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The Crystal Structure of Histamine Sulphate Monohydrate

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Histamine sulphate crystallizes in the space group $P2_1$ with four formula units, ($C_5H_{11}N_3^{2+}.SO_4^{2-}.H_2O$), in the unit cell of dimensions $a=13{\cdot}124$, $b=7{\cdot}037$, $c=10{\cdot}983$ Å and $\beta=104{\cdot}16°$. The structure was determined by the heavy-atom method and refined by least-squares calculations to $R=0{\cdot}089$. The imidazole ring is protonated and the bond angle C^{γ}–N^{δ}–C^{ε} in the protonated ring is larger than that for an unprotonated one. The skelton of the histamine molecule is roughly planar, although in histamine phosphate the imidazole ring and the aliphatic chain are nearly perpendicular to each other. There is a partial disorder associated with one of the water molecules. The hydrogen-bond scheme is complicated, there being three bifurcated hydrogen bonds and two C–H···O hydrogen bonds.

Introduction

The tertiary structures of many enzymes have been determined by X-ray diffraction, and it has become clear that histidine often plays a key role in the catalytic activity of enzymes. In particular, the imidazole group, the functional side chain of histidine, participates in the activity of many enzymes.

Accurate structure determinations of histidine have been done by Donohue & Caron (1964), Bennett, Davidson, Harding & Morelle (1970) and Madden, McGandy & Seeman (1972). On the other hand, only a few analyses have been reported for the structure of histamine which is obtained from histidine by decarboxylation. The substance has also an important physiological activity. The structure analyses of its phosphate and sulphate were therefore both performed in our laboratory. In this paper only the structure of histamine sulphate will be described, because the structure of the phosphate has already been reported by Veidis, Palenik, Schaffrin & Trotter (1969).

Experimental

The colourless and transparent crystals elongated along the monoclinic *b* axis were obtained by dissolving commercial histamine in 2*N* sulphuric acid. They are hygroscopic and deteriorate quickly on exposure to air: hence all the X-ray data were taken with the crystal coated in a collodion film.

The crystal data are summarized in Table 1. The systematic absence of 0*k*0 reflexions with *k* odd shows that the space group is either $P2_1$ or $P2_1/m$. The $N(z)$ test suggested the space group to be $P2_1$. The *h*0*l* reflexions are weak when $h+l$ is odd, so there exists a pseudo-*n*-glide symmetry.

Table 1. *Crystal data*

$C_5H_{11}N_3^{2+}.SO_4^{2-}.H_2O$
$a=13{\cdot}124$, $b=7{\cdot}037$, $c=10{\cdot}983$ Å, $\beta=104{\cdot}16°$
$V=983{\cdot}5$ Å^3, F.W. 227·24
$D_x=1{\cdot}535$ g cm^{-3} for $Z=4$
D_m (flotation) $=1{\cdot}52$ g cm^{-3}
$\mu=3{\cdot}31$ cm^{-1} (Mo $K\alpha$)
Systematic absence: 0*k*0, $k=2n+1$
Space group: $P2_1$

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Integrated intensity data were collected on a Rigaku automatic diffractometer, using Zr-filtered Mo $K\alpha$ radiation. The ω–2θ scan method was adopted. The 2θ scan range for each reflexion was from $\{2\theta(\alpha_1)-0{\cdot}70\}^\circ$ to $\{2\theta(\alpha_2)+0{\cdot}70\}^\circ$ with a scan speed of 2°/min. Background intensity was counted for 5 s at each end of the scan range. 1718 reflexions up to $\sin\theta/\lambda=0{\cdot}58$ were measured from a needle crystal of dimensions $0{\cdot}10\times0{\cdot}33\times0{\cdot}10$ mm.

The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was made because of the small cross sections and the small linear absorption coefficient of the crystal.

Structure determination

The coordinates of the two sulphur atoms in the asymmetric unit were obtained from a sharpened three-dimensional Patterson map. The carbon, nitrogen and oxygen atom positions were then found by a subsequent Fourier calculation.

The atomic scattering factors used for the calculation of the structure factors were those given for neutral sulphur, oxygen, nitrogen, carbon and hydrogen atoms in *International Tables for X-ray Crystallography* (1962). The refinement of the parameters was carried out by block-diagonal least-squares calculations. The

Table 2. *Fractional atomic coordinates and their standard deviations* (*in parentheses*) (*all* $\times 10^4$)

	x	y	z		x	y	z
S(1)	3390 (2)	0 (5)	339 (2)	S(2)	8361 (2)	1965 (5)	5794 (2)
O(11)	3079 (7)	−483 (14)	−998 (7)	O(21)	8147 (6)	3391 (13)	4790 (7)
O(12)	4509 (6)	449 (13)	689 (7)	O(22)	9497 (5)	1686 (14)	6269 (7)
O(13)	3143 (6)	−1554 (13)	1105 (7)	O(23)	7910 (5)	2558 (12)	6819 (7)
O(14)	2817 (6)	1743 (13)	566 (8)	O(24)	7875 (5)	177 (12)	5265 (8)
W(1)	7131 (10)	1300 (16)	2456 (8)	*W*(2′)	2655 (19)	2325 (29)	7040 (17)
				W(2″)	1948 (15)	2573 (38)	7433 (17)
N(11)	848 (6)	1957 (16)	4722 (7)	N(21)	4153 (7)	4962 (15)	842 (9)
C(12)	188 (7)	1929 (19)	3408 (8)	C(22)	4814 (8)	4687 (17)	2141 (10)
C(13)	891 (8)	1952 (19)	2477 (9)	C(23)	4093 (8)	4479 (17)	3006 (11)
C(14)	240 (7)	2129 (16)	1177 (8)	C(24)	4680 (8)	4426 (17)	4378 (11)
N(15)	736 (7)	2014 (15)	173 (7)	N(25)	4204 (6)	4584 (14)	5342 (7)
C(16)	3 (9)	2153 (19)	−885 (8)	C(26)	4896 (10)	4504 (17)	6441 (11)
N(17)	−921 (7)	2290 (18)	−645 (8)	N(27)	5815 (8)	4329 (15)	6182 (9)
C(18)	−800 (8)	2284 (18)	639 (11)	C(28)	5693 (8)	4305 (17)	4920 (11)

Table 3. *Anisotropic temperature factors and their standard deviations* (*in parentheses*) (*all* $\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	36 (1)	127 (5)	44 (2)	2 (6)	22 (3)	−1 (6)
S(2)	28 (1)	141 (5)	47 (2)	−10 (6)	20 (3)	8 (6)
O(11)	79 (6)	285 (27)	45 (7)	−44 (22)	17 (10)	−57 (22)
O(12)	41 (4)	242 (23)	62 (7)	−23 (17)	26 (9)	−19 (21)
O(13)	47 (5)	217 (21)	77 (8)	−41 (18)	42 (10)	57 (22)
O(14)	58 (5)	153 (19)	129 (10)	−7 (20)	43 (11)	−11 (26)
O(21)	70 (6)	212 (21)	56 (7)	−40 (20)	55 (10)	39 (21)
O(22)	29 (4)	297 (25)	54 (6)	4 (19)	33 (8)	−23 (23)
O(23)	23 (4)	220 (21)	66 (7)	20 (15)	31 (8)	6 (19)
O(24)	36 (4)	138 (17)	104 (8)	−43 (16)	26 (10)	−30 (22)
W(1)	146 (11)	271 (30)	76 (9)	6 (30)	−26 (15)	96 (27)
W(2′)	153 (22)	180 (51)	106 (20)	−124 (56)	44 (34)	43 (53)
W(2″)	77 (14)	485 (83)	97 (19)	−168 (59)	−120 (26)	164 (67)
N(11)	43 (5)	175 (21)	48 (7)	22 (23)	48 (10)	0 (25)
C(12)	44 (6)	181 (25)	32 (8)	35 (27)	33 (11)	37 (29)
C(13)	39 (6)	161 (24)	43 (8)	37 (26)	2 (11)	29 (30)
C(14)	33 (5)	97 (21)	45 (8)	−19 (21)	6 (10)	−36 (25)
N(15)	66 (6)	136 (19)	40 (8)	7 (23)	8 (10)	−15 (25)
C(16)	65 (7)	179 (29)	34 (9)	72 (29)	−24 (12)	−22 (31)
N(17)	32 (5)	269 (32)	87 (10)	3 (24)	−74 (11)	22 (30)
C(18)	33 (6)	154 (29)	100 (12)	−8 (24)	−15 (13)	34 (33)
N(21)	61 (6)	175 (23)	85 (10)	−83 (24)	93 (13)	−60 (28)
C(22)	49 (7)	133 (26)	65 (10)	3 (22)	44 (13)	−46 (27)
C(23)	26 (6)	167 (27)	87 (11)	−2 (22)	28 (13)	−20 (29)
C(24)	34 (6)	138 (25)	83 (11)	35 (21)	30 (13)	35 (27)
N(25)	37 (5)	176 (23)	48 (7)	12 (18)	19 (10)	40 (22)
C(26)	62 (8)	118 (26)	83 (12)	−9 (24)	−16 (15)	30 (28)
N(27)	59 (7)	197 (26)	62 (9)	−14 (23)	−50 (12)	11 (25)
C(28)	29 (6)	142 (25)	101 (13)	28 (22)	−21 (14)	15 (30)

function minimized was

$$\sum w(k|F_{\text{obs}}|-|F_{\text{cal}}|)^2 .$$

In the early stages of refinement, unit weight was assigned to all the observed reflexions. After several cycles of isotropic refinement, the R value decreased to 0·21. During the refinements, the temperature factor for $W(2)$, the oxygen atom of the water molecule, reached an extraordinarily large value of 13·0 Å^2. With the contribution of $W(2)$ omitted from the F_{cal}'s, anisotropic thermal parameters of the form

$$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$$

were then introduced for every atom and two cycles of refinement were carried out.

In the next Fourier map, two peaks of approximately one half of the expected height for the oxygen atom appeared near the position previously assumed for $W(2)$. It was therefore assumed that some sort of positional disorder involving the $W(2)$ atom must exist in the crystal. Most probably, the $W(2)$ atom seems to have equal probability of being located at $W(2')$ and $W(2'')$.

The difference-Fourier synthesis revealed the positions of all the hydrogen atoms with peak heights from 0·61 to 0·92 e Å^{-3}; four peaks with heights between 0·30 and 0·62 e Å^{-3} were assigned to the hydrogen atoms of the disordered water molecules, $W(2')$ and $W(2'')$, taking into account the hydrogen-bond scheme. Thus the hydrogen atoms were included in further refinement. In this calculation the following weights were adopted for each reflexion; $\sqrt{w}=\frac{1}{5}$ for $0<|F_{\text{obs}}|<5$, $\sqrt{w}=1$ for $5\le|F_{\text{obs}}|\le 25$, $\sqrt{w}=25/|F_{\text{obs}}|$ for $|F_{\text{obs}}|>25$. Isotropic temperature factors for all the hydrogen atoms were kept constant at 2·0 Å^2. All the parameters were refined until every shift became less than one fifth of each standard deviation. The standard deviations were estimated by the use of the diagonal terms of the inverse matrix. The final R value was 0·113 for the 1718 reflexions (or 0·089 for the 1565 non-zero reflexions). The reason for rather large value of R may be the disordered structure involving one of the water molecules.

Table 4. *Parameters of hydrogen atoms*

	Bonded to	x	y	z
H(111)	N(11)	0·133	0·321	0·508
H(112)		0·057	0·223	0·538
H(113)		0·142	0·071	0·496
H(121)	C(12)	−0·023	0·314	0·323
H(122)		−0·012	0·086	0·352
H(131)	C(13)	0·124	0·074	0·271
H(132)		0·132	0·309	0·255
H(15)	N(15)	0·137	0·242	0·044
H(16)	C(16)	0·009	0·235	−0·180
H(17)	N(17)	−0·151	0·239	−0·123
H(18)	C(18)	−0·141	0·206	0·090
HW(11)	W(1)	0·731	0·144	0·312
HW(12)		0·695	0·242	0·216
H(211)	N(21)	0·358	0·427	0·070
H(212)		0·452	0·477	0·032
H(213)		0·389	0·597	0·093
H(221)	C(22)	0·539	0·361	0·224
H(222)		0·518	0·612	0·223
H(231)	C(23)	0·356	0·339	0·274
H(232)		0·356	0·524	0·317
H(25)	N(25)	0·362	0·484	0·500
H(26)	C(26)	0·492	0·455	0·730
H(27)	N(27)	0·639	0·427	0·667
H(28)	C(28)	0·643	0·416	0·479
HW(2′1)	W(2′)	0·283	0·338	0·725
HW(2′2)		0·296	0·183	0·806
HW(2″1)	W(2″)	0·209	0·400	0·774
HW(2″2)		0·241	0·118	0·796

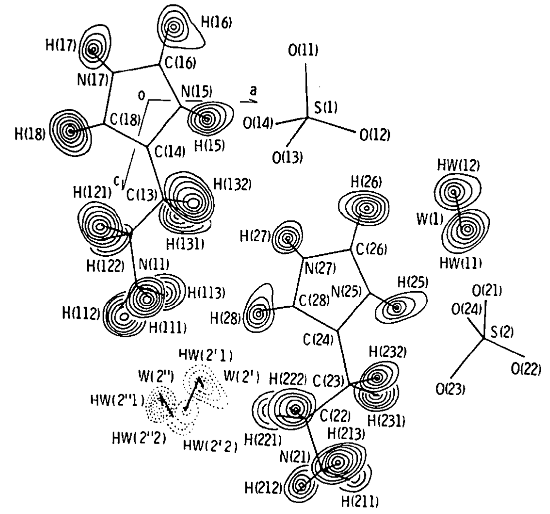


Fig. 1. Composite drawing of the three-dimensional difference map. First contour 0·25 e Å^{-3}; interval 0·10 e Å^{-3}. The peaks drawn by dotted lines correspond to the hydrogen atoms of the disordered water molecules.

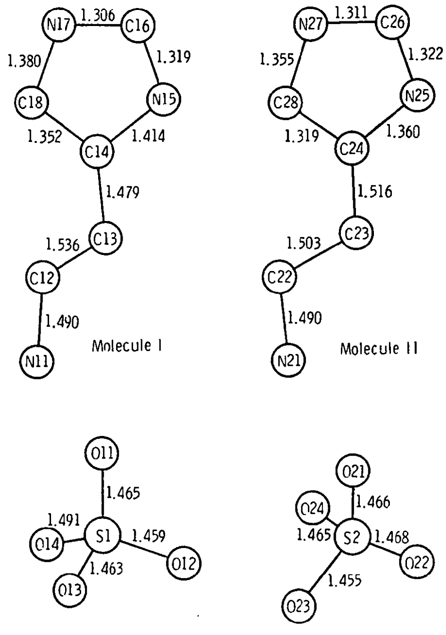


Fig. 2. Bond lengths.

The difference-Fourier map is drawn in Fig. 1. Tables 2 and 3 give the final atomic parameters with their standard deviations. The hydrogen parameters are listed in Table 4. Comparison of the observed and the calculated structure factors at the final stage is shown in Table 5.

Calculations were carried out on the FACOM 230-60 at the Data Processing Centre of Kyoto University and the NEAC 2200-500 at the Computer Centre of this university. Programs used in the calculations are as follows; *MFPM* for Patterson function calculation programmed by Professor N. Yasuoka, and *SFFR* for Fourier synthesis, *FBLS* for block-diagonal least-squares refinement, *DAPH* for calculations of distances and angles written by one of the authors (Ashida).

Table 5. *Observed and calculated structure factors* (× 5)

```
    K  FO  FC
H,L=  0   0
    2 136 138
    4 420 449
    6 118 113
    8  81  74
H,L=  1   0
    0  42  22
    1 237 232
    3  32  31
    4  46  47
    5  19  21
    6 151 154
    7  32  32
    8  12  24
H,L=  2   0
    0 116 130
    1 148 155
    2  87  84
    3  59  63
    4 155 152
    5  76  71
    6  59  60
    7  36  30
    8  50  56
H,L=  3   0
    0  10  24
    1  96  98
    2  80  79
    3  71  71
    4  28  19
    5  44  41
    6  47  48
    7  53  48
H,L=  4   0
    0  36  24
    1 275 284
    2  65  67
    3 169 171
    4  33  31
    5 177 184
    6  53  35
    7  18  18
H,L=  5   0
    0   8  11
    1 198 202
    2  79  74
    3 181 175
    4  50  54
    5  29  24
    6   0  25
    7 103 100
H,L=  6   0
    0  48  47
    1  88  83
    2  42  42
    3  46  33
    4  45  40
    5  36  30
    6  77  73
    7  15  27
H,L=  7   0
    0   0   8
    1 133 139
    2   0  12
    3  75  80
    4  87  97
    5  66  62
    6   0  20
    7  35  45
H,L=  8   0
    0 244 235
    1  78  80
    2  16  24
    3  32  45
    4  44  33
    5  78  74
    6  34  28
H,L=  9   0
    0  44  28
    1  65  66
    2 137 131
    3  78  75
    4 101 104
    5  41  45
    6   0   8
H,L= 10   0
    0  55  42
    1  60  58
    2  60  63
    3  56  53
    4   0  11
    5  33  30
    6  42  30
H,L= 11   0
    0  34  17
    1  78  81
    2 107 111
    3 108 118
    4   0  12
    5  22  16
H,L= 12   0
    0  98 109
    1  84  76
    2   8   7
    3   0  29
    4  85  94
H,L= 13   0
    0  23   1
    1   0   5
    2  87  88
    3  11  17
H,L= 14   0
    0  35  27
    1  39  20
    2   0  10
H,L=  0   1
    0   0  12
    1  48  55
    2 116 115
    3 132 138
    4 127 132
    5  13  21
    6  41  46
    7  18  22
    8  79  70
H,L=  1   1

    K  FO  FC
    0 249 236
    1 312 317
    2 126 129
    3  96  89
    4  83  84
    5 136 142
    6 145 152
    7  36  33
    8  25  18
H,L= -1   1
    0 133 144
    1 297 299
    2 186 190
    3  38  33
    4 151 152
    5 103 103
    6  80  76
    7  43  53
    8  32  44
H,L=  2   1
    0  66  65
    1 269 265
    2  59  64
    3 107 110
    4 164 168
    5   0  12
    6  41  50
    7  86  93
    8   0  27
H,L= -2   1
    0  39  43
    1 100 114
    2 415 443
    3 146 139
    4  82  77
    5  78  91
    6 122 116
    7   0  30
    8   0  18
H,L=  3   1
    0 195 191
    1  43  46
    2 126 124
    3  75  72
    4  71  81
    5  19  27
    6  77  75
    7  27   8
H,L= -3   1
    1 254 264
    2  31  49
    3 152 146
    4 206 203
    5  71  68
    6  83  87
    7  15  15
H,L=  4   1
    0  56  53
    1 220 227
    2  18  25
    3  67  58
    4  84  79
    5  56  53
    6  55  46
    7  51  44
H,L= -4   1
    0  95 101
    1 215 217
    2 210 203
    3  37  43
    4 110 111
    5   6   4
    6  49  51
    7  68  73
H,L=  5   1
    0 363 359
    1 140 148
    2  41  44
    3  93  94
    4  80  75
    5  84  87
    6  16  24
    7  44  22
H,L= -5   1
    0 311 315
    1 109 104
    2  76  69
    3  74  83
    4  39  33
    5  59  60
    6  46  44
    7   4  10
H,L=  6   1
    0  57  52
    1  42  34
    2 250 243
    3  85  86
    4  46  43
    5  19  21
    6  51  43
    7  27  31
H,L= -6   1
    0 113 111
    1 156 148
    2 147 145
    3  37  26
    4  45  45
    5  38  30
    6  45  50
    7  29  21
H,L=  7   1
    0  66  65
    1 223 218
    2  16  25
    3  52  51
    4  72  74
    5  47  52
    6  12  25
    7   0   8
H,L= -7   1
    0  64  63
    1 172 164
    2  88  86
    3  98  84
    4  25  38
    5 107 112

    K  FO  FC
    6  44  38
    7  31  28
H,L=  8   1
    0   9  26
    1 179 182
    2  29  29
    3 174 184
    4   0  11
    5  33  29
    6   1  16
H,L= -8   1
    0   0  18
    1 122 121
    2  77  71
    3 178 177
    4  90  93
    5   8   1
    6  36  21
H,L=  9   1
    0 119 116
    1  89  95
    2   0  12
    3  35  33
    4  49  42
    5  61  57
    6  31  36
H,L= -9   1
    0 114 112
    1   0  18
    2  50  49
    3  37  31
    4  53  55
    5  14  17
    6  61  53
H,L= 10   1
    0  23  24
    1  27  25
    2 105 106
    3  19  26
    4  70  76
    5   0  33
H,L=-10   1
    0  10  27
    1  56  53
    2  87  96
    3 111 115
    4  23  41
    5  66  63
    6  31  26
H,L= 11   1
    0  29  37
    1   0  10
    2  43  45
    3  20  11
    4  20  22
    5  61  45
H,L=-11   1
    0  18  15
    1  71  79
    2   0  20
    3  26  24
    4  30  25
    5  69  65
H,L= 12   1
    0  28  13
    1   0  15
    2  42  45
    3  32  46
    4  45  57
H,L=-12   1
    0  20   3
    1   0  24
    2  44  32
    3  41  48
    4  74  64
H,L= 13   1
    0  41  33
    1   0  17
    2  30  38
    3   0  11
H,L=-13   1
    0  31  29
    1  16  24
    2  36  33
    3   0  31
    4  30  27
H,L= 14   1
    0  27  15
    1   0  13
H,L=-14   1
    0  22   2
    1  13  31
    2  96  86
H,L=  0   2
    0 464 489
    1 207 207
    2 138 133
    3 166 170
    4 152 144
    5 102 113
    6 103 111
    7  40  37
    8   0  10
H,L=  1   2
    0  68  67
    1 240 242
    2 275 279
    3  84  78
    4 124 123
    5  76  79
    6  51  59
    7  39  37
    8  45  46
H,L= -1   2
    0  36  32
    1 126 118
    2 187 188
    3 110 108
    4  58  63
    5  35  40
    6  24  39
    7  41  57
    8  27  27
H,L=  2   2
    0 265 261
    1 308 323

    K  FO  FC
    2 243 241
    3 108 112
    4  54  55
    5 108 112
    6  47  41
    7   0  22
H,L= -2   2
    0 221 218
    1  89  85
    2 106 106
    3 130 122
    4  52  47
    5  23  26
    6 159 156
    7  23  21
    8   0   9
H,L=  3   2
    0  17   6
    1 168 167
    2  34  42
    3 106 111
    4  68  66
    5   0   7
    6  32  33
    7  30  28
H,L= -3   2
    0  11   4
    1  96 106
    2 184 191
    3  67  56
    4 177 176
    5  40  33
    6  31  37
    7  64  72
H,L=  4   2
    0 268 281
    1 173 162
    2 139 125
    3  46  42
    4  94 101
    5  42  54
    6  47  41
    7  48  42
H,L= -4   2
    0 119 126
    1 196 202
    2 107 106
    3  32  25
    4  47  52
    5 138 143
    6  42  39
    7  47  36
H,L=  5   2
    0   0  13
    1 142 146
    2 147 148
    3  84  88
    4  66  72
    5  40  35
    6  48  43
    7  48  64
H,L= -5   2
    0  46  41
    1  79  80
    2  99 102
    3 133 139
    4  20  18
    5  37  32
    6  24  32
    7  49  44
H,L=  6   2
    0 111 109
    1  29  26
    2  40  37
    3  74  75
    4  24  31
    5  52  61
    6  58  60
    7   0   4
H,L= -6   2
    0 125 122
    1 136 135
    2  92  91
    3  42  33
    4  13  16
    5  58  63
    6  40  36
    7   0  34
H,L=  7   2
    0  37  24
    1  64  49
    2  91  97
    3  11  29
    4  95  99
    5  15  30
    6  35  31
H,L= -7   2
    0  44  41
    1 131 132
    2 113 113
    3 123 125
    4  33  49
    5  41  51
    6  47  42
    7  71  68
H,L=  8   2
    0  56  54
    1 101 103
    2  34  46
    3  29  28
    4   0  12
    5  82  85
    6   0   5
H,L= -8   2
    0 233 225
    1  40  41
    2  47  55
    3 108 107
    4  76  83
    5  38  34
    6  46  48
H,L=  9   2
    0  21  35
    1  79  76
    2 106 107
    3 161 159

    K  FO  FC
    4  53  37
    5  30  36
    6  47  33
H,L= -9   2
    0  71  70
    1 109 106
    2 188 181
    3  39  46
    4  70  83
    5  69  61
    6  34  35
H,L= 10   2
    0  97  98
    1  64  67
    2  29  27
    3  39  28
    4  55  53
    5  43  44
H,L=-10   2
    0   9  29
    1 116 115
    2  56  45
    3  57  53
    4   0  17
    5  62  55
    6   0  31
H,L= 11   2
    0  25  16
    1  31  24
    2   0  32
    3  34  29
    4  23  30
H,L=-11   2
    0  49  60
    1  90  82
    2 114 108
    3  88  96
    4  59  68
    5   0  19
H,L= 12   2
    0  37  34
    1   0  14
    2  22  25
    3   8  21
    4  20  27
H,L=-12   2
    0 121 127
    1  51  42
    2  31  49
    3   0  24
    4  83  81
    5  43  20
H,L= 13   2
    0   0   3
    1  57  55
    2  70  68
H,L=-13   2
    0  31  10
    1  39  49
    2  56  49
    3  67  69
    4  13  13
H,L=-14   2
    0   9  13
    1  59  43
    2   0  18
    3  31  17
H,L=  0   3
    0 118 121
    1 107 120
    2 144 144
    3  98 105
    4  99 100
    5  41  43
    6  26   6
    7  24  39
H,L=  1   3
    1  78  73
    2 130 128
    3 158 152
    4  54  56
    5  17  18
    6  91  99
    7   0  22
H,L= -1   3
    1 268 270
    2 254 253
    3  94  93
    4  94  94
    5 112 120
    6  56  64
    7  54  39
H,L=  2   3
    0  81  80
    1  89  87
    2 161 158
    3  48  40
    4 126 134
    5  50  49
    6  13  34
    7  55  55
H,L= -2   3
    0   0   3
    1 204 208
    2 101 110
    3  58  58
    4  95  95
    5  53  45
    6  34  38
    7   0  10
H,L=  3   3
    0 122 116
    1  61  62
    2  47  52
    3  60  65
    4  19  12
    5  87  91
    6  74  74
    7  17  15
H,L= -3   3
    0 221 230
    1 124 116
    2 151 157
    3 113 114
    4  72  64
    5 113 119

    K  FO  FC
    6  69  76
    7  47  48
H,L=  4   3
    0  21   9
    1  77  83
    2  56  55
    3  63  62
    4  49  49
    5  49  44
    6  62  52
    7  19  12
H,L= -4   3
    0   0   0
    1 131 130
    2 196 190
    3  70  74
    4  93  90
    5  31  19
    6  13  38
    7  40  47
H,L=  5   3
    0  60  57
    1  56  56
    2  65  70
    3  16  13
    4  26  30
    5  92  90
    6   0   7
    7  52  40
H,L= -5   3
    0  14  10
    1  62  55
    2  29  32
    3  91  87
    4  69  70
    5  69  72
    6  62  65
    7  31  17
H,L=  6   3
    0  12  33
    1 105 106
    2  77  76
    3 137 140
    4  26  13
    5  20  16
    6   6  23
H,L= -6   3
    0  64  57
    1  16  19
    2 155 151
    3  59  60
    4  90  88
    5  36  31
    6  23  36
    7  65  66
H,L=  7   3
    0 199 199
    1  33  28
    2  47  44
    3  57  59
    4  84  86
    5  29  13
    6  20  32
H,L= -7   3
    0  77  80
    1  99  98
    2  85  79
    3  84  89
    4  28  30
    5  80  80
    6  68  69
    7   0  10
H,L=  8   3
    0   0  29
    1  76  73
    2 174 174
    3  91  94
    4  56  61
    5  33  32
    6  42  44
H,L= -8   3
    0  81  90
    1  95  98
    2 127 122
    3  76  75
    4  91  96
    5  62  63
    6  45  36
H,L=  9   3
    0  38  18
    1  85  82
    2  25  10
    3  33  27
    4  29  59
    5  38  54
H,L= -9   3
    0  40  40
    1  66  53
    2  20  16
    3  55  48
    4  64  55
    5  47  42
    6  18  10
H,L= 10   3
    0   0  11
    1  27   9
    2  84  81
    3  25  31
    4  57  58
    5  29  22
H,L=-10   3
    0  54  64
    1  62  74
    2  62  54
    3 115 119
    4  29  34
    5  35  50
    6  30  36
H,L= 11   3
    0  44  37
    1  44  34
    2  32  25
    3  48  53
    4  26  29
H,L=-11   3
    0  88  85

    K  FO  FC
    1  35  36
    2  19  12
    3  55  62
    4  45  54
    5  24  26
H,L= 12   3
    0   9   1
    1  74  67
    2  27  40
    3  70  65
H,L=-12   3
    0   0  25
    1  77  77
    2  79  88
    3  61  57
    4  52  52
    5  52  37
H,L= 13   3
    0  59  53
    1  39  33
    2  34  14
H,L=-13   3
    0  32   7
    1  63  63
    2  52  49
    3  25  49
    4  15  12
H,L=-14   3
    0  40  37
    1  49  35
    2  78  78
    3  11  32
H,L=  0   4
    0 109 106
    1 174 172
    2  69  72
    3  64  65
    4  48  56
    5 106 106
    6  30  39
    7  40  44
H,L=  1   4
    0 166 163
    1 158 158
    2  48  54
    3 111 110
    4  52  48
    5  77  75
    6  49  45
    7   0  31
H,L= -1   4
    0  89  83
    1 117 113
    2 125 128
    3  29  28
    4  96  99
    5  66  61
    6  38  38
    7  28  16
H,L=  2   4
    0  80  73
    1 131 116
    2 110 101
    3 145 145
    4  70  74
    5  53  51
    6  48  50
    7  64  63
H,L= -2   4
    1 134 137
    2 180 183
    3 236 229
    4  95  99
    5  80  77
    6  88  90
    7  30  35
H,L=  3   4
    0 178 177
    1 109 101
    2  82  84
    3  49  47
    4   8  27
    5   0  28
    6  29  14
    7  46  57
H,L= -3   4
    0  36  20
    1 216 217
    2 234 225
    3  98 101
    4  97  91
    5  62  60
    6  22  18
    7  47  58
H,L=  4   4
    0 123 116
    1  95  94
    2  89  85
    3  91  90
    4 103 103
    5  68  66
    6  69  73
    7  35  13
H,L= -4   4
    0  76  66
    1 159 155
    2  72  71
    3  49  44
    4  17  37
    5  73  69
    6  59  48
    7  25  30
H,L=  5   4
    0  95  91
    1 115 106
    2 247 250
    3 117 120
    4 100 105
    5  21  37
    6  71  71
H,L= -5   4
    0  17  11
    1  39  25
    2  65  66
    3  41  50
    4  55  62

    K  FO  FC
    5  57  53
    6  28  14
    7  32  31
H,L=  6   4
    0 102 109
    1 172 165
    2 110 110
    3  63  58
    4 115 116
    5  81  82
    6  36  32
H,L= -6   4
    0  48  54
    1 139 135
    2 151 148
    3 100 101
    4  62  60
    5 102 110
    6  60  63
    7  26  19
H,L=  7   4
    0  75  79
    1  90  92
    2   0  18
    3  82  81
    4  64  73
    5  12  13
    6  69  72
H,L= -7   4
    0 162 158
    1 161 164
    2   0  17
    3 146 146
    4 128 129
    5  35  41
    6  45  49
    7  36  50
H,L=  8   4
    0  15  13
    1  59  62
    2  34  41
    3  35  32
    4  34  30
    5  39  47
H,L= -8   4
    0  56  48
    1  42  30
    2  73  73
    3  81  77
    4  47  53
    5  48  49
    6  37  47
H,L=  9   4
    0  94  80
    1 126 142
    2  39  37
    3 142 145
    4  55  52
    5  51  41
H,L= -9   4
    0   0   8
    1  32  35
    2  82  84
    3  87  82
    4  38  33
    5   0  28
    6  32  51
H,L= 10   4
    0  83  86
    1 108 119
    2  48  57
    3  86  85
    4  79  68
H,L=-10   4
    0 139 144
    1  55  56
    2  74  71
    3 103 101
    4  86  96
    5   0  13
    6   6  24
H,L= 11   4
    0  38  33
    1  43  44
    2  95  96
    3  11  12
H,L=-11   4
    0  70  68
    1 137 135
    2 178 186
    3  53  46
    4  71  64
    5  60  68
H,L= 12   4
    0   0  38
    1  27  17
    2   0   6
H,L=-12   4
    0 100  99
    1 103 104
    2  38  34
    3  55  48
    4  33  49
H,L=-13   4
    0  54  66
    1  20  19
    2  21  23
    3  56  52
    4  13  19
H,L=-14   4
    0  31  35
    1  22  16
    2  21   5
    3  26  35
H,L=  0   5
    0 230 211
    1 126 125
    2  97  98
    3  83  79
    4  43  51
    5  36  26
    6  26  29
    7  37  45
H,L=  1   5
    0  68  67
    1  24  34
```

Table 5 (*cont.*)

```
    K  FO  FC
    2  72  69
    3 113 107
    4 109 113
    5  51  58
    6  68  67
    7  39  25
H,L= -1   5
    0 101 106
    1  52  44
    2 149 146
    3 189 184
    4  84  85
    5  36  48
    6  88  84
    7  55  49
H,L=  2   5
    0  37  40
    1 126 117
    2 134 132
    3  44  46
    4  85  93
    5  81  90
    6  56  55
    7   0   9
H,L= -2   5
    0  80  69
    1  34  32
    2 104 102
    3  49  43
    4  82  83
    5  72  65
    6  25  24
    7  19  34
H,L=  3   5
    0 140 137
    1 180 176
    2 108 106
    3  73  74
    4  78  73
    5  94  89
    6  25  35
    7  33  32
H,L= -3   5
    0   0   6
    1 127 123
    2  34  35
    3  36  35
    4 121 126
    5  67  71
    6   0  10
    7  24  31
H,L=  4   5
    0  79  83
    1  87  92
    2  60  60
    3  93  97
    4  94  74
    5  23  23
    6  33  38
H,L= -4   5
    0  36  38
    1  48  38
    2 140 140
    3  54  44
    4   0  18
    5  59  73
    6  66  71
    7  30  14
H,L=  5   5
    0  28  11
    1 115 118
    2  44  45
    3  26  27
    4  41  43
    5  61  54
    6  31  32
H,L= -5   5
    0 175 173
    1 147 145
    2  45  45
    3 148 141
    4 108 108
    5  85  92
    6  20  34
    7  41  50
H,L=  6   5
    0 150 147
    1  92  98
    2  61  50
    3 161 163
    4 110 103
    5  45  29
    6  11  10
H,L= -6   5
    0   0  19
    1 176 166
    2 134 133
    3 122 126
    4  79  69
    5  19  40
    6  28  27
    7  53  56
H,L=  7   5
    0  42  54
    1 106 104
    2 150 152
    3 105 113
    4  41  53
    5  66  71
H,L= -7   5
    0  51  47
    1 128 124
    2  45  37
    3  37  33
    4  34  35
    5  22  29
    6  29   8
H,L=  8   5
    0 122 121
    1 127 132
    2 143 130
    3  29  37
    4  34  34
    5  77  72
H,L= -8   5

    K  FO  FC
    0  90  85
    1  64  64
    2  85  87
    3  67  64
    4  74  78
    5  54  64
    6  31  28
H,L=  9   5
    0  99 107
    1  60  52
    2   0  17
    3  31  42
    4  18  34
H,L= -9   5
    0  67  70
    1  92  98
    2 172 168
    3 107 104
    4  64  61
    5  60  60
    6  54  67
H,L= 10   5
    0  40  40
    1  17  17
    2  26  15
    3  16  28
    4  53  47
H,L=-10   5
    0 194 204
    1 124 123
    2  99  96
    3  82  85
    4 119 128
    5  59  56
H,L= 11   5
    0  57  42
    1  22  22
    2   0  17
H,L=-11   5
    0  44  51
    1  56  58
    2  72  79
    3  56  52
    4   0  21
    5   2  11
H,L= 12   5
    0  40  34
H,L=-12   5
    0  41  42
    1  10  27
    2  49  40
    3  51  45
    4   0  29
H,L=-13   5
    0  52  54
    1  42  49
    2  22  28
    3  53  53
H,L=-14   5
    0   8  18
    1  72  72
    2  52  56
H,L=  0   6
    0 141 144
    1 153 152
    2  98 101
    3 104 104
    4  51  57
    5  43  43
    6  26  32
    7  22  11
H,L=  1   6
    0  76  81
    1  53  53
    2  23   7
    3  97  95
    4 103 103
    5  41  37
    6  31  17
    7  21   7
H,L= -1   6
    0 113 112
    1 152 150
    2 123 116
    3  56  54
    4  38  21
    5  68  71
    6  52  52
    7  24  28
H,L=  2   6
    0 111 117
    1  43  54
    2  75  79
    3 103  98
    4  93  94
    5   0  17
    6  41  37
H,L= -2   6
    0  92  90
    1 184 182
    2 153 153
    3 122 121
    4 142 140
    5 102 107
    6   0  16
    7  33  22
H,L=  3   6
    0  39  40
    1  80  76
    2  88  93
    3  95 101
    4  40  54
    5  64  59
    6  19  45
H,L= -3   6
    0  99  95
    1  65  56
    2  76  84
    3 126 130
    4  56  63
    5  31  34
    6  39  41
    7  33  35
H,L=  4   6
    0   0  23

    K  FO  FC
    1  83  86
    2  90  79
    3  41  34
    4  50  38
    5  56  54
    6  42  34
H,L= -4   6
    0 103  98
    1  48  45
    2  93  97
    3 102  93
    4  94  98
    5   0  18
    6  46  47
    7   0  31
H,L=  5   6
    0  59  61
    1  51  59
    2  62  66
    3  28  23
    4  39  34
    5  44  50
    6   0  21
H,L= -5   6
    0 100  99
    1  68  62
    2  77  74
    3  47  49
    4  74  78
    5  46  56
    6   0  34
H,L=  6   6
    0   2  17
    1  58  59
    2  60  57
    3  39  38
    4  52  55
    5  50  44
H,L= -6   6
    0  59  59
    1  52  62
    2  70  62
    3  60  60
    4  79  80
    5  45  35
    6  35  37
H,L=  7   6
    0 113 110
    1  35  28
    2  65  63
    3  83  83
    4  47  42
    5  43  43
H,L= -7   6
    0  84  87
    1  38  39
    2  81  77
    3  36  33
    4   0  25
    5  60  62
    6  45  35
H,L=  8   6
    0  31  34
    1  47  45
    2  37  32
    3  60  57
    4  36  33
H,L= -8   6
    0  36  37
    1  88  89
    2  58  52
    3   0   7
    4  30  39
    5  54  58
    6  23  16
H,L=  9   6
    0  39  50
    1  46  51
    2  31  21
    3  38  47
    4  51  49
H,L= -9   6
    0  88  90
    1  51  54
    2  56  63
    3  71  83
    4  48  51
    5  15  32
H,L= 10   6
    0  35  21
    1  52  39
    2  51  45
    3   5  25
H,L=-10   6
    0  48  31
    1  63  50
    2  20  25
    3  83  92
    4  37  35
    5  35   6
H,L= 11   6
    0   0   6
    1  41  48
H,L=-11   6
    0 111 111
    1  79  82
    2  44  40
    3  52  63
    4  65  67
    5  52  51
H,L=-12   6
    0   0   3
    1  23  29
    2  97  98
    3  26  13
    4  42  40
H,L=-13   6
    0  72  72
    1  59  64
    2  43  46
    3   0  17
H,L=-14   6
    0  27  26
    1  45  34
    2  20  17

    K  FO  FC
H,L=  0   7
    0 119 118
    1  87  93
    2  66  70
    3  37  56
    4  24  17
    5  82  88
    6  51  23
H,L=  1   7
    0  40  48
    1  67  57
    2  50  50
    3  25  30
    4  48  55
    5  35  34
    6  22  19
H,L= -1   7
    0 134 128
    1  47  53
    2 137 146
    3 134 143
    4  89  90
    5  22  36
    6   0  27
H,L=  2   7
    0  55  58
    1  27  26
    2  59  59
    3  32  29
    4  28  35
    5  43  39
    6  39  37
H,L= -2   7
    0 166 162
    1  44  44
    2  69  74
    3  84  91
    4  84  82
    5  37  43
    6  48  45
H,L=  3   7
    0  23  38
    1  70  74
    2 114 116
    3  51  46
    4  23  32
    5  69  66
    6  56  45
H,L= -3   7
    0 142 137
    1 123 124
    2 106 107
    3 128 121
    4 104 101
    5  29  21
    6   0  12
H,L=  4   7
    0 134 133
    1  44  50
    2  71  77
    3  90  94
    4  76  79
    5   6   4
H,L= -4   7
    0  34  25
    1 161 156
    2  99  95
    3  52  60
    4  23  30
    5  64  69
    6   0  24
H,L=  5   7
    0  61  65
    1  89  88
    2  38  43
    3  90  92
    4  70  67
    5  33  32
H,L= -5   7
    0  25   7
    1  95  91
    2 126 133
    3  63  71
    4  42  44
    5  66  65
    6  36  25
H,L=  6   7
    0  48  51
    1  86  95
    2  61  63
    3  33  41
    4  81  47
    5  17  36
H,L= -6   7
    0  84  81
    1   2   7
    2  39  43
    3  74  74
    4  44  55
    5  16  14
    6  52  45
H,L=  7   7
    0  19   7
    1   6  42
    2  87  89
    3  18  19
    4  29  28
H,L= -7   7
    0   0  28
    1  55  58
    2  64  68
    3  48  44
    4  60  62
    5  29  40
    6  26  19
H,L=  8   7
    0  92  94
    1  76  79
    2  51  50
    3  49  51
H,L= -8   7
    0 130 131
    1   0   9
    2  25  22
    3  82  79

    K  FO  FC
    4 102 104
    5  33  23
H,L=  9   7
    0  52  47
    1  65  67
    2  27   7
    3  54  51
H,L= -9   7
    0  39  38
    1  33  32
    2 103 102
    3  66  63
    4  30  50
    5  32  25
H,L= 10   7
    0  35  45
    1  18  35
H,L=-10   7
    0   0  30
    1  74  77
    2  45  40
    3   0  22
    4  41  49
    5  56  59
H,L=-11   7
    0  20  16
    1   0  26
    2  27  30
    3  23   4
    4  33  38
H,L=-12   7
    0  39  45
    1  80  83
    2  48  54
    3  43  40
    4   0   7
H,L=-13   7
    0   0  16
    1  57  55
    2  18  26
    3  90  80
H,L=-14   7
    0  49  61
    1  40  47
H,L=  0   8
    0  21   7
    1  90  95
    2  14  30
    3 101 104
    4  66  60
    5   0  19
    6  21  12
H,L=  1   8
    0  67  67
    1  31  17
    2  31  40
    3  70  68
    4  55  49
    5  30  30
    6  34  11
H,L= -1   8
    0 137 140
    1  90  84
    2  66  64
    3  64  92
    4  41  51
    5  49  61
    6  47  46
H,L=  2   8
    0  54  59
    1 136 141
    2  23  42
    3  99  99
    4  76  80
    5  53  47
H,L= -2   8
    0  34  18
    1 103 104
    2 177 180
    3   0  16
    4  55  51
    5  65  63
    6  56  44
H,L=  3   8
    0  41  47
    1 131 130
    2  75  72
    3  86  80
    4  25  23
    5  78  81
H,L= -3   8
    0  86  91
    1   0  27
    2  37  29
    3  60  61
    4  39  42
    5  29  29
    6  19  14
H,L=  4   8
    0  26  18
    1  50  48
    2  79  91
    3  16  29
    4  61  56
    5  33  36
H,L= -4   8
    0  27   6
    1  62  55
    2 113 119
    3  82  77
    4  65  67
    5  56  49
    6   0  21
H,L=  5   8
    0  81  74
    1  52  48
    2   7  20
    3   9  22
    4  66  56
H,L= -5   8
    0 178 168
    1  29  17
    2  57  50
    3  81  92
    4  63  74

    K  FO  FC
    5  43  46
    6  64  63
H,L=  6   8
    0  13   3
    1  29  34
    2   0   9
    3  63  60
    4   0  26
H,L= -6   8
    0  46  37
    1  95 104
    2  64  71
    3  85  84
    4  77  72
    5  36  33
    6  47  19
H,L=  7   8
    0  56  50
    1  55  53
    2  37  39
    3  29  35
H,L= -7   8
    0  35  39
    1  64  59
    2  50  42
    3  44  39
    4  44  42
    5  57  52
H,L=  8   8
    0  39  32
    1   0  13
    2  38  31
H,L= -8   8
    0   2   7
    1  73  64
    2  54  53
    3  41  45
    4  31  26
    5  22  17
H,L=  9   8
    0   0   6
    1   0  14
H,L= -9   8
    0   0   8
    1  87 101
    2  45  31
    3  54  62
    4   0  10
    5  61  54
H,L=-10   8
    0  12   2
    1  37  42
    2  96  91
    3  58  43
    4   0  11
H,L=-11   8
    0 138 139
    1  21  26
    2  11  31
    3  53  41
    4  58  63
H,L=-12   8
    0   0   5
    1  60  50
    2  61  57
    3  69  65
H,L=-13   8
    0  30   6
    1  88  63
    2  19  28
H,L=  0   9
    0   0  19
    1 156 165
    2  27  27
    3  90 100
    4  31  26
    5 100 100
H,L=  1   9
    0  28  37
    1  96  92
    2  84  85
    3 105  98
    4  39  31
    5  45  40
H,L= -1   9
    0  29   6
    1 119 122
    2  67  63
    3  80  79
    4  52  44
    5  12  38
H,L=  2   9
    0  31  27
    1  34  33
    2   0  10
    3  13  39
    4  52  42
    5  39  26
H,L= -2   9
    0  34   9
    1  69  68
    2  28  27
    3  10  24
    4  40  38
    5  20  10
H,L=  3   9
    0   0  10
    1  25  42
    2  65  65
    3   0  11
    4  35  24
H,L= -3   9
    0  29  23
    1 148 148
    2 132 122
    3 119 119
    4  51  38
    5   0   6
H,L=  4   9
    0  99 109
    1  35  15
    2   5  29
    3  57  67
    4  39  48
H,L= -4   9

    K  FO  FC
    0 267 271
    1 123 128
    2   0   4
    3  61  62
    4 122 128
    5  64  59
H,L=  5   9
    0   0   6
    1  59  58
    2  47  47
    3   0  30
H,L= -5   9
    0   0  10
    1  30  32
    2 213 214
    3  26  31
    4  55  52
    5  49  39
H,L=  6   9
    0   0  27
    1  71  69
    2  30  50
    3  18   9
H,L= -6   9
    0  95 100
    1  10  10
    2  44  39
    3  33  27
    4  51  49
    5  22  31
H,L=  7   9
    0  16  25
    1   0  10
    2  74  72
H,L= -7   9
    0   8   6
    1  37  26
    2  75  74
    3   0   9
    4   0  24
    5   0  13
H,L= -8   9
    0 100  97
    1  23  39
    2   0  22
    3  52  51
    4  44  53
H,L= -9   9
    0  37  19
    1  25  49
    2  35  34
    3  59  52
    4   0  16
H,L=-10   9
    0  74  82
    1  19  21
    2  30  21
    3   0  19
    4  23  26
H,L=-11   9
    0   0  21
    1  66  66
    2  16  43
    3  47  48
H,L=-12   9
    0  50  10
    1 101 106
    2  26  30
H,L=-13   9
    0   0  18
H,L=  0  10
    0   0   5
    1  31  33
    2  35  42
    3  25  27
    4  26   6
H,L=  1  10
    0  80  78
    1   0  30
    2  47  36
    3   9  34
    4  22  37
H,L= -1  10
    0  87  85
    1  46  41
    2  16  17
    3  34  14
    4  45  44
H,L=  2  10
    0  21  23
    1  79  75
    2  75  69
    3   0  29
    4  31  24
H,L= -2  10
    0   0   3
    1  93 103
    2  68  71
    3 102 104
    4   0  11
    5  42  15
H,L=  3  10
    0   0   2
    1  86  90
    2  36  31
    3  54  55
H,L= -3  10
    0  19  30
    1 126 130
    2  40  35
    3  43  39
    4  12  12
    5  74  71
H,L=  4  10
    0   0  17
    1  62  59
    2  69  70
    3  65  68
H,L= -4  10
    0   0  17
    1  51  36
    2  84  82
    3  30  45
    4  76  74
    5  12  19

    K  FO  FC
H,L=  5  10
    0 112 103
    1  29  20
    2  42  39
H,L= -5  10
    0  53  58
    1  32  30
    2   0  32
    3   0  35
    4  35  17
H,L=  6  10
    0   0   9
    1  32  31
H,L= -6  10
    0  29  24
    1  76  72
    2  66  72
    3  46  45
    4   0  11
H,L= -7  10
    0 138 137
    1  61  56
    2  14  18
    3   0   7
    4  78  74
H,L= -8  10
    0   0  16
    1  52  51
    2  79  81
    3  39  32
    4  11  18
H,L= -9  10
    0   0   7
    1  52  58
    2  25  12
    3  29  23
H,L=-10  10
    0   0  19
    1  22   3
    2  49  53
    3  23  11
H,L=-11  10
    0  61  64
    1  56  51
    2  36  26
H,L=-12  10
    0  20  10
H,L=  0  11
    0  22  23
    1  20  21
    2  22  18
    3  26  32
H,L=  1  11
    0   0   0
    1  51  62
    2   0  37
    3  67  55
H,L= -1  11
    0   0   6
    1   0   7
    2  42  38
    3  27  28
H,L=  2  11
    0  82  88
    1  21  33
    2  22  21
H,L= -2  11
    0  21  18
    1  61  61
    2  23  33
    3  13  25
    4  35  21
H,L=  3  11
    0  18  18
    1  41  39
    2  30  46
H,L= -3  11
    0  42  36
    1  69  75
    2  88  87
    3  43  61
    4  56  47
H,L=  4  11
    0   0  25
    1  57  67
H,L= -4  11
    0 123 123
    1  43  43
    2  27  26
    3  38  19
    4  39  35
H,L= -5  11
    0   0   0
    1  41  47
    2  43  43
    3  44  39
H,L= -6  11
    0  33  29
    1  42  45
    2  14   3
    3  23   6
H,L= -7  11
    0   0   8
    1  30  18
    2  63  66
    3  20   3
H,L= -8  11
    0  71  60
    1  23  29
    2  25  24
    3   0  17
H,L= -9  11
    0  23   9
    1  36  26
    2   0  12
H,L=-10  11
    0  61  64
    1   0  14
```

Discussion of the structure

Molecular structure

The bond lengths and angles found in the two crystallographically independent molecules are illustrated in Figs. 2 and 3 respectively. The standard deviations for the S–O, C–N and C–C bond lengths are 0·010, 0·017 and 0·018 Å respectively. The standard deviation of the bond angles is about 1·1°. The average bond lengths and angles involving hydrogen atoms are listed in Table 6.

Table 6. *Average bond lengths and angles involving hydrogen atoms and their standard deviations*

(*a*) Bond lengths

	max. (Å)	min. (Å)	av. (Å)	⟨σ⟩ (Å)
N–H	1·14	0·79	0·90	0·04
C–H	1·11	0·88	0·99	0·04
W–H	1·22	0·71	0·97	0·09

(*b*) Bond angles

	max. (°)	min. (°)	av. (°)	⟨σ⟩ (°)
H–N(sp^3)–X	122	100	113	4
H–C(sp^3)–X	133	93	109	2
H–N(sp^2)–X	145	103	124	3
H–C(sp^2)–X	146	106	126	3
H–N(sp^3)–H	124	82	106	5
H–C(sp^3)–H	121	90	110	6
H–*W*——H	126	89	106	11

The difference-Fourier map shows that the imidazole rings are protonated. The bond lengths and angles of the protonated imidazole rings in several crystal structures are listed in Table 7(*a*) with those of the unprotonated imidazole ring for comparison. The bond lengths and angles of the histamine cation in histamine sulphate are, as a whole, close to those found in histamine phosphate (Veidis, Palenik, Schaffrin & Trotter, 1969). The shapes of imidazole rings in various crystals are compared with each other in Table 7 and it is clear that the angle C^{γ}–N^{δ}–C^{ε} in the unprotonated ring is significantly smaller than that in the protonated one. The effect is similar to that found in many six-membered heterocyclic aromatic rings (Singh, 1965).

The bond angle C(3)–C(4)–C(8) is larger than the angle C(3)–C(4)–N(5) in both molecules. This tendency is similar to the other structures listed in Table 7(*b*). According to Bennett *et al.* (1970), this feature of the bond angle is attributed to the electronic structure

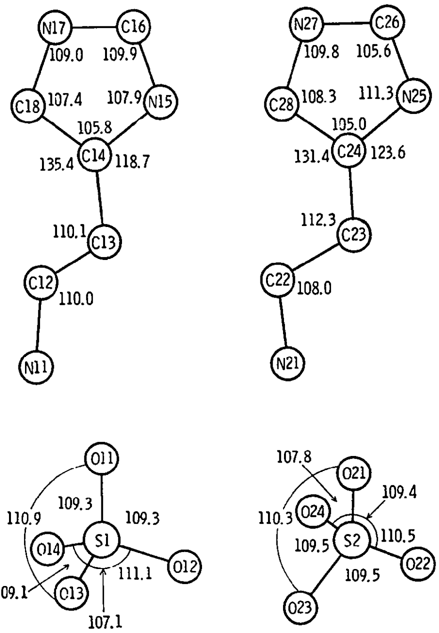


Fig. 3. Bond angles.

Table 7. *The bond lengths and angles in various imidazole rings*

(*a*) Bond lengths (Å)

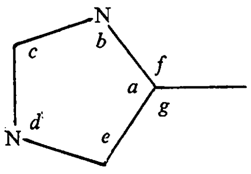
Name	Reference	C(4)–N(5)	N(5)–C(6)	C(6)–N(7)	N(7)–C(8)	C(8)–C(4)	⟨σ⟩
Molecule I	5	1·414	1·319	1·306	1·380	1·352	0·018
Molecule II	5	1·360	1·322	1·311	1·355	1·319	0·018
Histamine	1	1·379	1·332	1·314	1·373	1·349	0·004
DL-Histidine	2	1·403	1·306	1·331	1·381	1·355	0·01
L-Histidine	3	1·386	1·319	1·314	1·359	1·358	
L-Histidine*	4	1·382	1·327	1·339	1·374	1·361	0·003

(*b*) Bond angles (°)

Name	Reference	*a*	*b*	*c*	*d*	*e*	*f*	*g*	⟨σ⟩
Molecule I	5	105·8	107·9	109·9	109·0	107·4	118·7	135·4	1·1
Molecule II	5	105·0	111·3	105·6	109·8	108·3	123·6	131·4	1·1
Histamine	1	106·5	108·6	108·5	109·1	107·2	122·5	130·8	1·2
DL-Histidine	2	107·5	108·6	108·3	110·5	105·1	123·1	129·4	0·6
L-Histidine	3	106·2	108·5	108·7	109·6	106·9	122·1	131·6	
L-Histidine*	4	109·6	104·9	112·2	106·9	106·4	120·5	129·9	0·2

References

1. Veidis, Palenik, Schaffrin & Trotter (1969)
2. Bennett, Davidson, Harding & Morelle (1970)
3. Donohue & Caron (1964)
4. Madden, McGandy & Seeman (1972)
5. This work



* The imidazole ring is unprotonated.

around C(4). That is, the bond order of C(4)–C(8) is higher than that of C(4)–N(5). Therefore the electronic repulsion between the C(4)–C(8) bond and the C(4)–C(3) bond is stronger than that between the C(4)–N(5) bond and the C(4)–C(3) bond; hence the bond angle C(3)–C(4)–C(8) becomes larger than the C(3)–C(4)–N(5) angle.

The C(2)–C(3) bond length in molecule I is close to that of normal single bonds, while the corresponding one in molecule II is shorter but is closer to that in histamine phosphate (Veidis, Palenik, Schaffrin & Trotter, 1969). In the molecule I the bond C(3)–C(4) is fairly shorter than usual. These differences in the bond lengths may be caused by the correlation effect of pseudosymmetry.

The conformation of histamine is different in the two histamine crystals. The histamine cation is characterized by two planar groups. The first one is the imi-

Table 8. *Least-squares planes and deviations from the planes*

(*a*) Equations of the least-squares planes

	$X=ax+cz\cos\beta,\ Y=by,\ Z=cz\sin\beta$	Atoms
I	$0{\cdot}0888X+0{\cdot}9960Y+0{\cdot}0169Z=1{\cdot}5056$	C(14) N(15) C(16) N(17) C(18)
I′	$0{\cdot}0923X+0{\cdot}9953Y+0{\cdot}0281Z=1{\cdot}5022$	C(14) N(15) C(16) N(17) C(18) C(13)
II	$0{\cdot}0145X+0{\cdot}9993Y+0{\cdot}0338Z=1{\cdot}5060$	N(11) C(12) C(13) C(14)
III	$0{\cdot}0930X+0{\cdot}9956Y-0{\cdot}0097Z=3{\cdot}5285$	C(24) N(25) C(26) N(27) C(28)
III′	$0{\cdot}0932X+0{\cdot}9956Y-0{\cdot}0090Z=3{\cdot}5338$	C(24) N(25) C(26) N(27) C(28) C(23)
IV	$-0{\cdot}0227X+0{\cdot}9947Y+0{\cdot}1001Z=3{\cdot}4074$	N(21) C(22) C(23) C(24)

(*b*) Deviations ($\times 10^3$ Å) from the planes

I		I′		II		III		III′		IV	
C(14)	−7	C(14)	−24	N(11)	−38	C(24)	11	C(24)	12	N(21)	−37
N(15)	10	N(15)	2	C(12)	36	N(25)	−8	N(25)	−8	C(22)	29
C(16)	−9	C(16)	−2	C(13)	36	C(26)	3	C(26)	2	C(23)	55
N(17)	4	N(17)	13	C(14)	−33	N(27)	4	N(27)	3	C(24)	−45
C(18)	2	C(18)	−4			C(28)	−9	C(28)	−9		
C(13)*	49	C(13)	15			C(23)*	−3	C(23)	−1		
H(15)*	−347	H(15)*	−360			H(25)*	−132	H(25)*	−131		
H(16)*	−163	H(16)*	−146			H(26)*	−2	H(26)*	−3		
H(17)*	−2	H(17)*	16			H(27)*	−8	H(27)*	−9		
H(18)*	233	H(18)*	227			H(28)*	−5	H(28)*	−5		

* Atoms with asterisks are not included in the calculation of the planes.

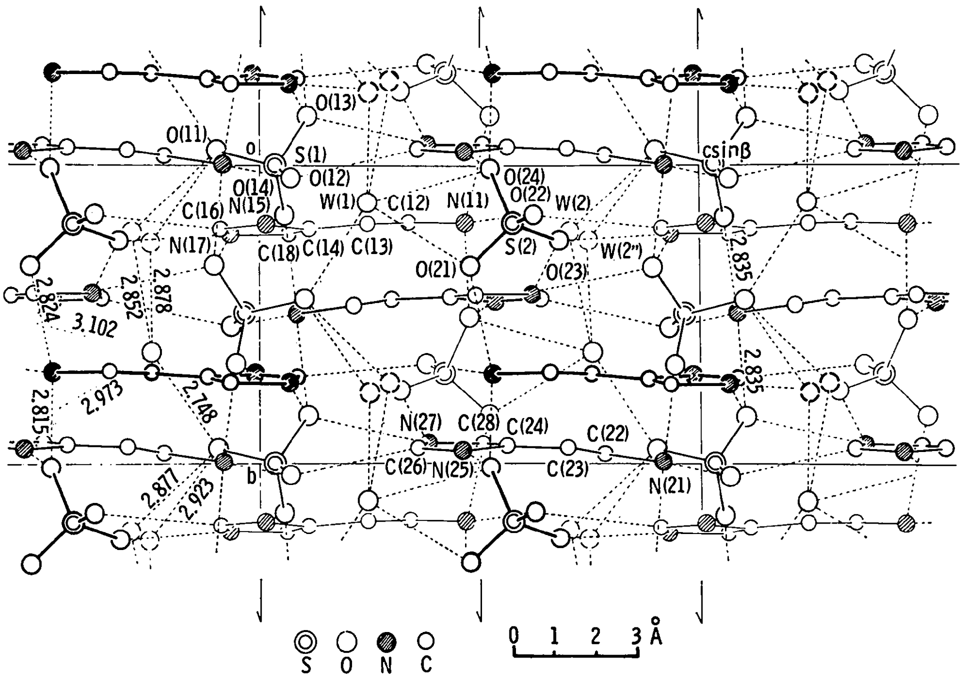


Fig. 4. The crystal structure viewed along the *a* axis.

dazole ring, and the second is the plane through the side chain atoms N(1), C(2), C(3) and C(4). Table 8 lists deviations of atoms from the least-squares planes. The dihedral angles between the two planes are 4·4° in molecule I and 9·2° in molecule II, while for histamine phosphate the angle is 82·5° (Veidis, Palenik, Schaffrin & Trotter, 1969). The two planes are therefore almost parallel in histamine sulphate, while they are almost perpendicular to each other in its phosphate. The differences in conformation may be attributed to the difference in hydrogen-bond schemes.

Crystal structure

The projections of the crystal structure along the *a* and *b* axes are shown in Figs. 4 and 5 respectively. Disordered water molecules are drawn as broken circles in the Figures. The hydrogen-bond scheme is depicted by dotted lines. All hydrogen atoms in the functional groups are involved in hydrogen bonds. The oxygen atoms in the sulphate groups are involved in the hydrogen bonds only as acceptors.

As mentioned previously, the pseudo-*n*-glide planes are clearly shown in the crystal structure. The deviations of atoms from the pseudosymmetry are larger in the sulphate anions than in the histamine cations.

Some of the closest intermolecular contacts neglecting hydrogen atoms are: 3·364 Å for N(17)· · · N(15^{viii}), 3·340 Å for C(28)· · · N(25^{i}), 3·036 Å for N(11)· · · *W*(2′) and 3·006 Å for N(11)· · · *W*(2″), the numbering by Roman numerals of the equivalent positions being listed in Table 9.

Though *W*(2) distributes in the two positions, *W*(2′) and *W*(2″) by disorder, the acceptor atoms for the hydrogen bonds from *W*(2′) and *W*(2″) are the same. The hydrogen-bond lengths are also not significantly different, that is, *W*(2′)· · · *W*(1) and *W*(2″)· · · *W*(1) are 2·852 and 2·878 Å respectively. It is also to be noted that the *W*(2′) and *W*(2″) atoms work only as donors of two hydrogen bonds, and that none of the water molecules have a hydrogen bond parallel to the *a* axis. All of these facts may be responsible for the occurence of the disorder of *W*(2). As is clear from Table 3, *W*(2′),

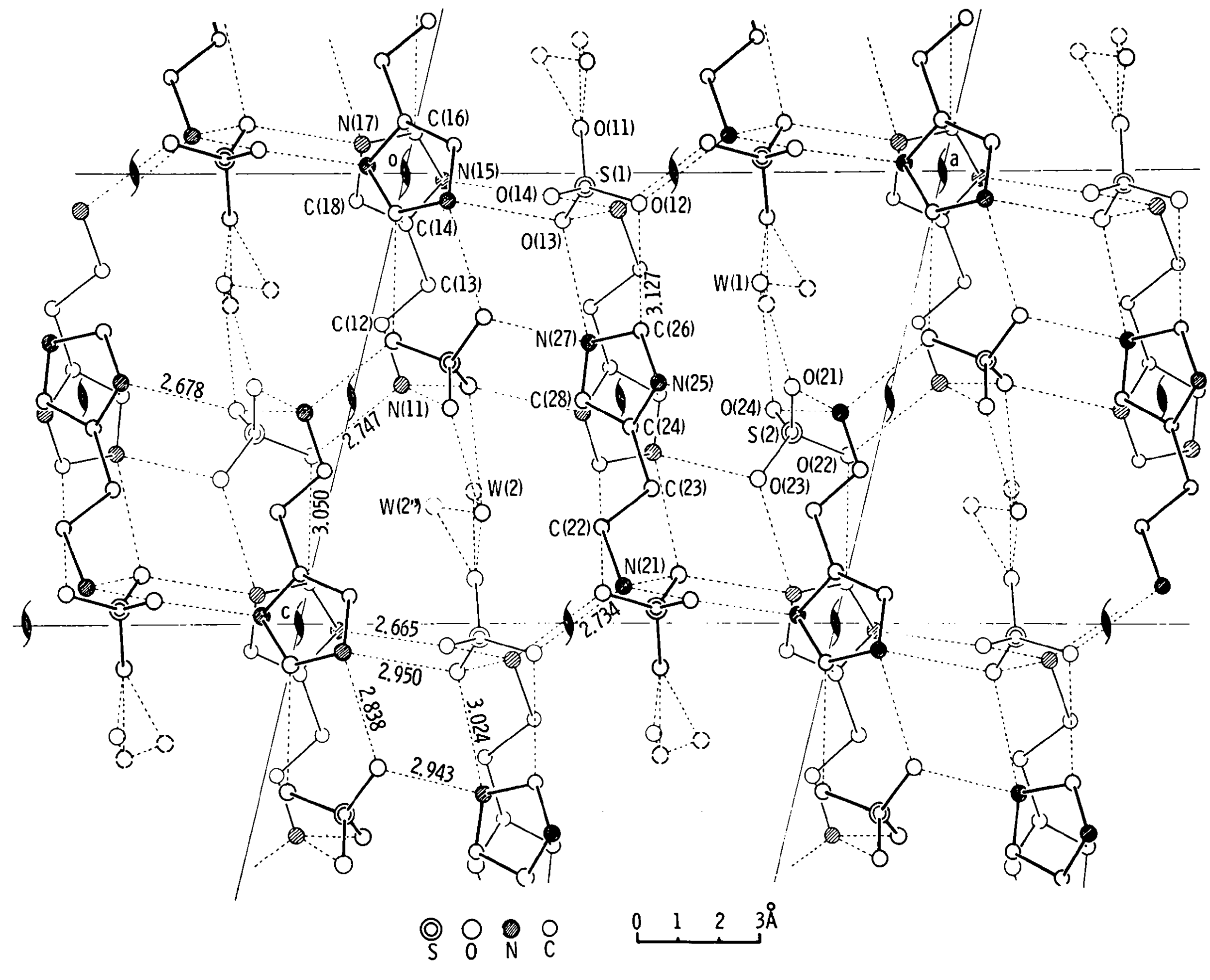


Fig. 5. The crystal structure viewed along the *b* axis.

Table 9. *Hydrogen bonds* (D–H$\cdots A$)

D	H	A	$D\cdots A$	H$\cdots A$	$\angle D$–H$\cdots A$
N(11)	H(111)	O(24^{i})	2·815 Å	1·83 Å	147°
N(11)	H(112)	O(22^{viii})	2·747	1·94	148
N(11)	H(113)	O(21^{ii})	2·824	1·73	159
N(15)	H(15)	O(14)	2·665	1·93	143
C(16)	H(16)	O(22^{vi})	3·050	2·12	146
N(17)	H(17)	{ O(23^{vi})	2·838	2·09	142
		O(13^{vii})	2·950	2·30	131
N(21)	H(211)	O(14)	2·835	2·03	152
N(21)	H(212)	O(12^{iv})	2·734	1·95	155
N(21)	H(213)	O(13^{iii})	2·835	2·03	180
N(25)	H(25)	O(24^{i})	2·678	1·93	159
C(26)	H(26)	O(12^{i})	3·127	2·24	157
N(27)	H(27)	{ O(23)	2·943	2·31	136
		O(13^{i})	3·024	2·44	130
W(1)	H*W*(11)	{ O(21)	2·973	2·34	149
		O(24)	3·102	2·46	151
W(1)	H*W*(12)	O(11^{iv})	2·748	1·95	154
W(2′)	H*W*(2′1)	*W*(1^{i})	2·852	2·08	164
W(2′)	H*W*(2′2)	O(11^{v})	2·877	1·92	138
W(2″)	H*W*(2″1)	*W*(1^{i})	2·878	1·96	144
W(2″)	H*W*(2″2)	O(11^{v})	2·923	1·72	167
	⟨e.s.d.⟩		0·015	0·13	12

i	$1-x, \frac{1}{2}+y, 1-z$	v	$x, y, 1+z$
ii	$1-x, y-\frac{1}{2}, 1-z$	vi	$x-1, y, z-1$
iii	$x, 1+y, z$	vii	$-x, \frac{1}{2}+y, -z$
iv	$1-x, \frac{1}{2}+y, -z$	viii	$x-1, y, z$

W(2″) and also *W*(1) show significantly larger temperature factors than those of other atoms.

The hydrogen-bond scheme in this crystal is very complicated, having three bifurcated hydrogen bonds. In these hydrogen bonds the lengths of $D\cdots A$ are rather long except for N(17)$\cdots$O(23^{vi}). The donor–acceptor lengths in bifurcated hydrogen bonds are usually longer than those in normal hydrogen bonds.

There are two short C–H$\cdots$O contacts in this sulphate crystal. Significantly short C–H$\cdots$O contacts are found in histamine phosphate (Veidis, Palenik, Schaffrin & Trotter, 1969) and in L-*N*-acetylhistidine monohydrate (Kistenmacher, Hund & Marsh, 1972). All the carbon atoms participating in these contacts are C^{ε} in the imidazole ring. Taking into account the geometries of these contacts in histamine sulphate the contacts may be hydrogen bonds rather than the interaction of neighbouring electronegative groups with the partial positive charge on the C^{ε} atom (Kistenmacher, Hund & Marsh, 1972).

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Kristallstruktur von Äthylen-1,2-dithiolato-di-(π-cyclopentadienyl)-Titan(IV)*

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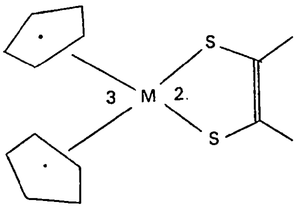
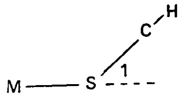
$(C_5H_5)_2TiS_2(CH)_2$ crystallizes with orthorhombic symmetry in the space group *Pcab*. The cell parameters are $a=22{\cdot}000$, $b=13{\cdot}470$, $c=7{\cdot}737$ Å and $Z=8$. The structure was determined by direct methods and refined with anisotropic temperature factors by full-matrix least-squares procedures. The final *R* value based on 2018 independent reflexions is 0·056. The plane TiS_2 of the molecule is folded out of the $S_2C_2H_2$ plane at an angle of 46·1°. Both the sulphur atoms and the cyclopentadienyl centroids give a distorted tetrahedral arrangement around the titanium atom. The bond S–C is distinctly shortened with respect to the sum of the atomic radii of these atoms. The spatial orientation of the cyclopentadienyl rings is staggered.

Einleitung

In früheren Arbeiten (Kutoglu & Köpf, 1970; Kutoglu, 1972) konnte gezeigt werden, dass zumindest in diesen Beispielen ein planares Strukturschema (McCleverty, 1968), wie dies allgemein für Metallocen-Dithiolen-Chelate vorgeschlagen wurde, nicht zutrifft.





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* Mitteilung III über Strukturbestimmungen an 'nichtlinearen' Metallocenen. II. Mitteilung: Kutoglu (1972). IV. Mitteilung: Debaerdemaker & Kutoglu (1973).