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91. Masao Nishikawa, Kazuhide Kamiya, Shigeru Kobayashi, Katsura Morita, and Yujiro Tomiie*2 : The X-ray Analysis of Lenthionine, an Odorous Substance of *Shiitake*, an Edible Mushroom.

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The chemical and stereochemical structure of lenthionine has been established by the X-ray method. Lenthionine crystallizes in the monoclinic system, space group $P2_1/a\text{-}C^5_{2h}$, with four molecules of $S_5(CH_2)_2$ in the unit cell. Using a three-dimensional Patterson function and minimum functions, all atomic positions were determined. The least squares method was adopted to distinguish CH_2 groups from sulfur by the temperature factors. Thus the three-dimensional molecular geometry has been elucidated to be in a chair form, having C_2 pseudo-symmetry.

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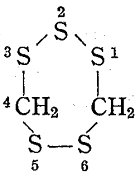
Lenthionine, $C_2H_4S_5$, is a new odoring substance first isolated from *Lenthinus edodes* (Berk.) Sing, by Morita and Kobayashi and its chemical structure has been established as 1,2,3,5,6-pentathiepane (I).1)



(I)

There have been recorded several eight-membered cyclic polysulfides, such as monoclinic2) and orthorhombic sulfur,3) hexasulfurdiimide, heptasulfurimide,4~6) and others,7,8) of which the conformations have been determined by X-ray diffraction studies. The present study, therefore, has been undertaken to establish the stereochemistry of lenthionine, because the compound appeared to provide a relevant status for the conformation of the seven-membered cyclic polysulfides.

Experimental

Single crystals for this work were obtained from a solution of lenthionine in methylene chloride. The crystals were pillar-shaped, beautifully formed and had the characteristic odor of the mushroom.

Equi-inclination multiple-film integrating Weissenberg photographs were taken of 9 layers about the *a* axis and 7 layers about the *b* axis with Cu $K\alpha$ radiation. A total of 2129 diffractions was obtained and intensities were estimated visually with the aid of standard intensity scales prepared by the exposure time method. Absolute values of the observed structure factors were then deduced by the ordinary procedure, and 1440 independent data were obtained. The corrections for absorption were made only for $(h0l)$ in an approximate way, the linear absorption coefficient for Cu $K\alpha$ radiation being $1/\mu = 78.4\,\text{cm}^{-1}$.

Results and Discussion

Unit Cell and Space Group——It was found from the X-ray examination that the crystal belongs to the monoclinic system, and the dimensions of the unit cell are as follows:

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1) K. Morita, S. Kobayashi : Tetrahedron Letters, **1966**, 573.

2) D.E. Sands : J. Am. Chem. Soc., **87**, 1395 (1965).

3) B.E. Warren, J.T. Burwell : J. Chem. Phys., **3**, 6 (1935).

4) J.C. Van de Grampel, A. Vos : Rec. trav. chim., **84**, 599 (1965).

5) H.G. Heal : Nature, **199**, 371 (1963).

6) J. Weiss : Z. Anorg. Allg. Chem., **305**, 190 (1960).

7) E.W. Lund, S.R. Svendson : Acta Chem. Scand., **11**, 940 (1957).

8) R.L. Sass, J. Donohue : Acta Cryst., **11**, 497 (1958).

$a=12.26 \pm 0.03$ Å
$b=7.72 \pm 0.02$ Å
$c=7.77 \pm 0.02$ Å
$\beta=111.2° \pm 0.4°$

The a axis is parallel to the elongated axis of the crystal. Systematic extinctions of (h0l) when h is odd and of (0k0) when k is odd lead to the space group $P2_1/a$, which requires four or a multiple of four molecules in the unit cell. The apparent systematic extinctions of (0kl) when $k+l$ is odd were also found. However, since these extinctions were not possible in monoclinic lattice, they may be attributed to a certain special arrangement of molecules in the unit cell.

The assumption of four molecules in the unit cell leads to the calculated density of 1.821 g cm^{-1}. This value would be a reasonable one since the densities of 1.96, 1.80, 1.85, 1.99 and 2.01 have been reported for monoclinic sulfur, orthorhombic sulfur, and three species of $S_6(NH)_2$,[4] respectively.

Determination of the Structure——The three-dimensional Patterson function was computed with sharpened coefficients $k^2F_0^2\exp[2(B-B')(\sin^2\theta/\lambda^2)]$, where k and B' were calculated by Wilson's method.[9] The Harker section $H(u\frac{1}{2}w)$ is shown in Fig. 1. As shown in the figure, most of the strong peaks are located at $w=0$ or $w=\frac{1}{2}$, which suggests a special situation of the molecular arrangement in the unit cell as mentioned above. Considering the symmetry restricted by the space group, this unusual feature of the map would be interpreted by assuming a majority of atomic positions to be near $z=1/4$ or $z=3/4$. Application of a minimum function, superposing the strongest peak at $u=1/4$, $v=w=\frac{1}{2}$ to the origin, did not definitely determine the coordinates of the atoms, especially of those which are located out of the particular plane at $z=1/4$ or $z=3/4$. In order to circumvent this difficulty, the superposition of the peak at $u=0.40$, $v=0.50$ and $w=0.16$ to the origin was tried. Thus, all atomic positions, except those of hydrogen, were found without any ambiguity and the structure of the seven-membered ring was elucidated.

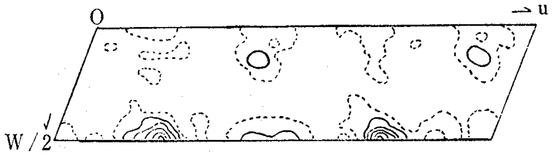

Fig. 1. Harker Section at $v=\frac{1}{2}$

To differentiate two CH_2 groups out of five sulfur atoms, the least squares treatment appeared promising. If one uses the same atomic scattering factors and temperature factors for all seven atoms in least squares refinement, the temperature factor of carbon would increase while that of sulfur would decrease.[10,11] Thus by using the atomic scattering factor of sulfur and temperature factor of 2.0 for all

TABLE I. The Atomic Coordinates and Temperature Factors after First Four Cycles of the Least Squares Treatment

No.	Atom	X	Y	Z	B
1	S	0.2469	0.4493	0.2315	1.39
2	S	0.3022	0.2564	0.4320	1.29
3	S	0.3055	0.0435	0.2757	2.36
4	S	0.4371	0.0367	0.2132	2.90
5	S	0.4491	0.2429	0.0843	1.45
6	S	0.5082	0.4458	0.2620	1.75
7	S	0.3718	0.5454	0.2636	3.69

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[9] A. J. C. Wilson: Nature, **150**, 152 (1942).

atoms, four cycles of the least squares treatment were made with diagonal approximation. The results are listed in Table I, from which the atoms No. 4 and No. 7 were assigned to carbon. Accordingly, in the subsequent five cycles of the least squares refinement, the scattering factor for carbon was introduced for these two atoms, resulting in a decreased *R*-value of 18.4%. The atomic coordinates and temperature factors thus obtained are listed in Table II.

Table II. The Final Atomic Coordinates and Temperature Factors

No.	Atom	X	Y	Z	B
1	S	0.2445	0.4523	0.2284	2.32
2	S	0.3016	0.2600	0.4217	1.91
3	S	0.3115	0.0400	0.2765	2.62
4	C	0.4496	0.0665	0.2418	1.56
5	S	0.4494	0.2433	0.0772	1.82
6	S	0.5035	0.4478	0.2496	2.19
7	C	0.3739	0.5725	0.2311	1.91

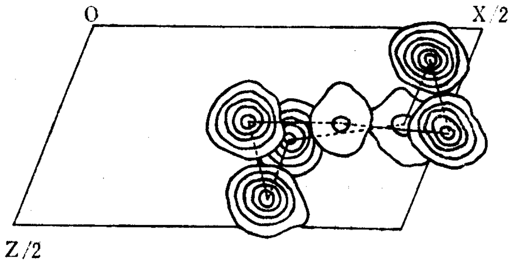

Fig. 2. The Final Three-dimensional Electron Density Distribution shown by Means of Superimposed Contour Section projected on (010)

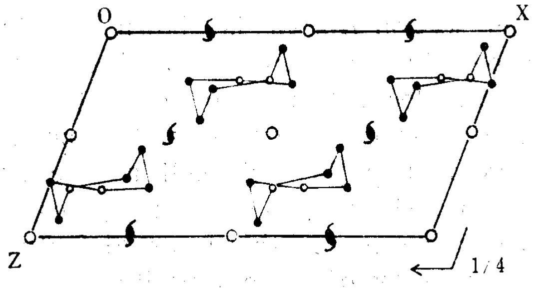

Fig. 3. Packing of the Structure seen down the *b* Axis

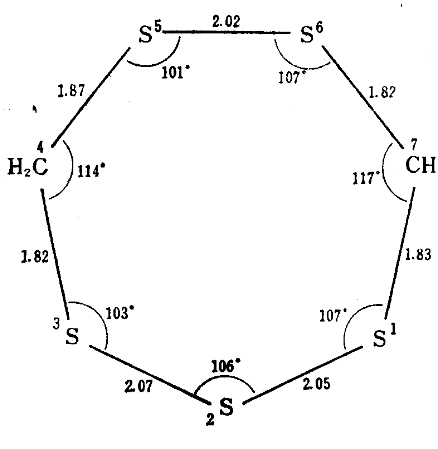

Fig. 4. Bond Distances and Angles

At this stage, a three-dimensional electron density map was computed for the first time. The results are shown in Fig. 2 by means of superimposed contour sections. The arrangement of atoms in the unit cell is given in Fig. 3. Bond distances and angles calculated from these results are shown in Fig. 4.

The standard deviations were calculated from the residuals in the final least squares refinement. The standard deviations in the coordinates of the five sulfur atoms ($\sigma=0.0046$ Å) are nearly equal and are about a quarter of those in the coordinates of the two carbon atoms ($\sigma=0.0176$ Å). Observed and calculated structure factors are listed in Table IV.

Discussion——From Figs. 2 and 3, a molecular conformation resembling the chair form is clearly seen. The conformation of the molecule is in C_2 pseude-symmetry.

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10) H.S. Yanai, W.N. Lipscomb: Tetrahedron, **6**, 103 (1959).

11) Y. Tomiie, *et al.*: Presented at the 18th Annual Meeting of the Chemical Society of Japan, April, 1965.

C (7) and the middle point of the S (3)–C (4) bond are on the pseudo two-fold axis which is nearly parallel to the *b* axis of the unit cell.

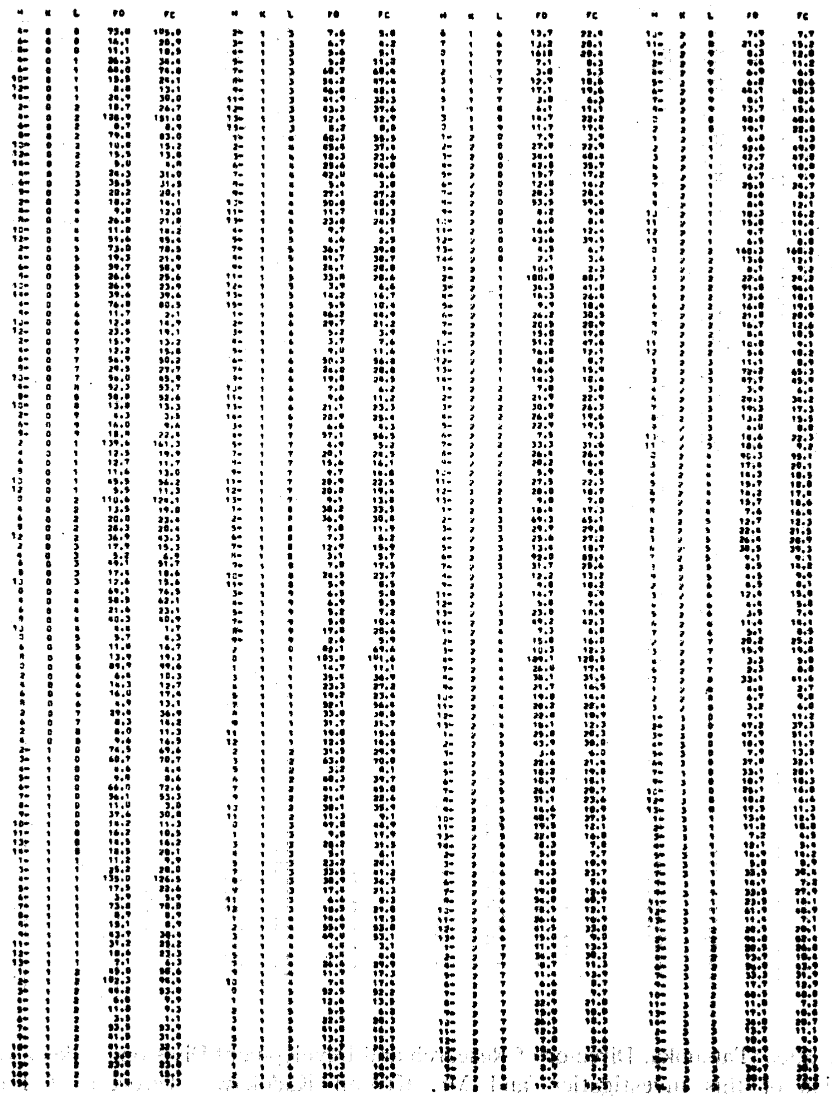
It is of interest that the pseudo two-fold axis bisects the molecule not at the S (2) position but, unexpectedly, at the C (7) position, and the two methylene groups become unequivalent in the crystal though they are equivalent in the chloroform solution as visualized by the NMR spectrum.[1]

The apparent systematic extinctions of (0*kl*) would be interpreted by this pseudo-symmetry and by the location of its axis at $z=1/4$ or $z=3/4$. If the *y* and *z* coordinates

Table III. Comparison of the Average Values of the Bond Lengths and Angles

Van de Grampel and Vos[4] (Å)	The present work (Å)	Van de Grampel and Vos[4]	The present work
S–S 2.04	S–S 2.05	S–S–S = 107°	S–S–S = 106°
S–N 1.73	S–C 1.85	S–N–S = 118°	S–C–S = 116°
		S–S–N = 110°	S–S–C = 105°

Table IV. Observed and Calculated Structure Factors (a)



for the atoms S(1), S(2), S(3), C(4), S(5), S(6), and C(7) of the molecule located upper left in Fig. 3 are shifted by $\frac{1}{2}$, they will approximately coincide with the y and z coordinates for the atoms S(6), S(5), C(4), S(3), S(2), S(1), and C(7) of the lower left molecule. Therefore, the condition for the systematic extinctions are approximately satisfied.

The relatively large value of the temperature factor for S(3) and the small value of that for C(4) may be interpreted by the existence of some disorder between these two atoms.

The valence angles of the carbon atoms are somewhat larger than the ordinary value. Such phenomenon has been observed also by Van de Grampel and Vos[4] in the case of $S_6(NH)_2$. In Table Ⅲ the average values of bond lengths and angles obtained in the present work are compared with those of $S_6(NH)_2$. They are in good agreement with each other though in the latter CH_2 is replaced by NH and the ring is an eight-membered one.

Table Ⅳ. Observed and Calculated Structure Factors (b)

H	K	L	FO	FC
11-	3	3	23.7	16.8
12-	3	3	7.9	8.0
13-	3	3	12.3	7.7
1-	3	4	26.2	21.2
2-	3	4	30.5	22.4
3-	3	4	12.4	12.3
4-	3	4	18.3	22.1
6-	3	4	73.9	65.7
7-	3	4	19.2	18.3
8-	3	4	11.4	10.2
9-	3	4	20.6	15.8
10-	3	4	38.1	29.5
13-	3	4	23.5	17.5
14-	3	4	22.5	13.2
2-	3	5	14.1	9.1
4-	3	5	90.5	61.3
7-	3	5	28.3	24.4
8-	3	5	47.5	54.1
8-	3	5	67.6	54.1
9-	3	5	26.8	20.0
11-	3	5	35.1	22.5
12-	3	5	18.3	13.8
13-	3	5	9.2	6.9
1-	3	6	30.6	27.8
2-	3	6	17.4	13.1
3-	3	6	12.2	8.6
4-	3	6	13.6	16.6
6-	3	6	22.9	13.5
7-	3	6	26.6	19.1
8-	3	6	16.8	14.4
9-	3	6	8.3	5.8
12-	3	6	9.6	7.4
13-	3	6	23.3	14.8
3-	3	7	7.5	6.0
4-	3	7	4.6	2.1
7-	3	7	6.2	7.2
9-	3	7	15.5	12.9
11-	3	7	23.9	15.5
12-	3	7	37.3	30.2
1-	3	8	22.8	21.2
2-	3	8	36.1	30.8
4-	3	8	6.6	10.3
5-	3	8	9.2	11.1
6-	3	8	37.4	31.7
7-	3	8	16.4	11.4
8-	3	8	8.0	9.5
9-	3	8	6.4	7.0
10-	3	8	20.2	12.2
11-	3	8	9.9	7.0
2-	3	9	6.3	2.4
4-	3	9	36.5	36.8
5-	3	9	4.7	5.5
7-	3	9	2.7	4.4
8-	3	9	6.4	4.7
2	3	0	46.0	37.3
0	3	1	47.1	53.2
3	3	1	17.6	16.2
4	3	1	102.4	101.2
5	3	1	29.3	27.2
6	3	1	12.5	12.4
7	3	1	37.8	36.8
8	3	1	54.5	45.9
9	3	1	28.1	19.5
10	3	1	8.2	6.0
11	3	1	13.0	12.9
12	3	1	19.1	12.7
1	3	2	11.2	13.0
2	3	2	20.3	14.6
3	3	2	35.9	37.6
6	3	2	43.8	45.8
7	3	2	17.2	16.2
8	3	2	8.2	9.4
9	3	2	20.3	15.6
11	3	2	9.3	3.9
12	3	2	8.5	8.3
0	3	3	135.9	128.8
1	3	3	13.4	7.0
3	3	3	22.2	23.2
4	3	3	46.8	44.2
5	3	3	15.0	14.8
6	3	3	12.4	11.7
7	3	3	21.1	22.7
8	3	3	20.4	24.5
9	3	3	10.7	8.3
2	3	4	57.5	50.8
3	3	4	30.2	31.3
4	3	4	4.6	6.3
5	3	4	3.9	0.1
7	3	4	17.9	17.4
8	3	4	7.2	10.0
9	3	4	10.8	7.8
10	3	4	31.5	38.8
2	3	5	12.2	11.5
3	3	5	9.3	11.1
4	3	5	14.4	14.4
5	3	5	10.5	12.0
6	3	5	9.4	9.0
7	3	5	9.8	11.6
8	3	5	6.5	7.1
1	3	6	6.1	10.6
2	3	6	29.7	26.5
3	3	6	24.6	26.8
4	3	6	4.2	8.9
5	3	6	4.5	3.7
6	3	6	20.4	26.5
7	3	6	5.6	9.2
0	3	7	10.6	15.3
1	3	7	7.7	6.6
2	3	7	12.5	14.1
3	3	7	8.3	10.8
4	3	7	20.7	30.5
5	3	7	5.7	9.3
1	3	8	7.5	10.3
3	3	8	3.3	11.8
1-	4	0	12.9	11.5
2-	4	0	11.5	15.1
3-	4	0	25.2	24.5
4-	4	0	37.9	35.7
5-	4	0	29.5	31.0
6-	4	0	4.9	6.7
7-	4	0	38.0	40.1
8-	4	0	30.8	33.6
9-	4	0	30.5	25.8
11-	4	0	32.3	24.7
12-	4	0	6.2	12.5
13-	4	0	6.4	7.7
1-	4	1	18.9	21.5
2-	4	1	26.1	20.3
3-	4	1	45.0	53.8
4-	4	1	14.1	17.1
5-	4	1	7.2	9.5
6-	4	1	48.6	48.0
7-	4	1	41.3	41.2
9-	4	1	19.4	13.2
10-	4	1	28.6	22.6
11-	4	1	20.3	15.1
12-	4	1	6.7	7.7
13-	4	1	18.0	17.4
1-	4	2	11.6	7.8
2-	4	2	21.0	19.1
3-	4	2	30.5	27.9
4-	4	2	65.8	60.2
5-	4	2	15.1	9.9
6-	4	2	5.2	3.4
7-	4	2	39.2	31.9
8-	4	2	44.4	42.1
9-	4	2	31.2	22.2
10-	4	2	11.2	7.8
11-	4	2	31.3	24.2
12-	4	2	6.9	3.3
13-	4	2	20.4	15.3
1-	4	3	23.2	20.7
2-	4	3	31.9	23.9
3-	4	3	25.7	21.4
4-	4	3	17.2	16.3
5-	4	3	22.4	20.5
6-	4	3	40.0	33.8
7-	4	3	35.8	29.6
8-	4	3	10.1	8.9
9-	4	3	27.8	22.3
11-	4	3	28.8	17.5
13-	4	3	30.5	23.0
2-	4	4	17.7	15.2
3-	4	4	24.8	20.4
4-	4	4	35.3	25.8
5-	4	4	11.5	11.1
7-	4	4	42.3	34.8
8-	4	4	8.3	4.1
9-	4	4	21.1	17.3
10-	4	4	7.9	5.2
11-	4	4	35.9	28.8
12-	4	4	37.2	30.3
13-	4	4	16.6	10.0
1-	4	5	24.0	24.0
2-	4	5	55.0	45.6
3-	4	5	18.4	16.4
4-	4	5	10.9	11.2
5-	4	5	9.4	12.2
6-	4	5	32.8	26.8
7-	4	5	29.7	22.2
8-	4	5	8.9	8.6
9-	4	5	25.1	15.3
10-	4	5	27.3	25.7
11-	4	5	14.4	6.9
13-	4	5	35.8	28.5
1-	4	6	8.0	5.0
2-	4	6	12.0	8.8
4-	4	6	41.8	36.0
5-	4	6	7.8	1.0
6-	4	6	8.3	0.7
7-	4	6	20.1	16.9
8-	4	6	28.7	19.5
9-	4	6	25.7	19.8
10-	4	6	10.1	4.9
11-	4	6	36.6	29.6
12-	4	6	28.2	19.5
1-	4	7	28.6	28.7
2-	4	7	23.5	19.0
4-	4	7	10.8	9.3
5-	4	7	17.2	19.9
6-	4	7	33.6	28.5
7-	4	7	26.8	22.2
8-	4	7	11.6	9.3
9-	4	7	6.7	8.5
10-	4	7	36.5	28.6
11-	4	7	16.5	10.3
2-	4	8	8.5	5.8
4-	4	8	28.0	24.2
5-	4	8	11.8	10.4
6-	4	8	6.2	2.2
8-	4	8	32.0	29.5
9-	4	8	9.0	5.6
5-	4	9	11.5	17.6
6-	4	9	9.6	16.3
0	4	0	80.2	101.9
2	4	0	13.0	15.1
1	4	1	13.6	9.5
2	4	1	72.4	67.9
3	4	1	56.6	62.6
4	4	1	9.1	11.1
6	4	1	15.9	10.5
7	4	1	28.0	25.5
8	4	1	3.9	2.8
9	4	1	19.4	18.6
10	4	1	32.1	37.9
11	4	1	16.1	11.0
12	4	1	5.2	5.9
0	4	2	8.6	4.0
1	4	2	7.1	5.9
2	4	2	11.1	9.5
3	4	2	35.4	38.7
4	4	2	33.2	35.4
5	4	2	27.2	28.7
6	4	2	6.8	6.8
7	4	2	33.2	37.7
8	4	2	3.9	1.6
9	4	2	10.6	8.9
11	4	2	13.3	10.1
0	4	3	4.1	4.1
1	4	3	15.4	11.9
2	4	3	25.2	28.5
3	4	3	43.6	46.3
4	4	3	4.5	6.8
5	4	3	5.5	7.6
6	4	3	26.1	34.9
7	4	3	22.9	22.3
8	4	3	14.8	17.1
0	4	4	10.9	2.5
1	4	4	10.2	4.0
2	4	4	5.3	1.4
3	4	4	24.2	26.2
4	4	4	34.1	36.0
5	4	4	13.7	15.4
6	4	4	6.8	7.7
7	4	4	17.9	18.3
8	4	4	20.2	23.1
9	4	4	3.5	5.5
1	4	5	8.3	6.5
3	4	5	40.3	45.3
6	4	5	17.8	20.9
7	4	5	16.7	19.5
8	4	5	3.0	5.8
0	4	6	45.6	46.6
1	4	6	11.1	1.6
3	4	6	13.5	14.3
4	4	6	5.4	3.7
5	4	6	12.2	15.7
6	4	6	6.4	4.9
1	4	7	12.8	13.3
2	4	7	24.0	25.8
3	4	7	22.5	28.9
4	4	7	2.4	1.3
0	4	8	9.2	12.5
1	4	8	4.4	3.6
2-	5	0	53.7	44.0
3-	5	0	5.7	0.6
4-	5	0	14.0	14.1
5-	5	0	6.5	2.0
6-	5	0	65.0	55.7
7-	5	0	8.3	4.8
10-	5	0	25.6	20.3
12-	5	0	8.4	8.6
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6-	5	1	11.4	11.1
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8-	5	1	21.1	16.3
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11-	5	1	8.1	3.5
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3-	5	2	18.0	13.4
4-	5	2	25.9	22.5
5-	5	2	10.6	12.5
6-	5	2	20.9	14.7
9-	5	2	7.5	6.5
10-	5	2	20.2	15.7
11-	5	2	14.5	9.2
1-	5	3	16.8	12.7
2-	5	3	23.3	16.3
3-	5	3	13.8	11.2
4-	5	3	50.5	43.2
5-	5	3	16.1	9.9
8-	5	3	50.6	44.5
9-	5	3	18.5	12.4
10-	5	3	15.5	8.8
11-	5	3	8.4	11.2
12-	5	3	46.7	38.7
1-	5	4	12.0	8.5
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7-	5	4	9.6	8.4
8-	5	4	19.7	13.5
9-	5	4	12.9	12.2
10-	5	4	39.6	30.9
11-	5	4	8.1	2.6
1-	5	5	7.8	5.7
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4-	5	5	36.2	30.3
5-	5	5	11.3	5.4
7-	5	5	7.9	7.9
8-	5	5	24.5	15.8
10-	5	5	8.4	5.8
12-	5	5	15.8	13.4
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8-	5	7	22.2	21.8
10-	5	7	10.5	6.7
2-	5	8	22.5	20.3
4-	5	8	8.4	12.4
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6-	5	8	6.4	7.7
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8-	5	8	9.9	14.2
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3	5	1	5.9	0.7
4	5	1	20.2	14.3
5	5	1	3.8	2.1
6	5	1	12.6	12.0
9	5	1	15.7	19.7
0	5	2	8.5	0.6
1	5	2	6.4	3.1
2	5	2	32.4	25.2
3	5	2	16.1	15.3
4	5	2	4.5	5.3
6	5	2	28.2	26.1
8	5	2	3.8	8.5
10	5	2	42.7	39.3
0	5	3	21.7	16.5
3	5	3	6.5	6.6
4	5	3	31.2	24.1
5	5	3	20.3	14.7
6	5	3	15.1	13.2
8	5	3	32.0	32.0
9	5	3	9.4	5.5
1	5	4	8.9	11.9
2	5	4	33.3	32.3
3	5	4	9.3	10.8
5	5	4	3.7	8.7
6	5	4	6.3	4.3
7	5	4	6.1	8.5
8	5	4	6.6	11.2
0	5	5	70.5	66.5
1	5	5	8.9	8.5
2	5	5	13.0	10.3
4	5	5	43.2	44.2
5	5	5	17.9	9.0
6	5	5	9.9	11.2
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4	5	6	5.7	8.2
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0	5	7	26.1	31.6
2	5	7	8.4	11.3
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3-	6	0	25.4	27.4
4-	6	0	23.5	20.5
5-	6	0	16.5	15.1
7-	6	0	35.2	31.5
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7-	6	2	45.5	38.0
8-	6	2	50.3	41.5
9-	6	2	28.9	23.6
11-	6	2	34.7	25.2
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3-	6	3	32.0	31.8
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6	6	1	8.5	1.5
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9	6	1	18.4	11.6
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3	6	2	15.5	13.0
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7	6	3	19.1	19.2
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2	6	4	12.3	4.6
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3	8	3	9.6	10.1
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0	9	3	3.4	8.9
1	9	3	6.5	8.5
		END		

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