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Stereochemistry of Macrolides. II.[1] Crystal Structure of *p*-Bromobenzoylpikromycin

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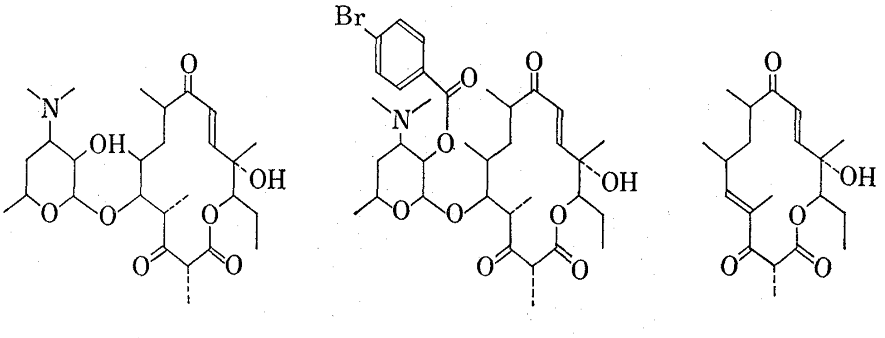
In order to elucidate the stereochemistry of 14-membered macrolactone, an X-ray crystal structural analysis of *p*-bromobenzoylpikromycin ($C_{35}H_{50}O_9NBr \cdot H_2O$) was carried out. The crystals are monoclinic with space group $P2_1$ and unit cell dimensions of $a = 19.027(9)$Å, $b = 14.876(5)$Å, $c = 7.148(3)$Å, $\beta = 108.97(8)°$, $Z = 2$. The crystal structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method including anisotropic thermal parameters to a final R value of 0.118.

The absolute configuration of pikromycin was determined on the D-desosamine moiety to be 2*R*, 4*R*, 5*S*, 6*S*, 8*R*, 12*S*, 13*R*, and 10*E*. A new "diamond lattice" conformation model D for *p*-bromobenzoylpikromycin is proposed based on the result of X-ray analysis.

Keywords——"Diamond lattice" conformation model; 14-membered macrolactone; X-ray analysis; absolute configuration; macrolide antibiotic

Pikromycin (amaromycin) is an antibiotic isolated from *Streptomyces flavochromogenese* by Hata, *et al.*,[3] and is active against gram-positive bacteria. The structure of pikromycin (**1**) has been elucidated as 10*E*-5-*O*-β-D-desosaminosyl-13-ethyl-12-hydroxy-3,9-dioxo-2,4,6,8,-12-pentamethyl-10-tridecenolide by chemical and spectroscopic methods,[4] and by X-ray analysis of kromycin.[5]



1 **2** **3**

Chart 1

Recently, we reported conformational studies on 14-membered macrolactone, derivatives of **1** and narbomycin by means of nuclear magnetic resonance (NMR) and circular dichroism (CD) spectra, and a new "diamond lattice" conformation model C for kromycin

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1) Part I: H. Ogura, K. Furuhata, H. Kuwano, and N. Harada, *J. Am. Chem. Soc.*, **97**, 1930 (1975).
2) Location: *a) Shirokane, Minato-ku, Tokyo 108, Japan; b) Hongo, Bunkyo-ku, Tokyo 113, Japan.*
3) T. Hata, Y. Sano, H. Tatsuta, R. Sugawara, A. Matsumae, and K. Kanamori, *J. Antibiot., Ser. A*, **8**, 9 (1955).
4) R.W. Rickards, R.M. Smith, and J. Majer, *Chem. Commun.*, **1968**, 1049; H. Muxfeldt, S. Schrader, P. Hansen, and H. Brockmann, *J. Am. Chem. Soc.*, **90**, 4748 (1968).
5) R.E. Hughes, H. Muxfeldt, C. Tsai, and J.J. Stezowski, *J. Am. Chem. Soc.*, **92**, 5267 (1970); C. Tsai, J.J. Stezowski, and R.E. Hughes, *J. Am. Chem. Soc.*, **93**, 7286 (1971).

TABLE I. Observed and Calculated Structure

K	FO	FC
H,L=-20		0
1	3	2
2	7	5
3	2	4
7	4	4
H,L=-19		0
0	9	8
3	3	1
4	5	1
5	8	9
6	6	4
H,L=-18		0
0	3	1
1	2	4
3	8	8
4	5	5
5	7	2
7	7	4
8	5	3
H,L=-17		0
0	3	4
1	10	9
3	16	15
5	7	6
9	4	3
H,L=-16		0
0	12	13
1	16	17
2	9	9
3	9	11
4	12	11
5	9	9
6	8	9
11	7	3
H,L=-15		0
0	3	6
1	6	5
2	13	13
3	11	12
6	6	2
7	6	3
9	7	7
10	6	7
11	8	5
H,L=-14		0
0	6	8
1	14	14
2	7	7
4	14	14
5	13	13
6	12	13
7	5	4
8	5	6
9	6	3
10	7	6
12	7	5
13	5	2
H,L=-13		0
0	4	4
1	18	18
2	18	15
3	16	18
4	13	13
5	12	15
6	12	10
7	9	13
8	7	10
9	6	6
10	6	4
11	6	8
12	8	6
13	4	3
H,L=-12		0
1	16	15
2	8	9
3	17	17
4	6	6
5	20	18
6	11	14
8	10	7
9	7	9
10	11	12
11	4	5
12	5	5
14	5	2
15	4	2
H,L=-11		0
1	17	20
2	14	15
3	9	10
4	20	23
5	6	7
6	9	8
7	5	4
9	9	11
10	16	17
11	4	7
12	9	10
14	6	5
H,L=-10		0
0	18	18
1	31	29
2	15	16
3	20	17
4	6	12
5	16	17
6	7	7
7	22	24
8	10	10
9	13	15
10	7	8
12	4	7
14	7	5
H,L=-9		0
0	28	28
1	6	6
2	28	27
3	14	19
4	20	24
5	17	16
6	15	16
7	8	13
8	20	24
9	7	8
10	13	14
11	8	6
12	9	10
14	4	5
H,L=-8		0
0	10	5
1	18	19
2	20	21
3	51	53
4	34	34
5	10	18
6	6	7
7	14	27
8	9	11
9	17	19
11	9	8
12	11	10
13	9	10
14	9	7
H,L=-7		0
0	27	28
1	35	37
2	48	55
3	54	55
4	38	33
5	24	24
6	18	21
7	6	10
8	14	18
9	7	13
10	15	14
11	10	13
13	6	9
16	6	2
H,L=-6		0
0	10	10
1	77	81
2	16	23
3	23	23
4	49	46
5	15	17
6	16	16
7	12	23
8	9	10
9	11	18
10	19	21
12	12	10
13	11	12
15	5	4
H,L=-5		0
0	46	43
1	49	46
2	60	56
3	51	48
4	31	53
5	49	46
6	36	42
7	17	19
8	29	30
9	31	30
10	20	22
11	20	19
12	11	11
H,L=-4		0
0	14	25
1	105	98
2	69	71
3	11	11
4	25	28
5	24	24
6	49	47
7	13	13
8	29	29
9	13	11
10	8	11
11	9	7
H,L=-3		0
0	43	53
1	53	62
2	53	51
3	11	11
4	57	61
5	12	11
6	24	40
7	18	17
8	18	16
9	39	39
10	2	1
11	5	6
H,L=-2		0
0	30	38
1	51	57
2	88	82
3	89	93
4	46	43
5	38	34
6	36	32
8	51	48
9	9	8
10	22	22
11	2	4
H,L=-1		0
0	10	1
1	25	21
2	16	18
3	64	55
4	42	40
5	57	52
6	33	37
7	48	44
8	35	31
9	24	24
10	14	12
11	9	9
H,L=0		0
2	133	117
4	77	71
6	34	36
8	12	12
10	5	4
H,L=-22		1
1	5	4
3	6	4
H,L=-20		1
3	6	6
4	4	4
8	4	5
H,L=-19		1
0	9	8
1	5	5
2	9	8
6	9	7
8	5	5
H,L=-18		1
2	9	10
5	5	3
6	5	3
7	4	2
9	5	4
H,L=-17		1
2	8	8
3	7	4
4	15	12
5	9	7
6	9	9
7	5	5
8	5	2
9	6	3
H,L=-16		1
1	16	15
2	9	10
4	12	14
5	8	7
6	11	13
7	6	6
10	6	6
11	5	5
H,L=-15		1
0	11	10
1	8	10
2	18	17
3	13	12
4	15	14
5	11	9
6	12	13
7	8	8
8	16	17
9	9	11
H,L=-14		1
0	25	24
1	7	10
2	18	16
3	12	12
4	16	18
5	10	12
7	5	7
8	8	9
9	7	5
10	6	5
H,L=-13		1
0	31	28
1	10	11
2	16	16
3	18	19
4	20	22
5	6	3
6	9	12
7	23	24
9	15	13
11	9	9
13	6	6
H,L=-12		1
0	25	25
1	6	6
2	12	11
3	14	12
4	25	24
6	21	22
7	16	17
9	14	13
10	7	8
H,L=-11		1
0	19	19
1	27	27
2	18	15
3	18	17
4	13	13
5	14	15
6	7	7
8	5	6
9	12	12
10	14	16
11	14	14
12	11	11
15	5	3
H,L=-10		1
0	49	48
1	29	27
2	41	40
3	5	5
4	4	22
5	16	18
6	21	21
7	16	17
8	8	7
10	8	6
12	9	11
13	7	8
14	7	8
15	4	2
16	4	2
H,L=-9		1
0	31	28
1	12	14
2	33	31
3	26	24
4	24	24
5	10	9
7	25	28
8	18	18
9	30	32
H,L=-8		1
0	10	11
1	22	25
2	58	58
3	54	47
4	36	37
5	15	14
6	25	28
7	9	7
8	27	26
9	14	14
10	19	19
11	12	11
12	11	10
13	5	5
14	6	6
17	5	4
H,L=-7		1
0	56	60
1	68	63
2	18	15
3	15	14
4	17	12
5	58	51
6	13	13
7	7	6
8	8	7
9	7	8
10	25	25
11	18	19
12	8	9
13	5	5
15	5	6
H,L=-6		1
0	48	49
1	7	6
2	46	45
3	41	43
4	31	28
5	27	27
6	22	25
7	30	32
8	10	11
9	5	3
10	8	7
11	22	22
13	6	7
15	7	5
16	5	7
H,L=-5		1
0	53	49
1	66	62
2	66	74
3	48	48
4	57	54
5	37	38
6	16	14
7	32	33
8	21	21
9	24	25
10	26	25
11	16	14
13	10	11
16	4	3
15	8	2
16	5	5
H,L=-4		1
0	88	89
1	82	81
2	58	53
3	27	29
4	53	54
5	47	43
6	20	18
7	16	11
8	29	27
9	13	13
10	20	19
11	15	14
12	6	5
13	7	7
14	9	10
15	5	5
H,L=-3		1
0	40	52
1	97	97
2	102	96
3	72	75
4	9	12
5	54	50
6	13	14
7	30	29
8	34	32
9	9	11
10	11	15
11	12	11
13	31	31
14	7	8
15	6	6
16	4	4
H,L=-2		1
0	27	26
1	106	107
2	57	47
3	78	76
4	30	29
5	44	40
7	43	41
8	11	11
9	11	11
10	12	13
11	18	18
12	14	12
13	14	14
15	5	5
H,L=-1		1
0	25	23
1	68	65
2	74	63
3	18	21
4	41	44
5	18	18
6	39	35
7	40	36
8	16	18
9	13	12
10	15	13
11	6	4
12	15	15
13	9	6
15	4	3
H,L=0		1
0	15	20
1	117	126
2	36	54
3	43	40
4	36	30
5	50	51
6	23	23
7	46	40
8	26	26
9	24	27
10	17	15
11	4	3
13	11	11
14	12	13
15	7	4
H,L=1		1
1	65	61
2	87	92
3	42	27
4	40	38
5	29	27
6	47	45
7	36	30
8	22	18
9	19	18
10	11	12
12	9	9
H,L=2		1
0	120	122
1	53	50
2	76	74
3	73	75
4	49	42
5	26	24
6	25	25
7	49	41
8	26	24
9	29	27
10	4	5
11	13	13
H,L=3		1
0	84	80
1	79	80
2	73	78
3	18	15
4	23	20
5	17	14
6	45	45
7	38	33
8	28	26
9	6	4
10	13	14
11	4	4
H,L=4		1
0	3	6
1	23	22
2	58	59
3	46	45
4	42	38
5	48	46
6	15	16
7	6	6
8	20	17
9	5	6
H,L=5		1
0	15	21
1	36	35
2	17	14
3	60	57
4	68	66
5	27	31
6	13	15
7	13	15
8	10	9
9	10	13
10	9	8
H,L=6		1
0	23	23
1	15	15
2	15	14
3	26	28
5	40	38
6	42	39
7	25	24
8	19	19
10	8	10
H,L=7		1
1	34	40
2	18	15
3	39	40
4	20	19
5	33	29
6	27	24
7	9	9
8	20	18
9	12	14
H,L=8		1
0	10	10
1	6	3
2	5	6
3	12	12
4	36	35
5	20	19
6	9	8
7	8	10
8	6	5
H,L=9		1
0	30	32
1	24	24
2	10	10
3	21	22
5	17	17
6	8	8
7	11	12
8	5	7
H,L=10		1
0	9	10
1	11	13
2	16	16
4	15	18
6	13	15
7	7	6
H,L=11		1
0	4	4
1	12	11
2	8	9
3	18	17
4	19	19
5	24	24
6	14	12
7	6	7
H,L=12		1
0	18	18
1	5	4
2	15	16
3	12	13
4	17	15
5	10	10
6	17	16
H,L=13		1
2	11	11
3	7	6
5	8	7
6	9	9
7	7	5
H,L=14		1
0	21	21
2	15	15
3	8	8
5	13	13
7	5	5
H,L=15		1
2	9	9
3	5	8
4	7	7
8	5	3
H,L=16		1
3	5	5
4	10	10
6	4	2
7	8	9
8	6	4
H,L=17		1
1	5	3
2	12	11
3	8	8
4	8	9
5	6	8
6	6	7
H,L=18		1
0	5	6
1	9	10
2	10	5
4	7	4
7	6	6
H,L=19		1
1	7	3
3	4	4
H,L=-23		2
0	5	7
H,L=-22		2
1	4	3
2	4	3
3	4	2
4	4	3
H,L=-21		2
1	7	6
5	7	4
H,L=-20		2
6	6	3
8	6	5
H,L=-19		2
0	9	6
1	6	4
3	6	7
4	5	3
6	6	5
7	6	4
8	5	5
9	5	3
H,L=-18		2
0	8	7
2	12	10
5	5	5
10	5	3
H,L=-17		2
1	17	17
2	9	5
3	15	15
4	7	6
5	10	10
6	7	4
7	7	4
8	6	8
9	5	5
12	4	4
H,L=-16		2
0	12	7
2	14	14
4	8	9
5	8	8
6	7	5
7	8	9
8	7	4
9	8	8
10	8	7
11	4	4
13	5	2
H,L=-15		2
1	8	7
2	8	7
3	14	13
4	11	11
5	12	10
6	8	9
7	19	19
8	8	8
9	7	6
12	5	3
H,L=-14		2
0	4	3
1	8	7
2	9	10
3	4	4
4	15	15
5	11	11
6	5	6
7	7	6
8	6	7
9	8	7
10	7	4
11	8	4
H,L=-13		2
0	17	16
1	46	44
2	16	19
3	5	9
4	7	8
5	5	5
6	16	17
7	8	8
8	11	10
11	8	8
14	5	7
15	4	5
H,L=-12		2
0	5	6
1	36	36
2	16	16
3	18	18
4	15	14
5	18	19
6	17	17
7	12	14
8	20	20
13	6	3
H,L=-11		2
0	6	3
1	18	15
2	4	1
3	18	15
4	21	23
5	6	6
6	11	12
7	7	8
8	7	7
10	15	16
11	5	3
13	6	7
14	5	3
H,L=-10		2
0	8	3
1	38	38
2	26	26
4	16	15
5	38	39
6	8	9
7	18	17
8	7	7
9	13	12
10	14	15
11	7	4
12	7	8
13	11	11
14	6	5
15	5	3
H,L=-9		2
0	66	64
1	21	21
2	53	54
3	17	15
4	35	35
5	15	13
6	4	9
7	11	10
8	19	19
9	7	5
10	7	8
11	6	6
15	5	1
16	5	4
H,L=-8		2
0	16	15
1	17	20
2	19	19
3	50	46
4	28	25
5	43	43
6	11	11
7	26	26
8	13	10
9	12	13
10	4	4
11	13	15
12	14	14
13	6	5
16	4	5
H,L=-7		2
0	60	61
2	17	16
3	20	17
4	41	39
6	9	11
7	11	10
8	6	9
9	12	14
10	23	20
11	8	8
12	13	14
13	5	8
14	6	9
15	6	4
17	6	2
H,L=-6		2
0	35	27
1	20	24
2	32	33
3	39	38
4	12	13
6	22	20
7	14	18
8	30	30
9	10	11
10	10	9
11	10	9
12	5	4
13	9	10
14	5	6
15	8	8
H,L=-5		2
0	8	11
1	53	54
2	79	85
3	36	37
4	44	48
5	17	17
6	17	16
7	26	24
8	28	30
9	8	8
10	18	20
11	19	20
12	11	12
13	9	8
14	7	9
15	8	6
H,L=-4		2
0	47	45
1	28	29
2	59	57
3	32	35
4	77	73
5	29	28
6	31	29
7	17	18
8	11	11
9	13	11
11	22	21
12	18	16
13	9	7
14	7	5
H,L=-3		2
0	53	57
1	29	27
2	10	8
3	48	42
4	45	42
5	9	13
6	41	41
7	24	23
8	14	14
10	9	11
11	7	5
12	9	9
14	10	10
15	5	6
H,L=-2		2
0	26	30
1	70	72
2	68	69
3	24	26
4	49	45
5	4	5
6	33	34
7	17	15
8	30	28
9	13	12
11	10	12
12	11	12
14	5	4
16	4	5
H,L=-1		2
0	10	8
1	35	31
2	53	52
3	33	33
4	35	32
5	10	10
6	47	45
8	15	14
9	32	31
10	7	7
11	26	25
12	11	10
13	17	18
14	6	2
15	5	4
H,L=0		2
0	26	28
1	70	69
2	29	34
3	17	15
4	31	28
5	15	14
6	50	48
7	17	16
8	12	13
9	23	19
10	9	8
11	6	7
13	7	6
H,L=1		2
0	23	16
1	38	40
2	28	23
3	24	23
4	10	5
5	51	50
6	22	18
7	35	31
8	9	11
9	14	14
11	10	11
14	5	4
15	9	11
H,L=2		2
0	19	21
1	46	45
2	45	40
3	37	40
4	32	31
5	26	24
6	55	49
7	5	4
8	17	18
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H,L=3		2
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H,L=4		2
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14	9	11
H,L=5		2
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14	7	7
H,L=6		2
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10	12	12
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H,L=7		2
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H,L=8		2
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H,L=9		2
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1	15	14
3	17	19
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6	27	26
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H,L=10		2
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H,L=11		2
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H,L=12		2
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11	6	6
H,L=13		2
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H,L=14		2
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H,L=15		2
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H,L=16		2
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H,L=17		2
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H,L=18		2
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5	5	4
H,L=19		2
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H,L=-23		3
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2	5	6
H,L=-22		3
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3	6	4
4	4	3
5	5	4
H,L=-21		3
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H,L=-20		3
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6	5	4
H,L=-19		3
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4	12	12
10	4	2
H,L=-18		3
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4	5	3
11	6	5
H,L=-17		3
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2	12	10
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4	13	10
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8	8	7
9	6	7
H,L=-16		3
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H,L=-15		3
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2	14	11
4	12	12
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11	5	7
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H,L=-13		3
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10	7	6
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H,L=-12		3
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H,L=-10		3
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14	5	2
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H,L=-8		3
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2	43	43
3	9	10
4	4	18
5	22	20
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7	15	16
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10	10	12

Factors for *p*-Bromobenzoylpikromycin (2)

K	FO	FC
11	17	20
12	6	4
13	7	7
14	5	6
16	4	5
H,L= -7 3		
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2	40	41
3	36	36
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10	12	12
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12	11	13
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16	7	6
H,L= -6 3		
0	37	35
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4	17	19
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9	13	13
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11	7	9
12	5	5
13	5	8
14	7	7
16	7	9
H,L= -5 3		
0	8	8
1	29	27
2	12	11
3	14	13
4	17	16
5	24	23
6	17	18
7	25	28
8	12	11
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10	19	20
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12	9	9
23	10	10
14	10	11
15	5	5
H,L= -4 3		
0	9	6
1	21	17
2	34	33
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4	8	8
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8	4	5
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10	9	8
12	18	18
13	6	5
16	4	4
H,L= -3 3		
0	9	5
1	45	45
2	32	31
3	30	31
4	15	15
5	28	27
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8	16	17
9	18	17
10	14	14
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14	11	13
15	5	5
H,L= -2 3		
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1	41	41
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6	14	11
7	23	23
8	19	18
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11	12	11
12	16	16
14	9	11
H,L= -1 3		
0	31	30
1	43	35
2	11	13
3	29	29
4	26	26
5	18	19
6	26	26
7	30	31
8	27	26
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10	15	17
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12	17	18
13	11	11
14	9	9
H,L= 0 3		
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1	36	34
2	25	25
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8	12	13
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14	4	4
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H,L= 1 3		
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1	27	25
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9	17	18
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H,L= 2 3		
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2	8	7
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8	9	9
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H,L= 3 3		
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7	15	14
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13	7	7
14	4	4
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H,L= 4 3		
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1	43	40
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5	18	17
6	15	15
7	7	8
8	7	7
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13	6	7
14	5	4
16	6	6
H,L= 5 3		
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1	10	7
3	19	21
4	14	15
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9	9	8
10	5	3
11	10	10
12	7	7
14	5	7
H,L= 6 3		
1	6	2
2	6	9
3	4	7
4	6	6
5	14	11
7	21	21
8	10	11
9	16	15
10	5	7
11	7	9
12	5	7
H,L= 7 3		
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1	9	13
2	9	9
3	9	11
4	13	13
6	6	6
7	13	13
9	11	13
10	2	6
12	6	5
14	6	6
15	4	2
H,L= 8 3		
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1	10	5
2	12	16
3	5	8
4	5	9
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7	6	9
8	9	10
10	6	6
13	7	4
H,L= 9 3		
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2	7	8
3	10	10
4	15	13
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6	17	16
7	13	14
9	4	2
10	6	5
12	4	7
13	4	2
14	5	5
H,L= 10 3		
0	9	10
1	9	8
3	7	4
5	5	6
6	9	9
8	5	7
10	6	3
13	4	2
H,L= 11 3		
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1	11	11
3	11	11
4	8	5
5	5	5
7	6	4
10	4	4
H,L= 12 3		
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1	12	15
2	9	11
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4	10	7
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6	6	5
7	4	5
8	8	7
10	6	4
H,L= 13 3		
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1	7	8
4	5	2
6	5	3
7	5	4
8	5	4
10	5	2
H,L= 14 3		
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2	10	13
4	10	7
7	5	3
9	4	2
10	4	2
H,L= 15 3		
3	5	7
4	7	8
5	5	5
7	5	3
H,L= 16 3		
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4	6	3
5	4	4
7	4	1
H,L= 17 3		
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5	6	3
H,L=-22 4		
1	6	5
4	4	6
H,L=-21 4		
0	4	3
1	5	3
4	5	5
5	4	3
6	5	5
7	4	3
H,L=-20 4		
0	6	5
4	5	1
8	4	2
H,L=-19 4		
3	8	9
7	4	6
8	7	4
9	6	3
H,L=-18 4		
0	8	7
1	8	5
2	7	8
3	8	7
4	5	5
6	6	6
7	6	8
8	5	4
10	7	6
H,L=-17 4		
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1	11	11
2	11	12
3	14	11
5	10	11
7	5	6
8	7	5
H,L=-16 4		
0	11	11
1	6	7
2	5	5
4	7	6
6	9	11
7	7	7
11	4	5
H,L=-15 4		
0	14	15
1	20	18
5	12	10
7	9	9
11	4	1
12	4	2
13	5	5
H,L=-14 4		
0	16	17
1	27	29
2	11	11
3	22	22
4	9	9
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7	8	7
9	6	6
10	8	8
12	4	3
H,L=-13 4		
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1	13	14
3	15	14
4	9	11
5	16	15
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7	9	9
8	7	7
9	10	10
14	5	3
H,L=-12 4		
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2	5	5
3	7	7
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6	8	9
7	14	15
8	13	16
10	5	7
11	9	10
12	5	4
13	4	3
H,L=-11 4		
0	8	6
1	15	16
2	11	10
3	11	10
4	8	5
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8	7	8
10	9	9
14	5	4
H,L=-10 4		
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1	11	12
3	26	26
4	13	15
5	5	8
6	11	12
7	6	5
8	10	12
9	8	11
10	17	19
14	4	4
15	4	3
H,L= -9 4		
0	17	17
1	14	14
2	16	18
3	8	12
4	12	13
5	8	7
6	15	15
8	16	15
9	8	8
10	7	6
11	7	10
12	8	7
H,L= -8 4		
0	15	17
1	10	9
2	8	6
3	7	9
4	6	4
5	10	8
6	12	14
7	5	5
9	13	13
11	7	9
12	8	10
13	6	2
14	4	2
H,L= -7 4		
0	12	9
1	14	15
2	14	15
3	7	8
4	22	22
6	19	21
7	8	9
8	15	16
9	5	8
10	16	16
12	10	11
H,L= -6 4		
0	10	9
1	16	17
2	12	13
3	4	3
4	26	26
5	13	11
6	11	11
7	7	7
8	10	12
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10	15	14
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14	9	9
15	5	6
H,L= -5 4		
0	30	28
1	10	9
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4	6	7
5	12	12
6	14	15
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8	13	12
9	16	14
10	11	14
11	9	12
H,L= -4 4		
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1	20	20
3	25	27
4	21	23
6	12	12
7	10	9
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12	5	3
13	4	4
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H,L= -3 4		
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7	16	16
8	20	19
9	14	14
11	9	12
14	4	5
H,L= -2 4		
0	27	28
1	21	20
2	8	7
3	15	13
4	9	8
5	14	14
6	11	10
7	9	15
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10	5	2
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12	10	7
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15	6	5
H,L= -1 4		
0	30	28
2	19	18
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4	13	14
6	19	18
7	17	17
8	12	15
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12	8	11
13	8	8
H,L= 0 4		
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1	22	21
2	26	27
3	8	8
4	29	31
7	7	7
8	9	8
9	10	10
10	13	13
12	4	3
14	5	5
H,L= 1 4		
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1	17	18
2	8	5
3	29	31
5	14	17
6	4	7
8	14	13
10	8	9
12	5	6
13	6	9
14	4	6
H,L= 2 4		
0	7	7
1	13	12
2	21	23
3	6	7
4	17	17
5	12	11
6	14	14
7	11	11
8	10	9
9	9	9
13	6	8
15	5	3
H,L= 3 4		
0	12	14
1	6	5
2	7	8
3	7	5
4	6	5
7	12	10
8	9	8
11	6	6
13	5	6
H,L= 4 4		
0	15	15
2	6	6
3	6	4
4	25	25
6	19	19
8	13	13
9	10	10
10	6	8
13	6	5
H,L= 5 4		
0	11	9
1	13	12
2	8	9
3	8	10
4	18	19
5	9	8
6	8	8
8	8	7
9	7	7
10	8	8
11	7	5
13	7	7
H,L= 6 4		
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1	22	22
2	5	4
3	7	10
4	7	4
5	7	7
7	11	12
9	7	7
10	7	7
11	8	7
12	5	2
13	4	7
H,L= 7 4		
0	10	9
1	8	10
3	5	6
5	5	6
7	13	12
8	4	3
9	11	9
12	8	6
13	6	6
H,L= 8 4		
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1	9	9
2	6	4
3	10	11
4	8	10
5	9	9
7	5	4
H,L= 9 4		
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2	9	10
3	13	11
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5	8	8
6	7	8
7	5	5
9	5	3
11	5	4
H,L= 10 4		
3	6	3
5	6	7
6	4	3
9	6	6
H,L= 11 4		
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1	10	8
3	8	6
4	5	5
5	8	5
6	10	8
8	6	2
9	6	4
H,L= 12 4		
2	4	6
3	5	6
6	5	2
H,L= 13 4		
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8	4	3
H,L= 14 4		
0	4	3
5	6	4
H,L= 15 4		
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1	4	2
2	4	2
3	4	1
H,L=-22 5		
0	6	6
H,L=-21 5		
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H,L=-20 5		
0	6	3
1	5	4
2	6	5
3	6	6
4	5	4
5	6	5
7	4	2
H,L=-19 5		
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2	8	7
3	4	3
6	6	4
H,L=-18 5		
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1	7	5
3	4	3
4	5	1
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9	7	6
H,L=-17 5		
0	11	8
1	8	5
2	7	7
3	5	4
5	8	8
6	5	6
9	5	3
H,L=-16 5		
0	9	7
1	7	7
3	9	8
4	5	6
7	4	4
8	5	2
11	6	2
H,L=-15 5		
0	18	20
1	7	8
2	8	8
3	7	11
6	10	9
H,L=-14 5		
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2	11	11
3	6	3
4	7	5
6	6	6
7	10	10
8	6	9
9	4	6
10	5	3
11	6	6
12	6	3
H,L=-13 5		
1	20	20
2	5	3
3	7	8
4	8	8
5	12	12
9	5	2
10	6	6
11	5	3
12	6	3
H,L=-12 5		
1	5	7
2	16	16
4	7	8
7	7	7
8	5	3
9	5	1
13	7	5
H,L=-11 5		
0	5	2
1	10	11
4	7	7
5	8	9
6	6	9
7	8	9
8	5	5
9	10	8
10	5	1
12	5	3
13	4	6
H,L=-10 5		
0	6	9
1	16	16
3	5	5
4	5	6
5	9	10
6	7	8
7	9	10
9	8	11
10	5	8
11	6	5
13	4	3
14	5	3
H,L= -9 5		
0	6	4
1	12	13
2	8	10
4	9	8
5	17	18
6	5	2
7	12	13
9	9	9
11	4	3
13	5	5
H,L= -8 5		
0	11	12
1	18	18
3	12	10
4	3	9
5	8	11
6	9	11
8	8	6
9	7	9
11	4	5
12	7	6
14	6	3
H,L= -7 5		
0	11	12
1	5	3
2	7	9
3	17	17
4	9	9
5	7	7
6	8	8
7	7	8
8	4	6
9	17	18
10	5	7
11	8	9
13	5	3
H,L= -6 5		
0	8	7
1	8	9
3	12	13
4	7	8
6	6	7
7	6	6
8	5	5
10	10	9
12	7	6
13	5	4
14	4	6
H,L= -5 5		
1	15	13
4	8	8
6	13	13
8	14	15
9	7	9
11	5	3
13	8	10
H,L= -4 5		
0	12	13
2	8	9
3	6	4
4	15	15
5	5	4
6	11	13
7	8	9
8	6	8
10	8	10
11	7	8
12	6	7
13	9	6
14	6	2
H,L= -3 5		
0	6	9
1	10	12
2	11	12
3	15	17
4	11	12
5	17	17
6	16	18
7	15	16
9	8	9
10	7	9
11	9	10
12	5	4
H,L= -2 5		
0	6	7
1	5	7
3	8	10
5	15	16
6	5	10
9	5	4
14	7	6
H,L= -1 5		
0	9	8
1	8	7
3	14	16
4	7	8
5	6	7
6	12	12
7	15	15
11	7	8
12	4	5
H,L= 0 5		
0	6	9
2	7	7
3	10	10
4	15	15
5	10	10
7	6	7
9	7	7
10	4	2
13	4	1
H,L= 1 5		
0	12	12
1	9	9
2	9	9
4	15	15
5	14	13
6	7	10
9	7	7
11	7	5
H,L= 2 5		
0	9	7
1	7	7
2	6	9
3	14	17
4	15	14
5	8	9
6	10	12
7	6	10
10	9	6
H,L= 3 5		
1	9	12
2	6	8
3	8	9
4	7	7
5	16	19
6	10	11
10	6	6
13	5	3
H,L= 4 5		
1	13	12
2	8	10
3	10	8
5	5	7
6	8	10
7	9	6
8	8	8
10	5	7
11	5	2
13	5	5
H,L= 5 5		
0	5	1
2	12	12
3	7	8
4	7	6
6	6	7
12	4	2
H,L= 6 5		
0	12	11
2	7	7
4	6	9
12	5	3
H,L= 7 5		
0	4	2
1	8	9
4	5	5
5	6	2
6	5	3
11	5	2
H,L= 8 5		
0	5	5
3	7	8
5	7	5
9	4	2
H,L= 9 5		
0	7	2
2	6	6
4	5	3
5	5	4
6	5	3
H,L= 10 5		
0	5	7
6	5	4
9	4	4
H,L= 11 5		
1	5	4
5	4	4
H,L= 12 5		
6	5	5
H,L= 13 5		
1	4	2
H,L=-19 6		
0	4	0
3	4	4
H,L=-17 6		
0	8	5
1	5	4
3	7	6
6	6	4
H,L=-16 6		
1	4	3
2	4	1
5	4	3
6	4	5
H,L=-15 6		
0	5	7
1	6	6
2	5	3
4	4	3
10	5	1
H,L=-14 6		
0	10	11
7	5	3
H,L=-13 6		
0	10	10
1	6	6
2	10	8
4	6	8
5	7	7
8	5	3
9	4	4
10	4	3
H,L=-12 6		
0	6	9
1	7	7
3	9	10
4	9	9
7	6	5
11	5	3
H,L=-11 6		
1	5	7
2	12	16
3	10	10
5	10	9
6	6	4
7	5	4
8	7	6
9	6	5
11	5	4
12	5	5
H,L=-10 6		
1	6	5
2	13	15
3	7	5
5	6	6
6	5	2
10	4	6
12	4	4
H,L= -9 6		
1	8	6
2	9	7
4	6	6
7	4	2
8	5	5
10	6	3
H,L= -8 6		
0	14	13
2	8	9
3	5	10
7	8	10
8	6	3
9	7	6
12	5	3
H,L= -7 6		
0	7	8
2	7	4
3	8	6
4	11	11
7	5	2
8	5	4
12	5	5
H,L= -6 6		
2	6	5
3	9	6
4	6	4
5	10	11
6	8	7
7	6	2
8	9	7
11	5	7
12	4	1
H,L= -5 6		
1	5	5
3	5	7
4	6	5
5	8	10
6	10	11
7	11	12
10	6	5
13	5	4
H,L= -4 6		
1	6	5
4	7	7
5	9	8
6	9	7
7	7	4
8	7	6
10	7	7
12	5	5
13	6	5
H,L= -3 6		
2	7	7
5	5	4
6	9	9
7	5	4
12	5	4
H,L= -2 6		
2	7	8
3	7	7
4	6	8
5	5	7
6	5	6
8	6	5
H,L= -1 6		
0	5	4
2	7	6
3	9	10
4	7	6
6	7	8
10	5	8
H,L= 0 6		
0	11	15
2	9	12
4	10	12
5	6	3
6	5	4
7	9	8
11	4	4
H,L= 1 6		
0	10	11
1	9	8
2	7	4
3	9	11
6	5	4
11	4	2
H,L= 2 6		
3	6	4
4	6	6
5	5	3
H,L= 3 6		
0	6	2
2	7	6
5	6	2
6	4	3
11	5	3
H,L= 4 6		
4	6	2
9	4	2
H,L= 5 6		
0	6	9
1	6	4
2	6	2
5	4	2
8	4	3
H,L= 6 6		
3	5	3
8	4	2
H,L= 7 6		
1	5	5
2	6	5
3	5	5
H,L= 8 6		
2	6	4
3	6	2
H,L= 9 6		
0	4	1
1	4	2
3	5	2
H,L= 10 6		
1	4	1
H,L=-16 7		
2	5	2
H,L=-15 7		
2	5	3
6	4	5
H,L=-14 7		
0	6	5
1	5	4
4	6	2
5	4	2
H,L=-13 7		
0	9	9
1	4	2
4	6	6
5	7	8
7	5	3
H,L=-12 7		
1	5	4
2	6	2
H,L=-11 7		
4	8	5
6	5	3
10	4	4
H,L=-10 7		
1	6	3
4	6	3
7	4	3
8	5	4
H,L= -9 7		
4	6	7
5	6	3
6	6	4
H,L= -8 7		
2	6	7
3	9	7
5	4	5
6	4	2
7	5	4
8	6	6
9	6	6
H,L= -7 7		
1	6	6
5	4	3
6	5	5
8	7	6
9	4	2
H,L= -6 7		
2	5	4
7	5	3
10	4	3
H,L= -5 7		
0	5	5
1	5	4
7	6	7
H,L= -4 7		
0	5	1
1	5	6
3	6	5
8	6	4
H,L= -3 7		
0	8	7
1	4	6
2	10	10
3	5	5
4	7	3
5	5	3
6	4	3
8	4	2
H,L= -2 7		
0	8	10
1	8	8
2	8	12
3	7	4
6	6	2
7	4	2
H,L= -1 7		
1	6	5
2	5	3
5	5	1
10	6	4
H,L= 0 7		
1	5	4
H,L= 1 7		
2	5	3
5	5	4
7	5	3
H,L= 2 7		
0	4	3
1	5	4
4	5	2
8	4	1
H,L= 3 7		
1	5	4
H,L= 4 7		
4	5	2
H,L= 6 7		
0	4	4
2	6	3
H,L=-11 8		
0	5	2
3	5	3
6	5	3
H,L=-10 8		
0	5	4
4	5	1
H,L= -7 8		
0	5	4
1	5	2
4	5	3
H,L= -6 8		
1	5	3
2	4	3
4	4	3
6	5	4
H,L= -5 8		
4	5	2
5	6	2
H,L= -4 8		
6	4	2
H,L= -3 8		
1	4	2
2	4	1
4	5	5
5	5	3
6	4	1
H,L= 0 8		
3	4	3

(3), 10,11-dihydrokromycin, deoxykromycin, and 10,11-dihydrodeoxykromycin was proposed.[1]

In the present paper, we describe the configurational and conformational studies on **1** and *p*-bromobenzoylpikromycin (**2**) based on the X-ray analysis. Since an attempted X-ray analysis of **1** with the symbolic addition method (MULTAN) failed, the X-ray analysis of **2** with the heavy-atom method was carried out. During the course of this work, another "diamond lattice" conformation model D for this 14-membered macrolactone was proposed.[6]

Experimental[7]

***p*-Bromobenzoylpikromycin** (**2**)——To a stirred solution of **1** (500 mg) in benzene (40 ml), a mixture of *p*-bromobenzoyl chloride (500 mg) in benzene (20 ml) and pyridine (0.2 ml) was added dropwise under cooling. After the reaction mixture was kept at room temperature for 4 hr, it was treated with MeOH to decompose the excess reagent. After removal of the solvent, the resulting precipitate was washed with benzene, dissolved in H_2O, the solution was neutralized with 2% $NaHCO_3$, and was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried over anhydrous Na_2SO_4, and evaporated to leave a white powder which was crystallized from EtOH as colorless prisms, mp 145—147°. *Anal.* Calcd. for $C_{35}H_{50}BrNO_9 \cdot H_2O$: C, 57.85; H, 7.21; N, 1.93. Found: C, 57.50; H, 7.15; N, 1.89. $[\alpha]_D^{18}$ +48.0° ($c=1.0$, EtOH). IR ν_{max}^{KBr} cm^{-1} 3480 (OH), 2790 (NMe_2), 1745 (ester), 1715 (lactone), 1675, 1630 ($-\underset{|}{C}=C-\underset{|}{C}O$), 1610, 1590 (phenyl). UV λ_{max}^{EtOH} nm (log ε): 243 (4.27).

Crystal Data——*p*-Bromobenzoylpikromycin (**2**), mp 145—147°, $C_{35}H_{50}BrNO_9 \cdot H_2O$, mol. wt. 726.71. Monoclinic, $P2_1$, $a=19.027(9)$Å, $b=14.876(5)$Å, $c=7.148(3)$Å, $\beta=108.97(8)°$, $V=1928.2$Å^3, $Z=2$. The density was measured by the floatation method in $CHCl_3$-hexane, and the calculated value was $\rho_{calcd}=1.254$ g cm^{-3} ($\rho_{obs}=1.26$ g cm^{-3}).

The diffraction intensities of a 0.2×0.2×0.3 mm parallel-piped crystal were measured on a Rigaku four-circle diffractometer in an ω-2θ scan mode (2°/min) using graphite monochromated CuKα radiation.

Accurate cel dimensions were determined by the least-squares method using the accurately measured 2θ values of the 24 strong reflections in the range of $16° \leq 2\theta \leq 35°$. The scan range of ω for each reflection was calculated by the formula $\omega=1.10°+0.5° \tan\theta$, and the backgrounds were measured at both ends of the scan range for 10.0 sec.

Three standard reflections were measured after every 50 reflections. The maximum deviation of the standard reflections from their mean values was 1.2%. These reflections having intensities exceeding 3 times the corresponding standard deviations were collected and corrected for Lorentz and polarization factors. A total of 2289 ($2\theta \leq 140°$) independent reflections with $|F_0|>3\sigma$ were measured.

Determination of the Structure——The structure was solved by the heavy-atom method. From the three-dimension Patterson map, position of the bromine atom could easily be deduced. The position of the bromine atom was found from the Harker section $P(u, 1/2, W)$ to be ($x=0.22$, $y=0.50$, assumed $z=0.26$).

A false mirror plane of symmetry was introduced into the first electron density map. Several attempts to destroy the pseudo-symmetry by selecting a reasonable atomic position allowed choice of atoms from one enantiomer.

Refinement of the positional parameters of the 46 atoms including the bromine atom was carried out by the block-diagonal matrix least-squares method, in which the anisotropic thermal vibration was assumed only for the bromine atom and all other non-hydrogen atoms were assumed to be carbon atoms. Six cycles of refinements gave an R-value of 0.187.

The oxygen atoms and nitrogen atom were assigned on the basis of the chemical consideration, the bond lengths and the unusually low values of thermal parameters under the assumption of those atoms being carbon, to give an R-value of 0.168.

A difference Fourier synthesis was performed at this stage and a water molecule was located. Two more cycles of block diagonal least-squares refinement with isotropic temperature factor were performed and R index reduced to 0.161. Finally, 5 cycles of block diagonal refinement with anisotropic temperature factor were calculated giving $R=0.118$ for 2289 non-zero reflections.[8] Observed and calculated structure factors from the last cycle are given in Table I, and the atomic coordinates and thermal parameters with their estimated standard deviations in Table II. Hydrogen atoms were not included in the refinement.[9]

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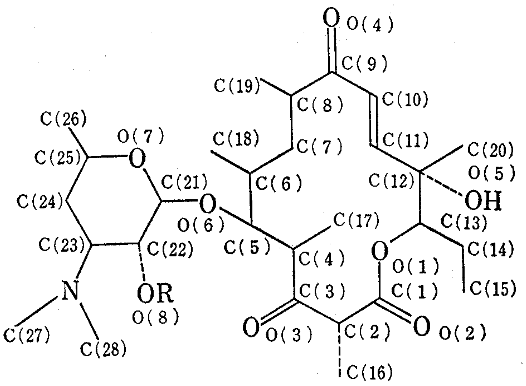
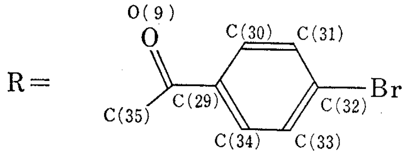
[6] H. Ogura, K. Furuhata, Y. Harada, and Y. Iitaka, *Abstr. Papers*, *20th Sym. Chem. Nat. Prod.*, **1976**, 16.

[7] Temperatures are uncorrected.

[8] The atomic scattering factors used in these calculations were taken from "International Tables for X-ray Crystallography," Vol. III, ed. by C.H. MacGillavry and G.D. Rieck, Kynoch Press, Birmingham, 1968, p. 201.

[9] The computer programs used in these calculations were 3DFANDFR and HLSQ by Y. Iitaka.





p-bromobenzoylpikromycin (**2**)

TABLE II. Final Atomic Parameters and Their Standard Deviations[a] ($\times 10^4$)

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	2229(2)	5000(0)	12631(7)	72(1)	112(2)	1142(19)	28(2)	154(4)	203(6)
C (1)	4681(11)	8577(13)	8206(29)	44(7)	35(10)	340(59)	15(7)	22(17)	9(19)
C (2)	4054(8)	8498(13)	8498(32)	14(5)	59(12)	506(73)	1(6)	33(15)	90(24)
C (3)	3423(9)	9088(14)	7956(28)	29(6)	57(11)	328(55)	−16(7)	23(15)	−3(21)
C (4)	3229(8)	9799(11)	9229(22)	23(5)	38(9)	211(40)	9(6)	31(11)	30(15)
C (5)	2659(7)	10482(11)	7841(24)	10(4)	31(8)	332(48)	1(5)	22(11)	−3(16)
C (6)	2762(10)	11483(12)	8605(27)	35(7)	42(10)	316(54)	−3(7)	40(15)	−49(19)
C (7)	3480(10)	11876(13)	8366(25)	48(8)	50(10)	212(46)	−13(8)	60(15)	−49(18)
C (8)	3360(8)	12144(11)	6152(23)	18(5)	42(9)	214(43)	−4(5)	9(12)	−17(16)
C (9)	4112(9)	12397(11)	6064(23)	35(6)	34(8)	191(41)	1(6)	38(13)	−7(15)
C (10)	4654(10)	11745(11)	5788(27)	38(7)	23(8)	330(55)	6(6)	46(16)	14(17)
C (11)	4513(9)	10857(11)	5548(23)	38(6)	39(9)	183(40)	8(6)	43(13)	5(16)
C (12)	5064(8)	10162(12)	5338(25)	21(5)	40(9)	279(47)	4(6)	26(12)	−10(17)
C (13)	5471(9)	9668(11)	7378(26)	30(6)	41(10)	270(47)	4(6)	29(14)	16(18)
C (14)	5996(11)	10262(14)	8969(28)	47(8)	66(15)	267(52)	6(9)	18(16)	3(22)
C (15)	6445(10)	9696(14)	10708(26)	37(7)	73(14)	244(49)	8(8)	27(15)	7(21)
C (16)	3764(14)	7483(17)	8781(48)	60(12)	57(14)	915(136)	−9(11)	115(34)	68(37)
C (17)	2912(9)	9339(14)	10692(26)	28(6)	28(6)	265(50)	11(8)	34(14)	79(22)
C (18)	2785(16)	11548(16)	10851(33)	118(16)	74(15)	326(66)	−7(13)	156(29)	−23(26)
C (19)	2803(11)	12865(13)	5337(27)	51(8)	44(11)	263(52)	20(8)	20(17)	−11(19)
C (20)	5655(12)	10508(15)	4504(27)	69(10)	67(13)	274(53)	15(10)	100(20)	50(22)
C (21)	1476(8)	10036(11)	5844(22)	27(5)	31(8)	200(39)	4(6)	29(12)	−9(15)
C (22)	779(9)	9548(13)	5961(26)	23(5)	53(10)	279(49)	6(6)	13(13)	−3(19)
C (23)	255(11)	9373(18)	3745(34)	34(7)	108(18)	441(73)	−15(10)	53(19)	−77(32)
C (24)	113(11)	10221(23)	2640(29)	38(8)	162(25)	217(49)	12(12)	4(15)	30(31)
C (25)	838(11)	10661(19)	2713(31)	30(7)	127(20)	315(59)	1(10)	26(10)	−27(30)
C (26)	712(15)	11624(22)	1715(37)	74(13)	151(13)	370(74)	25(15)	82(26)	140(38)
C (27)	−900(12)	9340(20)	4802(39)	40(9)	126(22)	591(93)	−25(12)	86(24)	−31(39)
C (28)	−875(15)	8603(37)	1843(52)	51(12)	369(60)	751(136)	−73(23)	66(33)	−299(77)
C (29)	1241(9)	7650(12)	9492(30)	27(6)	38(10)	401(65)	−9(6)	10(16)	−29(20)
C (30)	1610(12)	7100(14)	8546(38)	54(10)	46(12)	609(94)	−10(9)	85(25)	44(27)
C (31)	1934(14)	6290(17)	9474(44)	56(10)	74(16)	755(113)	2(11)	112(29)	75(36)
C (32)	1806(17)	6103(17)	11178(42)	45(9)	70(16)	726(111)	14(10)	53(26)	129(35)
C (33)	1434(15)	6619(20)	12224(38)	72(13)	106(21)	422(84)	6(14)	38(26)	54(35)
C (34)	1094(16)	7403(18)	11239(34)	96(15)	80(16)	345(73)	14(13)	85(28)	16(29)
C (35)	900(10)	8511(13)	8564(32)	40(8)	48(11)	433(70)	−8(8)	60(19)	−40(23)
N	−432(8)	8902(17)	3819(30)	22(6)	135(18)	555(70)	−14(9)	7(15)	−59(31)
O (1)	4874(6)	9440(7)	8150(17)	34(4)	24(5)	301(32)	3(4)	42(9)	−10(11)
O (2)	4995(8)	7959(8)	7672(23)	56(6)	28(6)	565(53)	−3(5)	79(15)	−13(15)
O (3)	3078(8)	9018(11)	6187(20)	53(6)	82(10)	333(42)	4(7)	−6(13)	−73(18)
O (4)	4315(7)	13202(8)	6339(22)	51(6)	33(7)	562(53)	−10(5)	111(15)	−20(15)
O (5)	4608(7)	9506(9)	4044(17)	46(5)	53(7)	253(33)	18(5)	−2(10)	−31(13)
O (6)	1274(6)	10809(8)	4743(16)	28(4)	60(8)	211(29)	2(5)	1(8)	−5(12)
O (7)	1919(5)	10232(8)	7684(14)	27(4)	52(7)	169(25)	−2(4)	16(8)	4(11)
O (8)	1032(6)	8706(9)	6835(19)	34(4)	59(8)	375(40)	2(5)	58(11)	−2(15)
O (9)	542(10)	8985(11)	9251(23)	93(9)	63(9)	452(52)	22(8)	109(18)	16(19)

[a] The anisotropic temperature factors are of the form; $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.
The estimated standard deviations are given in parentheses.

The absolute configuration was determined based on the absolute configuration of β-D-desosamine.[10] The structure of 2 is shown in Fig. 1, which illustrates a *c*-axis projection of the molecule. The absolute configurations of the asymmetric centers are consistent with those established for pikromycin.[5]

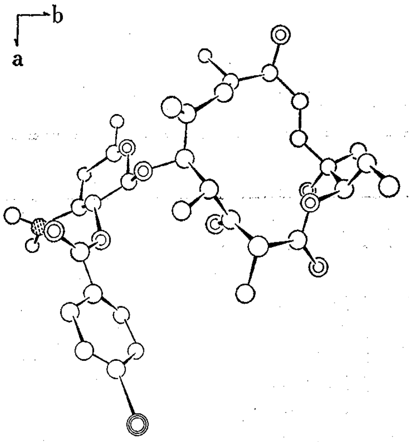
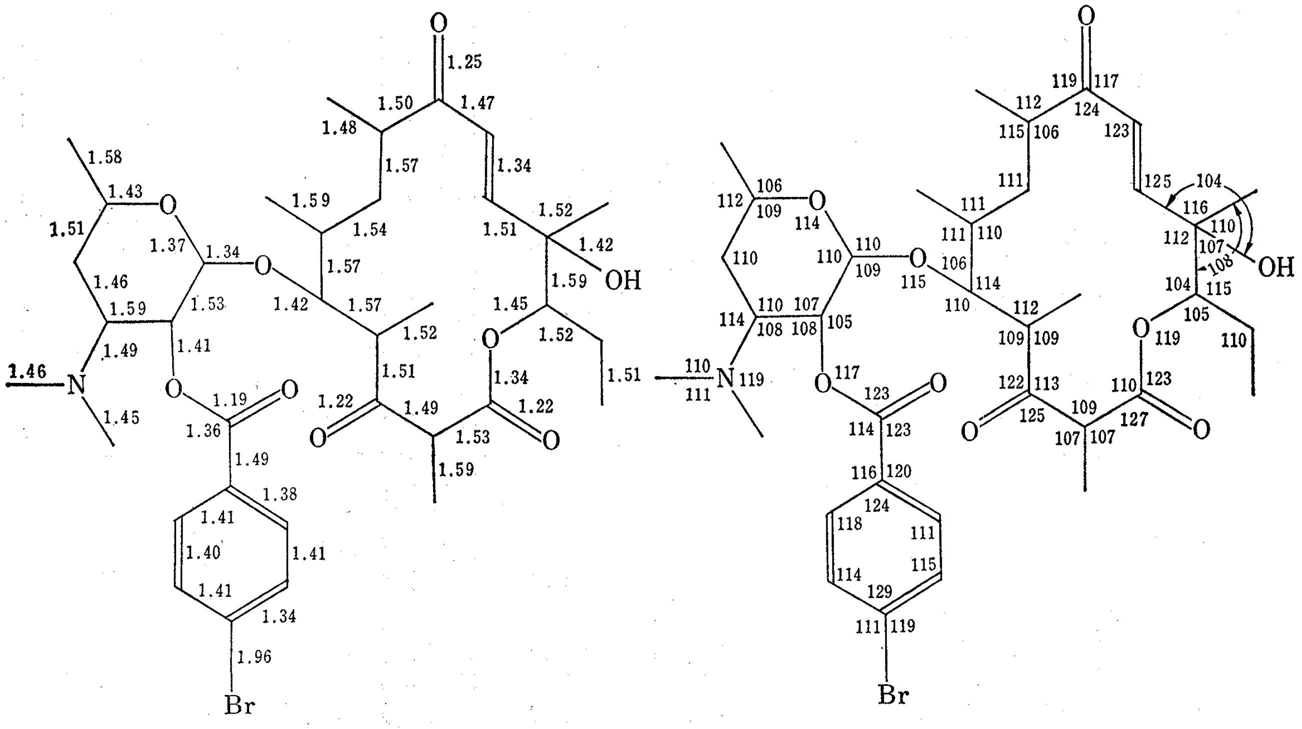


Fig. 1. Conformation of *p*-Bromobenzoylpikromycin (2)

Table III. Some Torsional Angles (°)

C (13)-O (1)-C (1)-C (2)	178.9
O (1)-C (1)-C (2)-C (3)	54.9
C (1)-C (2)-C (3)-C (4)	−120.8
C (2)-C (3)-C (4)-C (5)	170.5
C (3)-C (4)-C (5)-C (6)	144.9
C (4)-C (5)-C (6)-C (7)	71.4
C (5)-C (6)-C (7)-C (8)	77.5
C (6)-C (7)-C (8)-C (9)	−172.6
C (7)-C (8)-C (9)-C (10)	85.2
C (8) C (9) C (10) C (11)	1.3
C (9)-C (10)-C (11)-C (12)	−177.6
C (10)-C (11)-C (12)-C (13)	98.1
C (11)-C (12)-C (13)-O (1)	174.6
C (12)-C (13)-O (1)-C (1)	110.3
C (13)-O (1)-C (1)-O (2)	1.9
O (2)-C (1)-C (2)-C (3)	−127.6
C (1)-C (2)-C (3)-O (3)	60.2
O (3)-C (3)-C (4)-C (5)	−10.5
O (3)-C (3)-C (2)-C (1)	60.2
C (3)-C (4)-C (5)-O (6)	95.6
O (4)-C (9)-C (10)-C (11)	177.7
C (10)-C (11)-C (12)-O (5)	−147.0
C (11)-C (12)-C (13)-C (14)	−67.6
O (5)-C (12)-C (13)-O (1)	−66.5



Bond lengths (Å) Bond angles (°)

Fig. 2. Bond Lengths and Angles

Discussion of the Structure

The molecular structure of *p*-bromobenzoylpikromycin (2) determined by the present analysis is shown in Fig. 1. As expected from chemical and spectroscopic studies, C-2 position has the *R*-configuration. The bond lengths and angles of molecule are shown in Fig. 2. Some important torsion angles are listed in Table III.

As shown in a packing cell (Fig. 3), H_2O molecules exist near dimethylamino group of the desosamine moiety.

In conclusion, the most favorable "diamond lattice" conformation model D for compound 2 is proposed in Fig. 4.

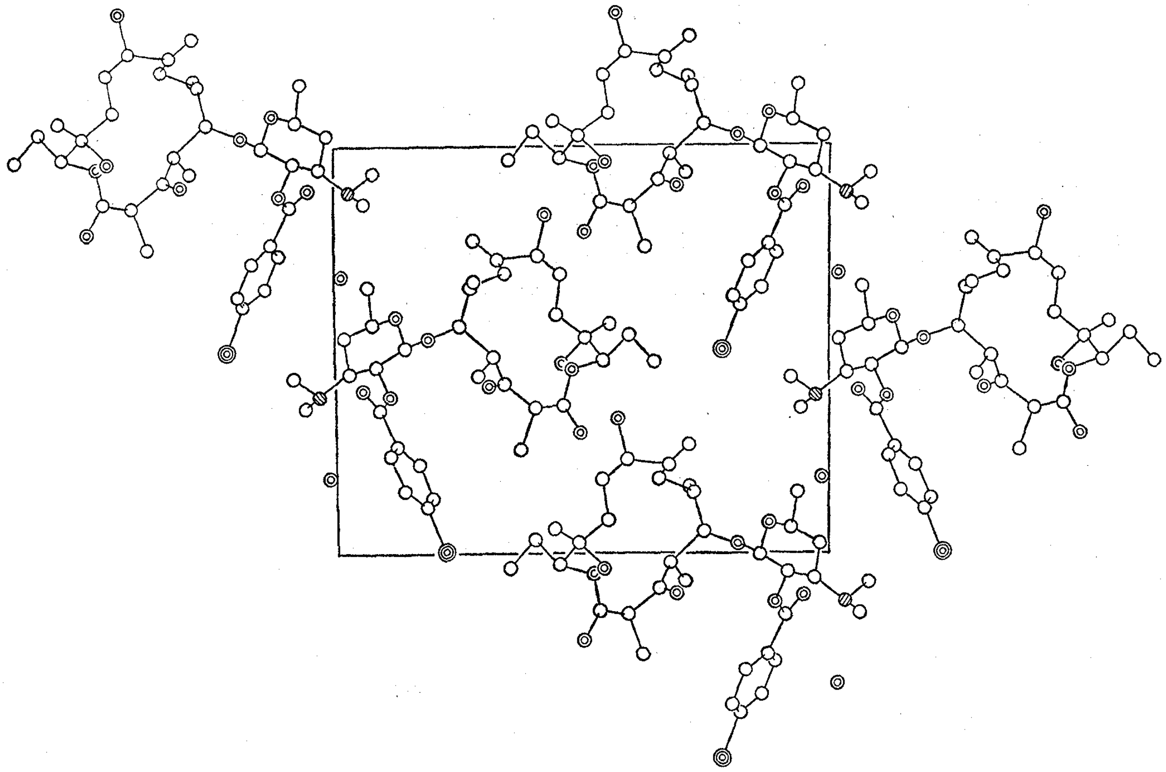


Fig. 3. The Packing of the Molecules Viewed Along the c Axis

○, carbon; ◎, oxygen; ◍, nitrogen; ●, bromine.

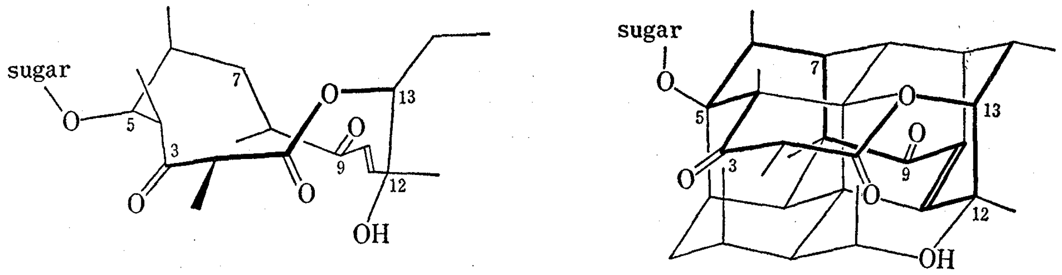


Fig. 4. A New "Diamond Lattice" Conformation Model D for *p*-Bromobenzoylpikromycin (2)

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10) W. Hofheinz, H. Griseback, and H. Friebolin, *Tetrahedron*, **18**, 1265 (1962); D.V. Lemal, P.D. Pacht, and R.B. Woodward, *Tetrahedron*, **18**, 1275 (1962).