-18
8	22	21
10	51	-52
11	28	-25
12	37	36
H,L=	-1	2
0	51	-51
1	14	12
2	148	162
3	194	-209
4	127	-134
5	123	129
6	106	108
7	95	-99
8	76	-76
9	58	57
10	68	69
11	31	-29
12	53	-51
13	34	30
14	32	33
H,L=	-1	3
1	37	-34
3	20	-19
4	54	-53
5	15	11
6	38	36
7	31	32
8	23	-25
10	23	-22
H,L=	-1	4
0	213	-206
1	11	11
2	160	155
3	21	21
4	177	-181
5	32	30
6	96	96
8	76	-78
10	71	73
12	30	-31
14	27	27
H,L=	-1	5
1	17	16
4	31	34
6	12	2
8	29	30
9	16	15
11	21	-26
H,L=	-1	6
1	105	-100
2	82	78
3	119	112
4	82	-82
5	99	-98
6	77	77
7	58	59
8	60	-62
9	57	-56
10	21	24
11	39	38
12	32	-30
13	27	-30
H,L=	-1	7
1	12	10
4	43	-42
5	32	-31
H,L=	-1	8
1	114	-109
2	24	-21
3	89	87
4	12	-13
5	67	-63
7	46	45
8	25	25
9	37	-38
11	27	28
H,L=	-1	9
3	17	-15
9	17	18
H,L=	-1	10
0	72	70
1	43	-43
2	62	-63
3	36	36
4	56	54
5	23	-24
6	45	-44
7	30	28
H,L=	-2	0
0	234	-237
1	69	66
2	187	186
3	10	-11
4	198	-199
5	119	113
6	120	118
8	75	-75
10	54	53
12	41	-43
14	30	27
H,L=	-2	1
1	129	124
2	42	-40
3	23	21
4	10	-8
5	17	-20
6	46	42
8	23	24
9	37	-37
10	27	-31
12	17	22
H,L=	-2	2
0	284	-282
1	332	-337
2	268	271
3	136	136
4	123	-125
5	123	-126
6	92	94
7	64	66
8	59	-59
9	81	-80
10	29	30
11	32	30
12	47	-46
13	15	-6
14	30	26
16	17	-12
H,L=	-2	3
0	11	0
2	97	-94
3	97	-100
5	37	37
6	11	-14

K	FO	FC
7	40	-40
8	11	-2
10	20	-25
11	21	22
12	18	18
H,L=	-2	4
0	40	-42
1	150	-166
2	44	-47
3	113	122
4	38	38
5	95	-101
6	11	-10
7	127	128
8	21	22
9	71	-69
10	14	12
11	49	49
13	21	-26
H,L=	-2	5
1	12	11
2	37	37
4	20	18
5	28	26
6	26	30
7	21	-20
8	13	-16
9	14	21
11	17	-19
H,L=	-2	6
0	156	150
1	139	-133
2	100	-96
3	102	102
4	75	75
5	74	-73
6	86	-89
7	55	57
8	50	54
9	36	-33
10	50	-52
11	29	25
12	25	25
13	25	-27
H,L=	-2	7
1	20	19
2	15	9
3	19	-21
4	37	-35
5	13	13
6	25	25
11	17	-15
H,L=	-2	8
0	118	111
1	16	14
2	91	-87
3	43	-42
4	68	66
5	35	35
6	65	-67
7	29	-31
8	65	66
10	35	-38
H,L=	-2	9
3	14	-11
4	32	-28
5	17	-9
6	32	32
7	25	25
8	20	-19
H,L=	-2	10
0	23	21
1	42	40
2	34	-30
3	41	-39
4	27	28
5	56	56
6	36	-33
7	30	-31
8	35	32
H,L=	-2	11
2	16	-6
H,L=	-3	0
1	178	-172
3	158	154
5	96	-96
7	117	115
9	61	-58
10	14	14
11	48	47
13	32	-35
15	19	14
H,L=	-3	1
1	24	27
2	16	-14
3	41	-37
4	19	13
5	70	68
6	33	31
7	19	-21
8	15	-15
H,L=	-3	2
0	47	46
1	120	-114
2	39	-36
3	87	83
4	88	85
5	99	-94
6	115	-111
7	114	113
8	44	43
9	106	-107
10	49	-47
11	50	50
12	27	27
13	17	-19
15	24	18
H,L=	-3	3
1	33	-30
2	114	-107
3	32	42
8	14	-15
9	30	-31
10	24	24
11	23	20
15	15	-5
H,L=	-3	4
0	109	109
2	149	-145
4	167	169
5	14	-13
6	103	-107
8	81	84
9	18	-16
10	49	-48
11	14	-14

K	FO	FC
12	49	50
13	25	23
14	39	-32
H,L=	-3	5
1	31	-30
2	17	-17
3	15	-14
4	13	14
6	12	11
7	26	-25
9	13	11
10	13	12
12	20	-17
H,L=	-3	6
0	71	78
1	83	94
2	84	-94
3	59	-63
4	82	90
5	75	83
6	58	-60
7	34	-30
8	44	49
9	38	38
10	42	-43
11	22	-24
12	24	22
14	18	-14
H,L=	-3	7
1	33	32
3	11	15
5	16	-18
7	14	13
9	21	-26
10	19	-7
11	15	12
H,L=	-3	8
1	78	71
2	24	19
3	113	-115
5	74	78
7	66	-70
9	41	43
11	31	-35
H,L=	-3	9
2	16	-18
3	23	-23
H,L=	-3	10
0	62	-60
1	46	44
2	49	49
3	48	-49
4	38	-39
5	42	43
6	24	27
8	20	-19
H,L=	-3	11
4	19	17
H,L=	-3	12
0	48	-45
2	54	51
H,L=	-4	0
2	179	-174
3	15	11
4	141	134
5	29	-28
6	83	-82
8	93	91
10	47	-47
12	39	37
H,L=	-4	1
1	16	-15
2	14	13
4	50	45
13	18	13
H,L=	-4	2
0	172	166
1	88	83
2	134	-128
3	74	-75
4	147	141
5	70	69
6	89	-87
7	18	-16
8	32	31
9	37	35
10	42	-39
11	26	-23
12	16	17
13	18	18
H,L=	-4	3
2	15	-19
3	68	65
6	16	14
8	46	-46
9	16	-20
10	20	18
H,L=	-4	4
0	25	-27
1	205	195
2	13	-11
3	207	-205
5	93	95
7	91	-91
8	24	-25
9	52	54
11	43	-41
12	25	26
13	36	32
H,L=	-4	5
1	85	-82
3	58	55
4	18	15
5	26	-26
6	15	-13
7	21	25
11	17	17
13	15	-2
H,L=	-4	6
0	72	-68
1	79	75
2	70	73
3	30	-32
4	53	-54
5	63	65
6	62	62
7	43	-44
8	50	-54
9	42	39
10	36	38
11	31	-29
12	16	-11
H,L=	-4	7
3	15	10
4	14	13
6	17	-17

K	FO	FC
8	25	28
9	21	-19
10	16	-17
H,L=	-4	8
0	96	-108
2	90	103
4	72	-82
6	51	63
8	50	-55
10	32	32
12	29	-31
H,L=	-4	9
2	35	-37
4	20	22
6	14	-19
7	15	-9
8	15	11
H,L=	-4	10
0	41	-40
1	51	-53
2	18	15
3	35	36
5	39	-42
6	26	24
7	41	44
8	21	-20
9	33	-36
H,L=	-4	11
4	17	15
5	18	14
7	22	-23
H,L=	-4	12
1	30	-32
3	34	31
H,L=	-5	0
1	111	109
2	53	-54
3	84	-83
4	13	16
5	79	79
6	24	-24
7	95	-94
8	24	26
9	65	66
11	36	-37
H,L=	-5	1
2	17	17
3	16	-10
6	13	11
7	13	15
8	16	17
H,L=	-5	2
0	74	-74
1	89	85
2	76	75
3	46	-45
4	49	-48
5	75	73
6	59	59
7	50	-50
8	36	-35
9	36	37
10	20	19
11	39	-36
12	17	-19
H,L=	-5	3
2	19	-16
3	39	37
4	20	17
5	20	-20
6	23	-24
7	16	-17
8	18	15
H,L=	-5	4
0	97	-95
1	23	20
2	77	72
3	32	-33
4	71	-68
6	95	93
7	29	-29
8	96	-95
9	29	28
10	55	53
11	15	-4
12	33	-30
14	17	14
H,L=	-5	5
1	13	-16
2	41	39
3	25	25
4	33	-30
7	20	-20
9	20	21
H,L=	-5	6
0	104	-98
1	71	-66
2	61	61
3	64	66
4	59	-58
5	56	-61
6	50	54
7	30	32
8	37	-40
9	17	-16
10	30	33
11	31	28
13	38	-33
H,L=	-5	7
2	25	25
4	13	14
H,L=	-5	8
1	73	-70
2	22	21
3	73	73
5	52	-56
7	46	51
9	36	-32
11	24	25
H,L=	-5	9
5	16	11
8	16	-15
11	19	-14
H,L=	-5	10
0	32	37
1	35	-39
2	41	-50
3	26	33
4	38	41
5	32	-36
6	26	-31
7	22	26
9	26	-26
10	22	-15
H,L=	-5	12
0	35	33
2	39	-40

K	FO	FC
4	39	40
H,L=	-6	0
0	92	-94
1	33	33
2	101	100
3	38	-38
4	86	-86
6	44	46
7	28	-28
8	26	-24
9	32	30
10	17	17
H,L=	-6	1
3	27	-29
4	10	12
5	11	14
6	25	-23
7	18	17
H,L=	-6	2
0	78	-76
1	51	-49
2	74	72
3	64	63
4	87	-85
5	41	-39
6	51	53
7	42	41
8	34	-33
9	31	-28
10	31	33
11	17	15
12	22	-17
H,L=	-6	3
8	16	18
12	18	11
H,L=	-6	4
0	15	-14
1	104	-100
2	46	46
3	102	100
5	70	-69
6	12	11
7	34	32
8	18	-19
9	31	-31
11	25	22
H,L=	-6	5
3	21	-17
4	34	-34
5	26	27
6	20	-22
7	33	-34
9	19	20
13	19	12
H,L=	-6	6
0	40	39
1	65	-63
2	80	-80
3	79	77
4	58	59
5	60	-61
6	43	-44
7	22	24
8	43	43
9	19	-17
10	17	-19
11	32	29
12	19	11
13	23	-25
H,L=	-6	7
2	35	37
3	21	-20
6	17	17
H,L=	-6	8
0	55	54
1	16	7
2	45	-44
4	45	50
6	41	-42
8	34	40
10	29	-33
12	19	11
H,L=	-6	9
8	20	-22
H,L=	-6	10
0	44	42
1	32	31
2	38	-38
3	40	-40
4	33	34
5	24	26
6	30	-25
7	24	-26
8	15	14
9	25	23
10	17	-15
H,L=	-6	11
1	15	-15
3	20	19
H,L=	-6	12
0	19	-17
1	20	22
5	18	24
H,L=	-7	0
1	29	-26
2	15	18
3	32	32
4	18	-17
5	50	-50
7	31	31
9	31	-32
H,L=	-7	1
9	19	13
H,L=	-7	2
0	29	27
1	64	-62
2	40	-38
3	52	55
4	16	15
5	48	-49
6	16	-16
7	54	55
8	29	31
9	30	-32
10	22	-17
H,L=	-7	3
4	15	14
6	14	12
8	15	-10
H,L=	-7	4
0	63	63
2	43	-43
4	44	47
6	49	-49
8	33	31
10	31	-29
H,L=	-7	5

K	FO	FC
2	16	15
4	16	-16
H,L=	-7	6
0	48	46
1	31	29
2	41	-41
3	18	-16
4	44	45
6	55	-55
7	29	-26
8	47	46
9	21	23
10	26	-26
H,L=	-7	7
3	22	-21
6	15	-16
H,L=	-7	8
1	72	69
3	39	-37
5	39	39
7	31	-28
9	25	22
H,L=	-7	9
1	15	10
H,L=	-7	10
0	16	-15
1	29	29
2	22	22
3	31	-30
5	26	24
6	16	18
7	22	-25
H,L=	-7	12
0	46	-43
2	30	29
4	23	-24
6	21	21
H,L=	-8	0
0	59	61
2	38	-40
4	27	28
6	26	-31
H,L=	-8	1
2	14	-14
6	15	4
H,L=	-8	2
0	64	67
1	23	22
2	55	-59
3	22	-21
4	36	35
5	16	16
6	23	-24
8	26	29
H,L=	-8	4
1	51	50
2	15	-14
3	46	-47
5	53	55
7	31	-30
9	29	23
H,L=	-8	5
1	18	13
H,L=	-8	6
0	25	-24
1	49	50
2	29	26
3	45	-49
4	22	-20
5	19	17
6	18	14
7	24	-22
9	17	16
H,L=	-8	7
4	21	19
5	19	-16
6	17	-23
7	22	22
H,L=	-8	8
0	33	-32
2	38	40
4	52	-52
6	37	37
H,L=	-8	10
2	18	16
3	14	15
4	18	-21
5	17	-11
9	23	-14
H,L=	-8	12
2	16	2
3	20	23
5	17	-21
H,L=	-9	2
3	24	-27
5	22	22
H,L=	-9	3
0	15	0
H,L=	-9	4
0	37	-32
2	34	35
4	31	-29
5	22	24
6	28	24
H,L=	-9	6
4	22	-17
5	16	-14
6	18	16
H,L=	-9	8
1	27	-25
2	16	5
3	21	21
5	23	-24
6	17	21
H,L=	-9	9
5	18	-10
H,L=	-9	10
0	24	23
1	24	-26
2	22	-16
3	16	13
H,L=	-10	4
0	20	-23
H,L=	-10	5
2	15	3
H,L=	-10	6
3	17	20
H,L=	-10	8
0	29	26
2	22	-23

$k=2n+1$, indicate the space group to be $P2_1/c$. From measuring the 2θ setting angles for 14 reflections on the diffractometer with Mo-$K\alpha$ radiation, the unit cell dimensions were determined to be $a=7.89$, $b=12.01$, $c=9.71$ Å, and $\beta=121.0°$. The density measured by the flotation method, with a mixture of benzene and ethylene bromide, was 1.84 gcm^{-3}, whereas the calculated density on the assumption of four molecules in the unit cell is 1.84 gcm^{-3}. Three-dimensional intensity data were collected on a full automatic four-circle diffractometer (Rigaku Denki Co. Ltd.) with Zr-filtered Mo-$K\alpha$ radiation. For the intensity measurement, a plate-like crystal with approximate dimensions of $0.12\times0.20\times0.40$ mm was used and the c-axis was mounted as coincident to the ϕ axis of the goniostat. A total of 2244 independent reflections accessible in $\sin\theta/\lambda$ less than 0.65 were scanned by the ω-2θ technique at a scan speed of 4° per minute through the scan range from $\{2\theta(\alpha_1)-0.65°\}$ to $\{2\theta(\alpha_2)+0.65°\}$ for all reflections, in which a value of 0.65° was determined by measuring the scan range for a sufficiently strong and low order reflection. Background counts of five seconds duration were taken at both sides of each peak. In order to correct the intensities for coincidence loss, the counting rate was kept less than 10000 counts per second with an automatic attenuator mechanism. During the data collection, the intensities for three standard reflections (080), (006), and (800) were measured periodically to check the stability of the electronics and the damage on crystal lattice. After 1187 of all reflections, which have the net intensity exceeded three times of its estimated standard deviations, were recorded and corrected for the usual Lorentz and polarization effects, these data were converted to the absolute scale by means of the usual averaging process.

Structure Determination and Refinement

A three-dimensional Patterson function was calculated, and this easily revealed bromine atom position. Since y paprameter of bromine atom is nearly 1/4, however, the first Fourier synthesis phased on the bromine atom position brought about the pseudo mirror plane at $y=1/4$. To avoid such a trouble, the useful two-dimensional (0 1 0) Fourier synthesis was carried out, and all the non-hydrogen atoms except the terminal ethyl carbon could be assigned. Subsequent Fourier synthesis phased on these positions showed the complete structure including the terminal ethyl carbon.

Three-dimensional refinement was then carried out by block-diagonal least-squares method with unit weight factors for all reflections. The positional parameters of all the non-hydrogen atoms and anisotropic thermal parameters of the bromine atom were initially refined to drop R-index ($\sum||F_o|-|F_c||/\sum|F_o|$) to 0.08. At this stage, a difference Fourier map clearly revealed the positions of all the hydrogen atoms. Finally, all positional parameters, together with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, were refined, and the R-index decreased to 0.052 for all observed reflections.

Final atomic coordinates and thermal parameters together with the corresponding standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 2.

Results and Discussion

The intramolecular bond lengths and angles are shown in Fig. 1. Within the experimental errors, these values except hydrogen atoms are in good agreement with the values found in other uracil derivatives; 1-methyluracil[6] and 1-methylthymine.[1] The only remarkable deviations were found in the C(2)-N(3) bond length, which is about 0.02 Å longer than those of the above-mentioned derivatives, and in the N(3)-C(4)-C(5) angle which is significantly less here (113.3°) than in 1-methyluracil (116°)[6] and 1-methylthymine (116.1°)[1]. A similar value of this angle is also found in the form II (112.7°) of 1-ethyl-5-bromouracil.[7] Such a smaller angle is commonly found in crystal structures of 5-halogenated uridines; 5-fluoro-2′-deoxy-β-uridine (112.6°)[8], 5-chlorouridine (113.7°),[9] 5-bromo-2′-deoxyuridine (112.4°) and 5-bromouridine (112.8°).[10] Therefore, it seems likely this angle is certainly affected by halogen substitution at C(5).

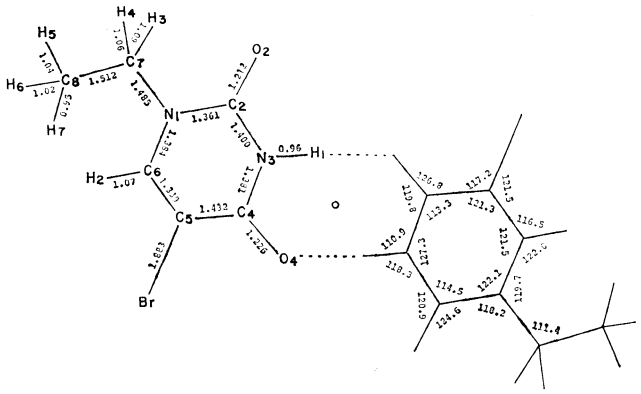

Fig. 1. Bond lengths and bond angles of 1-ethyl-5-bromouracil. The standard deviations are 0.008 Å in bond lengths and 0.6° in bond angles between non-hydrogen atoms.

The best plane through the six ring atoms, as calculated by the least-squares method, is defined by the equation. The distances from the non-hydrogen atoms to

$$-0.89763x + 0.32294y + 0.29995z + 1.30399 = 0.$$

Table 3. Deviations of atoms from the least-squares plane through the six ring atoms

Atom	Deviation (Å)	Atom	Deviation (Å)
Br	−0.008	N(1)	−0.005
C(2)	−0.007	N(3)	0.022
C(4)	−0.022	O(2)	−0.036
C(5)	0.006	O(4)	−0.043
C(6)	0.006	C(7)	−0.068

6) D. W. Green, F. S. Mathews, and A. Rich, *J. Biol. Chem.* **237**, 3573 (1962).
7) T. Tsukihara, T. Ashida, and M. Kakudo, This Bulletin **45**, 909 (1972).
8) D. R. Harris and W. M. MacIntyre, *Biophys. J.* **4**, 203 (1964).
9) S. W. Hawkinson and C. L. Coulter, *Acta Crystallogr*, **B27**, 34 (1971).
10) J. Iball, C. H. Morgan, and H. R. Wilson, *Proc. Roy. Soc., Ser. A*, **295**, 320 (1967).

this plane are listed in Table 3. Both exocyclic oxygen atoms O(2) and O(4) are significantly displaced on the same side of the plane. The substituent carbon atom C(7) is also markedly displaced by 0.068 Å from this plane. Such deviations from the base are frequently observed in crystal structures of purine and pyrimidine derivatives.

The arrangement of the molecules in the crystal is shown in Figs. 2 and 3. The basic molecular unit in this crystal is a dimer formed by two molecules which are joined together in pairs around a center of symmetry, with two N–H···O hydrogen bonds connecting the N(3) atom with the carbonyl oxygen O(4) at a distance of 2.85 Å. It is of particular interest that hydrogen bonded pairing system of the form I is quite different from that of the form II, in which N(3)–H and the carbonyl oxygen O(2) in place of O(4) are used for the hydrogen bond formation.[5,7]

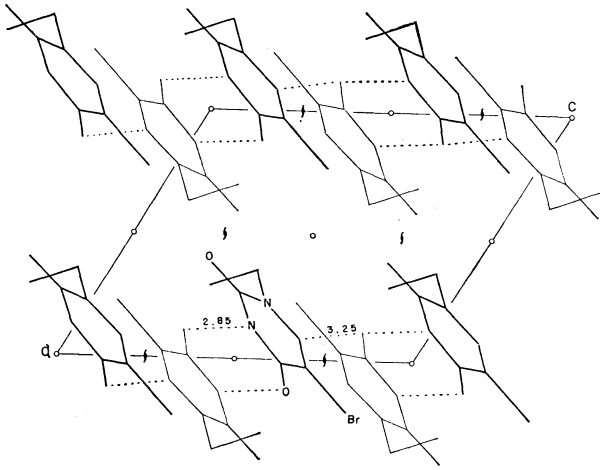

Fig. 2. The crystal structure viewed down the *b* axis.

Figures 2 and 3 show the stacking mode of the adjacent pyrimidine rings related by the *c*-glide plane, forming an infinite stack along the direction of the *c*-axis. This stacking is characterized by the following two points; one is the characteristic arrangement of the adjacent pyrimidine rings tilting to one another with the dihedral angle of 38.° The other is very little overlap of the bases and, therefore, main contact is due to the interactions between the bromine substituent and the adjacent pyrimidine ring as shown in Fig. 3. The distance from the bromine atom to this plane is 3.5 Å. Such a bromine-base contact is frequently found in crystal structures of halogenated purines and pyrimidines.[11]

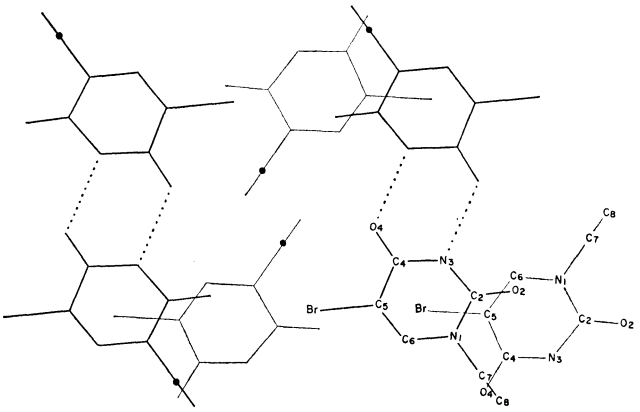

Fig. 3. The stacking of molecules viewed perpendicular to the plane (101).

The closest C···O intermolecular distance in the crystal is found between C(6) and the carbonyl oxygen O(4) of the adjacent molecule, and this distance is 3.25 Å, with the H···O distance 2.24 Å and the C–H–O angle 157.8°, which seems to be a weak hydrogen bond. A similar C–H···O contact has been reported in pyrimidine nucleotides; uridine residue of β-adenosine-2′-β-uridine-5′-phosphoric acid (3.18 Å),[12] calcium thymidine-5′-phosphate (3.42 Å)[13] and barium uridine-5′-phosphate (3.17 Å)[14], and in uracil derivatives; 1-methylthymine (3.11 Å)[1] and uracil (3.19 and 3.28 Å).[15] These values agree quite well with those suggested by Sutor as to the existence of C–H···O hydrogen bond in the solid state.[16]

11) C. E. Bugg, J. M. Thomas, M. Sundaralingam, and S. T. Rao, *Biopolymers*, **10**, 175 (1971).
12) E. Shefter, M. Barlow, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **B25**, 895 (1969).
13) K. N. Trueblood, P. Horn, and V. Luzzati, *ibid.*, **14**, 965 (1961).
14) E. Shefter and K. N. Trueblood, *ibid.*, **18**, 1067 (1965).
15) G. S. Parry, *ibid.*, **7**, 313 (1954).
16) D. J. Sutor, *J. Chem. Soc.*, **1963**, 1105.