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The Crystal Structure of 2,7-Dimethylthiachromine-8-ethanol Dihydrate

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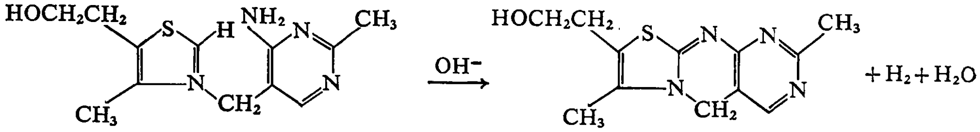
The molecular dimensions of 2,7-dimethylthiachromine-8-ethanol (thiochrome) are compared with those of its precursor, thiamine. Next to the overall conformation, the greatest changes which are introduced by oxidative ring closure occur in the bond lengths and angles of the five-membered thiazole ring. However, it still manifests to a smaller degree characteristics of the thiazolium ring. Most of the parameters of the pyrimidine ring are essentially unchanged by ring closure. The β-hydroxy oxygen of the ethanol side chain participates in an intramolecular interaction with the ring sulfur atom which has not been observed previously in other thiamine structures although the S···O interaction with the 2-(α-hydroxyethyl) side chain in thiamine derivatives is a characteristic feature. Thiochrome dihydrate ($C_{12}H_{14}N_4OS.2H_2O$) grew as triclinic crystals in space group $P\bar{1}$ with $Z=2$ and unit-cell dimensions $a=7{\cdot}314\,(5)$, $b=8{\cdot}971\,(5)$, $c=11{\cdot}499\,(8)$ Å, $\alpha=86{\cdot}90\,(5)^\circ$, $\beta=108{\cdot}51\,(5)^\circ$ and $\gamma=98{\cdot}50\,(5)^\circ$. The intensities were measured by the $\theta:2\theta$ scan technique on a 4-circle automated diffractometer using graphite monochromated Cu $K\alpha$ radiation. The structure was refined by full-matrix anisotropic least-squares techniques to an agreement index, R, of 0·036 for 2323 observed reflections.

Introduction

Heating an aqueous alkaline solution of thiamine converts it spontaneously into thiochrome:



This reaction is used in the quantitative determination for thiamine since neutral or alkaline solutions of thiochrome exhibit a blue fluorescence which is enhanced in isobutyl alcohol. We have determined the crystal structures of thiamine base (Pletcher, Sax, Sengupta, Chu & Yoo, 1972) and of thiochrome in order to observe the changes that occur in the molecular parameters after oxidative ring closure.

Experimental

Thiochrome (Nutritional Biochemicals Corporation) was crystallized from hot water as the dihydrate in the form of yellow acicular crystals elongated in the direction of the *a* axis. The lack of symmetry and systematically absent reflections in oscillation and Weissenberg photographs indicated that the crystals were triclinic with space group either $P1$ or $P\bar{1}$. Since the E-value statistics from the intensity data correspond to a centrosymmetric system, the space group was assigned as $P\bar{1}$. This assignment was later confirmed by the successful refinement of the crystal structure. The crystal data are summarized in Table 1. The intensity data were collected and the cell parameters were measured from a crystal having a cross section 0·19 mm by 0·22 mm along **b** and **c** respectively and cut to 0·15 mm along **a** using a Picker FACS-1 4-angle diffractometer system equipped with a scintillation detector. The crystal was mounted with its a axis roughly parallel to the φ axis. The unit-cell parameters were obtained from a least-squares fit to the angular settings for 12 centered reflections with 2θ values between 39° and 52° (Picker, 1972) using graphite monochromated Cu $K\alpha$ radiation. The integrated intensities were measured using a $\theta:2\theta$ scan over a 1·8° range in 2θ at a rate of 1° min^{-1}. The background count was accumulated for 20 s at each end of the scan range. Three standard reflections, which were monitored after every 40 reflections, fluctuated within a 4% range during the data collection. The intensity data were corrected by means of the observed variations in the standards (Shiono, 1971*a*). A total of 2323 independent reflections within a complete hemisphere for $\sin\theta/\lambda<0{\cdot}5805$ were measured. (Of these independent reflections, 208 were measured twice; the $0kl$ reflections and their symmetry equivalent reflections.) As it was measured each intensity was reduced to its structure amplitude using the appropriate Lorentz-polarization factor for graphite monochromated ($2\theta m=26{\cdot}16^\circ$) radiation (Picker Corporation FACS-1 Disk Operating System, 1972). The equivalent reflections in the $0kl$ zone were compared and found

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to agree within 0·9%. The average of individual pairs of equivalent reflections were used in the analysis. Of the independent reflections, 165 were considered unobserved when $|F| \le 6\sigma(F)$ where $|F|$ is the structure amplitude and $\sigma(F)$ is given by $(1/2\text{Lp}|F|)\,\sigma(I)$; Lp is the Lorentz-polarization factor, $\sigma(I)=[I_t+k^2B]^{1/2}$, $I=I_t-B_t$, $B_t=kB$, $B=(b_1+b_2)$, $k=2t_2/t_1$, $I_t=(10S+5)$, $b_1=(10\ C_1+5)$, $b_2=(10\ C_2+5)$, S = the number of decacounts accumulated during the scan requiring time t_1, and C_1 and C_2 are the background decacounts accumulated in time t_2 at either end of the scan range.

Table 1. *Crystal data*

2,7 Dimethylthiachromine-8-ethanol dihydrate
$C_{12}H_{14}N_4OS.2H_2O$ M.W. 298·36
$a=$ 7·314 (5) Å $\lambda(\text{Cu } K\alpha_1\alpha_2)=1{\cdot}54178$ Å
$b=$ 8·971 (5) Data measured at ambient temperature,
$c=$ 11·499 (8) $\simeq 22\,^\circ$C
$\alpha=$ 86·90 (5)°
$\beta=$ 108·51 (5) $V=707{\cdot}6$ (8) Å^3
$\gamma=$ 98·50 (5) $Z=2$
Space group $P\bar{1}$ $F(000)=316$
$\varrho_o=1{\cdot}406$ by flotation in benzene–chloroform
$\varrho_c=1{\cdot}400$
$\mu(\text{Cu } K\alpha)=21{\cdot}46$ cm^{-1}
m.p. 226–228°C (not corrected) – Thermolyne melting point apparatus. Loss of birefringence due to a loss of water of crystallization occurs from 95–115°C.

The structure had been solved previously using data that were later found to contain errors as a result of an intermittent malfunction in the Picker four-angle programmer diffractometer system.* With the initial data set the X-RAY 67 system of programs (Stewart, 1967) was used conveniently for converting $|F|$'s to $|E|$ values, for determining the signs of 246 reflections and for synthesizing an E-map (Karle, Hauptman, Karle & Wing, 1958). The E-map revealed the image of the molecule and provided coordinates for the 20 nonhydrogen atoms. The remaining 18 hydrogen atoms were located in a difference Fourier synthesis. The parameters of the 38 atoms were refined by the full-matrix least-squares program, *ORFLS*, in the X-RAY 67 system (Stewart, 1967) with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms. These parameters were used as the initial values for full-matrix least-squares refinement (Shiono, 1971*b*) utilizing the new data set. The quantity minimized was $\sum w(|F_o|-k|F_c|)^2$ where k is a single scale factor and w, the weight, is that defined by Hughes (1941) with $\sigma = F_o/3{\cdot}6$ when $F_o > 3{\cdot}6$ and $\sigma=1$ when $F_o \le 3{\cdot}6$. For the unobserved reflections and four reflections affected by extinction, w was assigned as 0. The atomic scattering factors for C, N, O and S were taken from *International Tables for X-ray Crystallography* (1962) while that for H is from Stewart, Davidson & Simpson (1965). The anomalous dispersion correction ($\Delta f'$ and $\Delta f''$) for S was taken from Cromer (1965). The refinement converged to $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}036$ for the observed reflections only and 0·042 over all the reflections. Of the 165 unobserved reflections, $F_c > F_o$ for 98. However, in no case did $||F_o|-|F_c||$ exceed $6\sigma(F)$ based on counting statistics. The maximum shift/error ratio in the final cycle of refinement for all the nonhydrogen parameters was 0·82 while the average ratio for all the parameters was 0·25. A difference Fourier synthesis at the end of the refinement was essentially featureless. The two largest peaks in the map at 0·35 and 0·23

Table 2. *Positional and thermal parameters*

Positions are designated in fractional coordinates of unit-cell axes; estimated standard deviations in parentheses.

(*a*) Nonhydrogen atoms. All values × 10⁴. Thermal vibration coefficients are for the expression

$$\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\sin^2\theta/\lambda^2\}$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	1457 (0·6)	1523 (0·4)	5838 (0·4)	467 (3)	251 (3)	355 (3)	−33 (2)	116 (2)	−53 (2)
C(2)	1934 (2)	3313 (2)	5275 (1)	281 (7)	268 (8)	344 (8)	1 (6)	81 (6)	−56 (6)
N(3)	2444 (2)	4326 (1)	6190 (1)	334 (7)	252 (7)	325 (7)	−10 (5)	98 (5)	−45 (5)
C(4)	2436 (2)	3721 (2)	7341 (2)	325 (8)	321 (9)	338 (8)	2 (7)	95 (6)	−52 (7)
C(5)	1949 (2)	2212 (2)	7313 (2)	411 (9)	305 (9)	336 (8)	−17 (7)	112 (7)	−40 (7)
C(6)	3034 (3)	5937 (2)	5994 (2)	378 (9)	241 (9)	403 (9)	−6 (7)	120 (8)	−60 (7)
C(7)	2936 (2)	6204 (2)	4680 (2)	268 (8)	294 (9)	367 (9)	37 (6)	87 (6)	−33 (6)
C(8)	2295 (2)	5032 (2)	3807 (2)	264 (7)	281 (8)	366 (9)	19 (6)	87 (6)	−45 (6)
N(9)	2180 (2)	5313 (2)	2633 (1)	365 (8)	361 (8)	343 (8)	41 (6)	101 (6)	−21 (6)
C(10)	2696 (2)	6734 (2)	2309 (2)	320 (8)	367 (9)	435 (10)	56 (7)	115 (7)	25 (7)
N(11)	3369 (2)	7903 (2)	3078 (1)	469 (8)	355 (8)	460 (9)	34 (6)	143 (7)	38 (6)
C(12)	3469 (3)	7603 (2)	4251 (2)	432 (9)	283 (9)	436 (10)	−11 (7)	133 (6)	−36 (7)
N(13)	1776 (2)	3558 (2)	4108 (1)	428 (8)	279 (7)	338 (7)	−15 (6)	103 (6)	−50 (6)
C(14)	2484 (3)	7031 (3)	988 (2)	578 (12)	519 (12)	424 (11)	66 (10)	145 (9)	85 (9)
C(15)	2896 (3)	4762 (2)	8400 (2)	521 (11)	376 (10)	343 (10)	−24 (9)	134 (8)	−76 (8)
C(16)	1885 (3)	1167 (2)	8376 (2)	677 (13)	354 (10)	394 (10)	−6 (9)	191 (9)	3 (8)
C(17)	409 (3)	−244 (2)	8042 (2)	524 (11)	402 (10)	578 (12)	13 (9)	237 (10)	44 (9)
O(18)	1048 (2)	−1189 (2)	7335 (1)	506 (8)	361 (7)	679 (9)	−51 (6)	206 (7)	−89 (6)
O(19)	4888 (3)	938 (2)	2585 (2)	575 (10)	355 (9)	1255 (17)	84 (8)	305 (11)	55 (9)
O(20)	2470 (3)	2952 (2)	1053 (1)	791 (11)	536 (9)	460 (8)	68 (8)	156 (8)	−56 (7)

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* The preliminary structure was reported at the American Crystallographic Association meeting, March, 1970, New Orleans, Louisiana. Although refinement converged to an R of 5·1%, the data set contained a number of reflections which deviated significantly from their calculated values.

Table 2 (*cont.*)

(*b*) Hydrogen atoms. All values $\times 10^3$. Thermal vibration coefficients are for the expression $\exp[-(8\pi^2 U)\sin^2\theta/\lambda^2]$

	x	y	z	U
H(61)	207 (3)	648 (3)	618 (2)	46 (5)
H(62)	435 (3)	625 (2)	650 (2)	36 (5)
H(121)	395 (3)	848 (3)	482 (2)	48 (6)
H(141)	117 (7)	689 (5)	47 (4)	131 (15)
H(142)	303 (5)	638 (5)	69 (3)	105 (13)
H(143)	320 (7)	801 (6)	93 (4)	133 (14)
H(151)	195 (4)	548 (3)	822 (2)	65 (7)
H(152)	283 (4)	429 (3)	906 (3)	64 (7)
H(153)	410 (3)	534 (3)	856 (3)	45 (8)
H(161)	154 (4)	178 (3)	896 (3)	63 (7)
H(162)	325 (4)	71 (3)	877 (2)	63 (7)
H(171)	−89 (3)	7 (3)	758 (2)	52 (5)
H(172)	39 (4)	−84 (3)	888 (2)	64 (7)
H(181)	−3 (5)	−196 (4)	699 (3)	77 (9)
H(191)	455 (4)	11 (4)	271 (2)	59 (7)
H(192)	579 (5)	97 (4)	244 (3)	85 (11)
H(201)	221 (5)	349 (4)	153 (3)	80 (10)
H(202)	317 (5)	234 (4)	154 (3)	76 (11)

e Å^{-3} were located directly over the S atom at distances of 0·6 and 1·3 Å respectively. These may possibly result from the anomalous dispersion correction which was applied to the S atom. The third largest peak at 0·2 e Å^{-3} is located at a distance of 1·0 Å from O(20) and may represent a disordered hydrogen although this position is not favorable for hydrogen-bond formation. The remaining peaks all have a density of 0·1 e Å^{-3} or less.

The final positional and thermal parameters with their estimated standard deviations are listed in Table 2. The observed and calculated structure factors are given in Table 3. The structure of the molecule showing the thermal vibration ellipsoids is presented in Fig. 1. Fig. 2 shows the interatomic bond distances and angles along with the atomic numbering scheme.

Discussion

The tricyclic fused-ring system in thiochrome dihydrate deviates slightly but significantly from a strictly planar arrangement which is in sharp contrast to the conformation in thiamine where the planar thiazolium and pyrimidine ring systems are nearly at right angles (Pletcher, Sax, Sengupta, Chu & Yoo, 1972). The planarity in this structure is apparent from the data in Table 4 where are listed the displacements of atoms from various least-squares planes that have been fitted to the tricyclic system, to each of its three component rings and to the respective halves of the tricyclic system containing the thiazole and pyrimidine rings. The torsion angles (Table 5) within the rings and at the junctions between the rings deviate from 0° (180°) by 3·5° at most.

A comparison of the molecular parameters in thiochrome with those in thiamine base is given in Table 6. These data show that ring closure alters the dimensions of the five-membered ring much more drastically than those of the pyrimidine ring. Although these shifts in bond lengths are consistent with the differences in their chemical formulae, the structural data do imply that the five-membered ring still exhibits some of the electronic characteristics of the thiazolium ring. Thus, the

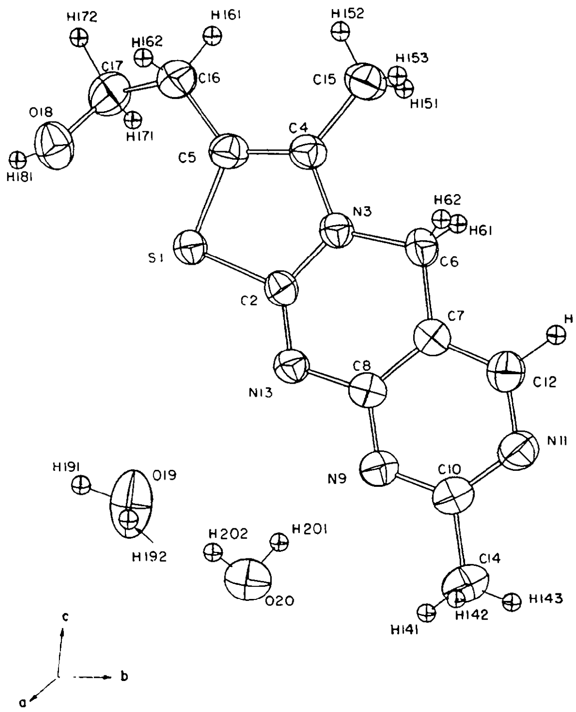

Fig. 1. A single molecule of thiochrome dihydrate as drawn by *ORTEP* program (Johnson, 1965) with the thermal ellipsoids of the nonhydrogen atoms at the 50% probability level. The hydrogen atoms are represented by spheres having a fixed arbitrary radius.

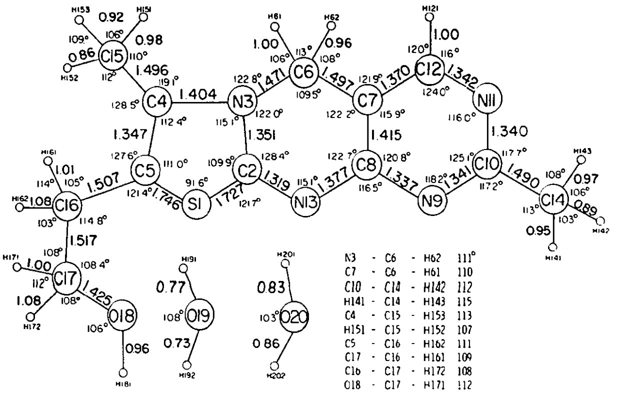

Fig. 2. A schematic representation of the molecule showing the atomic numbering scheme and the final bond distances and angles. The estimated standard deviations in bond lengths between nonhydrogen atoms range from 0·002 to 0·003 Å while those involving hydrogen atoms range from 0·02 to 0·05 Å. The estimated standard deviations in bond angles range from 0·1 to 0·2° for angles defined only by nonhydrogen atoms and from 1·0 to 4·0° for angles including hydrogen atoms.

Table 3. *Observed and calculated structure factors*

Columns are l, $10|F_o|$ and $10|F_c|$. The unobserved reflections are marked with * and the 4 reflections affected by extinction which were assigned zero weight are marked with †.

	FOBS	FCAL
H= 0 K=-10		
-3	36	34
-2	87	86
-1	79	82
0	23	27
1	36	88
2	52	52
H= 0 K= -9		
6	66	65
5	90	90
4	130	135
3	44	44
2	53	56
1	24	26
0	23	26
-1	96	94
-2	144	145
-3	35	55
-4	23	24
-5	7*	2
-6	1*	5
H= 0 K= -8		
-8	27	27
-7	27	26
-6	9*	6
-5	86	85
-4	39	38
-3	102	103
-2	121	121
-1	101	106
0	94	94
1	27	25
2	78	75
3	132	131
4	69	69
5	15	14
6	40	42
7	111	111
H= 0 K= -7		
9	15	15
8	43	42
7	77	77
6	69	67
5	22	20
4	38	139
3	10	9
2	173	175
1	106	106
0	23	21
-1	123	124
-2	23	19
-3	51	52
-4	144	140
-5	158	155
-6	80	73
-7	63	60
-8	22	19
-9	32	31
H= 0 K= -6		
-10	13	10
-9	82	78
-8	109	109
-7	48	51
-6	179	184
-5	171	170
-4	155	151
-3	254	253
-2	108	112
-1	89	83
0	129	133
1	66	71
2	57	53
3	100	100
4	210	207
5	10	7
6	73	75
7	17	14
8	32	29
9	33	36
10	43	45
H= 0 K= -5		
11	30	29
10	74	75
9	50	53
8	103	102
7	58	62
6	24	23
5	139	142
4	145	142
3	195	191
2	131	114
1	205	206
0	108	118
-1	189	188
-2	61	62
-3	24	21
-4	56	158
-5	9*	4
-6	33	32
-7	23	19
-8	44	42
-9	45	38
-10	22	23
-11	33	29
H= 0 K= -4		
-11	81	83
-10	32	30
-9	104	101
-8	122	128
-7	20	14
-6	181	180
-5	134	139
-4	72	57
-3	54	48
-2	93	87
-1	71	66
0	262	263
1	576	614
2	275	270
3	92	85
4	77	75
5	67	63
6	130	79
7	172	174
8	127	126
9	35	35
10	12	8
11	38	38
H= 0 K= -3		
12	44	47
11	43	40
10	48	53
9	[illegible]	49
8	[illegible]	54
7	223	225
6	26	27
5	25	12
4	172	174
3	367	376
2	27	19
1	346	365
0	168	163
-1	10	19
-2	311	313
-3	8	3
-4	42	31
-5	275	277
-6	80	73
-7	167	172
-8	11	[illegible]
-9	182	182
-10	25	33
-11	38	42
-12	[illegible]	70
H= 0 K= -2		
-12	[illegible]	49
-11	7*	8
-10	[illegible]	134
-9	362	354
-8	358	368
-7	110	114
-6	208	202
-5	4*	2
-4	228	235
-3	521	594
-2	411	455
-1	126	130
0	120	116
1	205	208
2	64	65
3	548	612
4	224	236
5	417	419
6	76	73
7	50	50
8	93	98
9	98	102
10	199	204
11	82	89
12	17	19
H= 0 K= -1		
12	46	50
11	6*	13
10	12	12
9	96	93
8	187	192
7	38	30
6	126	105
5	238	205
4	324	360
3	206	200
2	19	17
1	165	173
0	281	310
-1	468†	584
-2	427	486
-3	102	110
-4	50	44
-5	178	171
-6	90	99
-7	141	134
-8	107	94
-9	33	37
-10	28	26
-11	84	82
-12	27	28
H= 0 K= 0		
-12	85	86
-11	5*	6
-10	70	72
-9	134	128
-8	81	89
-7	269	265
-6	470	480
-5	102	98
-4	108	106
-3	161	163
-2	374	422
-1	434†	611
H= 1 K= 10		
0	60	60
-1	121	123
H= 1 K= 9		
-5	35	34
-4	34	34
-3	42	44
-2	44	42
-1	78	77
0	77	75
1	37	40
2	12	16
3	12	9
4	106	105
5	115	117
H= 1 K= 8		
7	53	58
6	24	21
5	1*	2
4	19	22
3	38	30
2	20	20
1	103	102
0	10*	8
-1	12	11
-2	46	54
-3	66	51
-4	13	11
-5	28	29
-6	94	91
-6	94	91
-7	20	18
H= 1 K= 7		
-9	61	64
-8	92	93
-7	51	51
-6	67	65
-5	40	46
-4	182	189
-3	172	172
-2	116	117
-1	6*	6
0	45	46
1	149	148
2	418	437
3	231	229
4	88	81
5	46	50
6	24	21
7	46	48
8	83	91
H= 1 K= 6		
9	20	20
8	96	98
7	122	124
6	99	100
5	178	163
4	190	194
3	68	76
2	203	205
1	274	283
0	244	265
-1	45	44
-2	113	115
-3	81	82
-4	150	146
-5	101	99
-6	85	89
-7	15	15
-8	88	96
-9	13	14
-10	36	34
H= 1 K= 5		
-11	77	64
-10	84	64
-9	59	61
-8	28	26
-7	330	318
-6	210	209
-5	87	91
-4	175	176
-3	25	15
-2	15	10
-1	204	209
0	170	170
1	53	56
2	58	64
3	90	97
4	140	144
5	145	151
6	77	76
7	85	90
8	100	96
9	[illegible]	[illegible]
10	5*	5
H= 1 K= 4		
11	44	45
10	54	51
9	85	82
8	90	91
7	70	71
6	12	11
5	27	21
4	54	55
3	166	165
2	94	97
1	174	168
0	84	87
-1	362	360
-2	308	312
-3	206	211
-4	64	65
-5	154	159
-6	19	16
-7	302	303
-8	181	184
-9	68	87
-10	21	21
-11	8*	8
H= 1 K= 3		
-12	52	51
-11	21	21
-10	47	46
-9	46	45
-8	67	67
-7	180	189
-6	92	86
-5	141	139
-4	22	16
-3	168	163
-2	173	185
-1	235	260
0	150	152
1	20	22
2	294	271
3	304	314
4	345	341
5	163	159
6	94	97
7	27	30
8	11	6
9	88	89
10	67	66
11	81	83
H= 1 K= 2		
11	40	38
10	93	94
9	124	119
8	52	48
7	98	100
6	104	104
5	230	226
4	101	98
3	436	431
2	20	18
1	297	311
0	65	75
-1	197	195
-2	348	347
-3	272	270
-4	228	230
-5	39	42
-6	113	114
-7	41	45
-8	6*	6
-9	122	124
-10	85	91
-11	83	80
H= 1 K= 1		
-12	51	53
-11	38	33
-10	43	41
-9	100	103
-8	147	139
-7	40	47
-6	118	114
-5	206	188
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2	120	128
3	83	88
4	59	58
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6	60	62
7	185	186
8	15	14
9	13	12
10	44	41
11	42	42
H= 1 K= 0		
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11	59	59
10	27	23
9	29	26
8	184	183
7	76	72
6	43	36
5	71	74
4	282	280
3	112	97
2	140	149
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H= 1 K= -1		
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2	112	103
3	235	237
4	228	214
5	278	293
6	147	144
7	75	90
8	29	32
9	86	70
10	52	52
11	16	15
12	70	74
H= 1 K= -2		
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10	15	18
9	24	21
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6	52	50
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3	21	25
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H= 1 K= -3		
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6	128	134
7	66	71
8	137	135
9	111	109
10	82	84
11	42	39
H= 1 K= -4		
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7	1*	11
6	177	177
5	209	203
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H= 1 K= -5		
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2	193	196
3	157	157
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5	21	18
6	176	175
7	300	299
8	82	80
9	43	43
10	3*	7
H= 1 K= -6		
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8	61	61
7	127	124
6	230	226
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H= 1 K= -7		
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3	46	45
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5	32	30
6	59	57
7	49	48
8	11	10
H= 1 K= -8		
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6	103	102
5	44	40
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3	130	132
2	129	129
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2	59	54
3	53	48
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5	1*	4
H= 1 K=-10		
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H= 2 K=-10		
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0	26	28
1	31	30
2	30	32
H= 2 K= -9		
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4	48	46
3	58	60
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-3	65	60
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-6	57	54
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H= 2 K= -8		
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-3	72	70
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-1	49	47
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1	73	77
2	22	20
3	84	84
4	103	102
5	35	36
6	46	47
H= 2 K= -7		
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7	44	42
6	68	65
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4	30	29
3	139	136
2	99	103
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-2	30	29
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-7	98	100
-8	83	85
-9	59	57
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H= 2 K= -6		
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-8	67	67
-7	19	19
-6	79	81
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-4	49	49
-3	30	35
-2	18	15
-1	21	29
0	26	26
1	40	39
2	71	73
3	117	117
4	1*	2
5	1*	7
6	1*	4
7	40	39
8	36	33
9	46	47
H= 2 K= -5		
9	12	12
8	68	67
7	95	95
6	98	98
5	158	156
4	12	11
3	30	30
2	114	104
1	344	347
0	178	176
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-2	25	33
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-4	89	90
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-6	103	101
-7	119	118
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H= 2 K= -4		
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-6	47	43
-5	54	59
-4	58	54
-3	60	55
-2	51	49
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1	149	146
2	202	199
3	254	259
4	83	81
5	42	45
6	119	122
7	12	9
8	89	88
9	2*	7
10	11	5
H= 2 K= -3		
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9	80	83
8	140	138
7	77	81
6	68	72
5	168	166
4	140	135
3	181	199
2	317	317
1	22	18
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-2	260	260
-3	258	267
-4	285	291
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-8	119	128
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-11	93	90
-12	18	19
H= 2 K= -2		
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-12	63	62
-11	62	61
-10	25	26
-9	232	232
-8	211	204
-7	121	120
-6	201	212
-5	72	72
-4	61	63
-3	101	99
-2	168	157
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0	176	190
1	9	10
2	183	171
3	90	102
4	40	44
5	159	136
6	20	24
7	70	68
8	74	75
9	19	15
10	88	94
11	38	45
H= 2 K= -1		
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10	26	30
9	92	87
8	156	154
7	35	26
6	269	267
5	336	319
4	173	171
3	123	116
2	227	235
1	196	198
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-3	94	88
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-5	50	45
-6	228	222
-7	245	237
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-9	67	69
-10	109	107
-11	43	36
-12	38	40
-13	51	57
H= 2 K= 0		
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-12	56	45
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-8	195	201
-7	129	125
-6	397	379
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-3	73	67
-2	108	99
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1	542	573
2	262	273
3	74	88
4	74	85
5	159	159
6	53	49
7	45	48
8	47	42
9	7*	9
10	12	12
11	40	40
H= 2 K= 1		
11	73	70
10	27	21
9	173	164
8	281	279
7	207	209
6	83	77
5	172	172
4	44	41
3	232	234
2	361	379
1	180	182
0	224	236
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-2	377	398
-3	270	277
-4	278	293
-5	128	131
-6	120	102
-7	87	82
-8	75	75
-9	44	53
-10	133	135
-11	151	161
-12	88	93
-13	26	29
H= 2 K= 2		
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-10	115	121
-9	35	34
-8	230	234
-7	175	176
-6	160	157
-5	228	224
-4	173	169
-3	10	12
-2	257	253
-1	422	449
0	163	159
1	166	166
2	78	68
3	208	209
4	249	254
5	214	208
6	21	18
7	18	19
8	122	119
9	175	171
10	53	56
H= 2 K= 3		
10	55	58
9	10	9
8	148	141
7	154	160
6	68	66
5	40	43
4	106	116
3	24	20
2	109	115
1	329	343
0	70	63
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-2	461	465
-3	238	235
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-6	19	18
-7	62	55
-8	123	123
-9	149	148
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-12	10	8
H= 2 K= 4		
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-9	42	36
-8	130	134
-7	86	91
-6	85	77
-5	267	269
-4	174	164
-3	116	109
-2	204	194
-1	147	137
0	162	159
1	231	237
2	36	37
3	56	56
4	60	63
5	32	28
6	53	56
H= 2 K= 5		
3	155	151
H= 2 K= 6		
7	40	41
8	55	46
9	18	17
10	48	44
H= 2 K= 5		
9	15	14
8	76	71
7	64	67
6	85	87
5	142	148
4	144	154
2	129	132
1	34	30
0	193	199
-1	50	52
-2	127	128
-3	199	204
-4	189	189
-5	80	79
-6	42	41
-7	63	62
-8	19	16
-9	36	35
-10	16	15
-11	36	38
H= 2 K= 6		
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-9	50	53
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-7	41	38
-6	8*	3
-5	101	96
-4	8*	11
-3	174	174
-2	198	201
-1	15	12
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1	81	80
2	15	11
3	111	108
4	229	225
5	87	83
6	87	92
7	74	69
8	31	29
H= 2 K= 7		
7	31	30
6	45	47
5	24	23
4	7*	4
3	59	57
2	112	109
1	17	18
0	5*	10
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-2	2*	4
-3	116	112
-4	132	130
-5	20	20
-6	74	69
-7	56	53
-8	87	87
-9	5*	4
H= 2 K= 8		
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-6	123	122
-5	144	146
-4	40	39
-3	77	78
-2	59	59
-1	22	28
0	69	64
1	194	195
2	37	37
3	54	57
4	47	46
5	34	34
H= 2 K= 9		
3	52	55
2	35	30
1	60	61
0	35	35
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-3	86	84
-4	54	55
-5	33	35
H= 3 K= 9		
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-1	52	50
0	4*	3
H= 3 K= 8		
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3	76	79
2	22	21
1	39	35
0	68	67
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H= 3 K= 7		
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-2	80	85
-1	44	37
0	94	93
1	41	42
2	137	137
3	74	74
4	38	39
5	47	48
H= 3 K= 6		
7	99	105
6	79	79
5	44	47
4	20	20
3	187	181
2	347	344
1	275	279
0	123	119
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-2	36	37
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-4	241	240
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-10	84	83
H= 3 K= 5		
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-10	23	27
-9	72	74
-8	86	83
-7	176	173
-6	20	30
-5	115	114
-4	135	137
-3	160	160
-2	48	44
-1	[illegible]	16
0	106	[illegible]
1	201	203
2	7*	7
3	107	104
4	211	211
5	40	44
6	[illegible]	33
7	122	122
8	7*	4
H= 3 K= 4		
8	35	30
7	12	13
6	15	17
5	108	105
4	56	59
3	16	20
2	19	22
1	14	14
0	246	254
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-2	116	110
-3	116	127
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-5	62	66
-6	174	164
-7	362	364
-8	184	192
-9	6*	[illegible]
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-11	63	66
H= 3 K= 3		
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-10	31	30
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-8	184	178
-7	18	13
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-5	181	184
-4	69	72
-3	101	93
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0	186	190
1	43	40
2	127	133
3	62	59
4	8*	20
5	82	81
6	108	108
7	72	68
8	77	77
9	10	10
H= 3 K= 2		
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8	46	48
7	32	31
6	1*	2
5	46	44
4	251	243
3	420	435
2	59	64
1	10	9
0	10	11
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-2	58	57
-3	251	251
-4	132	133
-5	70	63
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-7	97	96
-8	56	56
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-12	10	7
H= 3 K= 1		
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-8	53	50
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0	26	24
1	132	135
2	114	119
3	6*	10
4	65	64
5	146	137
6	68	69
7	1*	[illegible]
8	55	[illegible]
9	39	38
10	7*	4
H= 3 K= 0		
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9	17	15
8	86	87
7	155	152
6	137	135
5	8*	6
4	16	17
3	20	19
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0	286	[illegible]
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-4	66	71
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-11	10	13
-12	117	115
-13	51	51
H= 3 K= -1		
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-10	66	68
-9	132	132
-8	189	193
-7	108	109
-6	29	23
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-4	169	183
-3	92	97
-2	153	153
-1	15	22
0	241	246
1	9	16
2	26	28
3	125	129
4	128	130
5	22	20
6	57	56
7	106	106
9	16	14
H= 3 K= -2		
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H= 3 K= -2		
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6	84	78
H= 3 K= -2		
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8	74	75
7	46	46
6	8*	6
5	130	126
4	104	107
3	30	30
2	14	18
1	29	23
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-6	68	71
-7	16	17
-8	141	142
-9	33	33
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H= 3 K= -3		
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-11	50	49
-10	58	54
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-8	37	41
-7	14	7
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-5	286	287
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0	106	[illegible]
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2	164	163
3	106	112
4	37	34
5	22	23
6	95	92
7	88	88
8	48	48
9	47	47
H= 3 K= -4		
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8	111	108
7	113	113
6	34	33
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4	20	15
3	40	39
2	80	86
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-12	60	61
H= 3 K= -5		
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-6	29	31
-5	73	70
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-3	182	195
-2	208	212
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1	212	203
2	3*	4
3	101	100
4	107	105
5	130	129
6	35	35
7	120	115
8	33	33
H= 3 K= -6		
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7	140	139
6	201	199
5	82	81
4	40	39
3	77	78
2	85	87
1	255	250
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-3	14	17
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-6	68	67
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-8	47	45
-9	21	20
-10	35	34
-11	48	46
H= 3 K= -7		
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-9	8*	7
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-7	9*	3
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-5	197	200
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-3	62	67
-2	135	131
-1	43	42
0	7*	8
1	123	120
2	114	109
3	45	41
4	58	56
5	91	91
6	130	128
7	27	28
H= 3 K= -8		
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4	92	90
3	77	75
2	74	75
1	39	40
0	11	10
-1	163	159
-2	288	287
-3	186	185
-4	113	107
-5	16	14
-6	57	56
-7	82	83
-8	133	132
-9	93	95
H= 3 K= -9		
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-6	48	47
-5	8*	9
-4	113	[illegible]
-3	[illegible]	[illegible]
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-1	76	76
0	6*	12
1	21	20
2	71	73
3	56	57
4	28	27
H= 3 K=-10		
0	19	20
-1	51	52
-2	7*	6
-3	14	15
H= 4 K= -9		
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1	37	37
0	1*	1
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-2	10	10
-3	81	77
-4	69	69
-5	5*	5
-6	39	38
H= 4 K= -8		
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2	60	61
3	36	36
4	14	12
H= 4 K= -7		
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2	2*	6
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-2	17	18
-3	51	49
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-5	62	62
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-2	62	65
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2	27	27
3	89	86
4	43	44
5	67	65
6	53	55
7	30	36
H= 4 K= -5		
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6	16	16
5	38	39
4	23	21
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2	154	153
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-3	31	31
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-5	62	67
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-11	38	35
H= 4 K= -4		
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2	129	126
3	61	59
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6	57	56
7	81	79
8	34	37
H= 4 K= -3		
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7	31	29
6	36	38
5	81	74
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-6	9*	17
-5	23	21
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3	55	60
4	136	120
5	206	198
6	24	24
7	65	65
8	81	80
9	52	53
H= 4 K= -1		
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8	70	68
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1	116	120
2	82	80
3	66	65
4	45	45
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6	91	86
7	148	146
8	135	131
9	34	32
H= 4 K= 1		
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2	149	145
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-3	221	217
-4	9*	9
-5	89	82
-6	12	5
-7	14	16
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-9	142	140
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-11	101	107
-12	8	1
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-9	136	138
-8	47	50
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-6	29	25
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-2	268	271
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0	184	178
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2	58	53
3	17	19
4	7*	11
5	67	64
6	51	52
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4	34	35
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-3	203	198
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-5	108	109
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H= 4 K= 4		
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0	95	99
1	[illegible]	[illegible]
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3	10	9
4	132	129
5	68	67
6	27	27
7	39	39
H= 4 K= 5		
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4	51	49
3	197	192
2	86	86
1	8*	7
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H= 4 K= 6		
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-6	58	57
-5	63	59
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2	51	48
3	7*	5
4	52	52
5	56	59
H= 4 K= 7		
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2	67	67
1	61	67
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-6	86	90
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H= 4 K= 8		
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1	31	33
H= 5 K= 7		
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0	34	36
H= 5 K= 6		
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2	132	136
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2	202	200
3	25	23
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H= 5 K= 3		
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2	69	71
3	13	13
4	80	83
5	47	48
6	32	35
H= 5 K= 2		
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6	61	63
5	86	86
4	106	102
3	25	26
2	110	109
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-3	61	58
-4	57	55
-5	88	91
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H= 5 K= 1		
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3	209	207
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H= 5 K= 0		
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3	25	23
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7	18	19
H= 5 K= -2		
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3	113	113
2	20	17
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-11	48	44
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H= 5 K= -3		
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3	88	88
4	99	97
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7	16	19
H= 5 K= -4		
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2	52	57
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H= 5 K= -5		
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3	10	13
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H= 5 K= -6		
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H= 5 K= -7		
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3	84	83
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H= 6 K= -8		
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H= 6 K= -7		
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H= 6 K= -6		
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[illegible]	71	69
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H= 6 K= -3		
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2	32	31
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H= 6 K= -2		
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H= 6 K= -1		
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3	17	15
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H= 6 K= 3		
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H= 6 K= 4		
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H= 6 K= 5		
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H= 7 K= 3		
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H= 7 K= 2		
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H= 7 K= 0		
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H= 7 K= -1		
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H= 7 K= -2		
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H= 7 K= -3		
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3	4*	4
H= 7 K= -4		
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H= 7 K= -5		
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0	18	16
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H= 7 K= -6		
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H= 7 K= -7		
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H= 8 K= -4		
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H= 8 K= -3		
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H= 8 K= -2		
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H= 8 K= -1		
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H= 8 K= 0		
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-4	12	12
-3	7*	11

length of C(2)–N(3) is closer to that of the corresponding bond in a thiazolium ring than to a carbon–nitrogen single bond as depicted by its standard formula. In thiamine the C(6) methylene bridge effectively reduces electronic interaction between the aromatic pyrimidine and thiazolium rings. The ring closure which results from the bond formation between the thiazolium C(2) and the pyrimidine amino N(13) introduces the possibility of resonance between the two original rings. Indeed, the residual thiazolium character of the five-membered ring along with the observed bond lengths for C(2)–N(13) and N(13)–C(8), which are respectively longer and shorter than the standard carbon–nitrogen double and single bond lengths, do suggest that some electronic charge is transferred to N(13) and the pyrimidine ring. Although many resonance forms are required to account for the observed bond lengths, the predominant forms contributing to the interaction between the two rings all contain components such as $\mathrm{N^{+}(3){=}C(2){-}N^{-}(13)}$ and $\mathrm{N^{+}(3){=}C(2){-}N(13){=}C(8){-}N^{-}(9)}$. With the exception of N(13)–C(8) and C(8)–N(9) the bonds in the pyrimidine ring do not differ significantly between the two compounds.

Table 4. *Some least-squares planes through groups of atoms*

Coefficients $\times 10^4$ in $Ax+By+Cz-D=0$, referred to the crystallographic axes (x,y,z in Å). Displacement from the plane (Å $\times 10^3$). Bold-face type indicates atoms included in the plane.

A	*B*	*C*	*D*	Displacements
−9654	3021	1135	2149	**S(1)** −70, **C(2)** 6, **N(3)** 39, **C(4)** 31, **C(5)** −38, **C(6)** 34, **C(7)** 4, **C(8)** 25, **N(9)** 29, **C(10)** 7, **N(11)** −51, **C(12)** −50, **N(13)** 32, C(14) 65, C(15) 126, C(16) −138, C(17) 480, O(18) −420.
−9710	2588	1111	657	**S(1)** −1, **C(2)** 4, **N(3)** −6, **C(4)** 5, **C(5)** −2, C(6) −77, N(13) 24, C(15) 56, C(16) −65, C(17) 615, O(18) −149.
−9644	3033	1094	2217	**C(2)** −20, N(3) 10, **C(6)** 7, **C(7)** −16, **C(8)** 8, **N(13)** 11, S(1) −101, C(4) −5, N(9) 18, C(12) −65.
−9612	3327	1197	4196	C(7) 12, **C(8)** −7, **N(9)** −4, **C(10)** 12, **N(11)** −7, **C(12)** −5, C(6) 44, N(13) −41, C(14) 67.
−9702	2760	1176	1587	**S(1)** −26, **C(2)** 3, **N(3)** 15, **C(4)** 26, **C(5)** −5, **C(6)** −31 **N(13)** 18, C(7) −73, C(8) −26, C(15) 101, C(16) −76, C(17) 578, O(18) −205.
−9612	3238	1112	3344	**C(6)** 23, **C(7)** 2, **C(8)** 1, **N(9)** 13, **C(10)** 21, **N(11)** −14, **C(12)** −22, **N(13)** −24, C(2) −57, N(3) −5, C(14) 87.

Table 5. *Torsion angles in the rings and at the* I/II *and* II/III *junctions*

Φ in part *A* is the torsion angle about the specified bond. The other two atoms required to define the angle are attached to the ends of the bond and are in the ring in question. The sign convention for the torsion angle is that of Klyne & Prelog (1960). The torsion angles in the other enantiomorph are opposite in sign.

A. Intra-ring angles

Ring I	Φ	Ring II	Φ	Ring III	Φ
S(1)–C(2)	0·5 (1)	C(2)—N(3)	−3·7 (3)	C(7)—C(8)	−1·8 (2)
C(2)–N(3)	−1·1 (2)	N(3)—C(6)	0·7 (2)	C(8)—N(9)	0·3 (2)
N(3)–C(4)	1·3 (2)	C(6)—C(7)	1·9 (2)	N(9)—C(10)	1·6 (3)
C(4)–C(5)	−0·8 (2)	C(7)—C(8)	−2·1 (3)	C(10)–N(11)	−1·8 (3)
S(1)–C(5)	0·2 (1)	C(8)—N(13)	−0.5 (2)	N(11)–C(12)	0·1 (3)
		N(13)–C(2)	3·5 (3)	C(12)–C(7)	1·6 (3)

B. Inter-ring junctions

I/II junction	Φ	II/III junction	Φ
C(5)–S(1)–C(2)—N(13)	−179·1 (2)	C(2)—N(13)–C(8)—N(9)	179·0 (1)
S(1)–C(2)–N(13)–C(8)	−176·9 (1)	N(13)–C(8)—N(9)—C(10)	−179·2 (2)
S(1)–C(2)–N(3)—C(6)	176·7 (1)	N(13)–C(8)—C(7)—C(12)	177·7 (2)
C(5)–C(4)–N(3)—C(6)	−176·5 (2)	N(3)—C(6)—C(7)—C(12)	−177·9 (2)
C(4)–N(3)–C(6)—C(7)	178·3 (1)	C(6)—C(7)—C(12)–N(11)	−178·6 (2)
C(4)–N(3)–C(2)—N(13)	178·5 (2)	C(6)—C(7)—C(8)—N(9)	178·4 (2)

C. Extranuclear angles

	Φ		Φ
C(2)—S(1)–C(5)—C(16)	−177·4 (2)	C(2)—N(3)—C(4)—C(15)	−177·3 (2)
S(1)—C(5)–C(4)—C(15)	177·6 (2)	C(4)—C(5)—C(16)–C(17)	150·5 (2)
S(1)—C(5)–C(16)–C(17)	−32·2 (2)	C(5)—C(16)–C(17)–O(18)	69·4 (2)
N(3)—C(4)–C(5)—C(16)	176·6 (2)	C(8)—N(9)—C(10)–C(14)	−177·7 (2)
C(6)—N(3)–C(4)—C(15)	4·9 (2)	C(12)–N(11)–C(10)–C(14)	177·5 (2)
C(15)–C(4)–C(5)—C(16)	−4·9 (3)		

Table 6. *A comparison of bond lengths between thiochrome and thiamine base*

Bond	Thiochrome	Thiamine* (Pletcher *et al.*, 1972)
S(1)—C(2)	1·727 (2)	1·667
C(2)—N(3)	1·351 (2)	1·311
N(3)—C(4)	1·404 (2)	1·392
C(4)—C(5)	1·347 (2)	1·353
C(5)—S(1)	1·746 (2)	1·731
N(3)—C(6)	1·471 (2)	1·496
C(6)—C(7)	1·497 (2)	1·490
C(7)—C(8)	1·415 (2)	1·412
C(8)—N(9)	1·337 (2)	1·349
N(9)—C(10)	1·341 (2)	1·337
C(10)–N(11)	1·340 (2)	1·330
N(11)–C(12)	1·342 (2)	1·343
C(12)–C(7)	1·370 (2)	1·371
C(8)—N(13)	1·377 (2)	1·338
C(10)–C(14)	1·490 (3)	1·496
C(4)—C(15)	1·496 (2)	1·490
C(5)—C(16)	1·507 (3)	1·493
C(16)–C(17)	1·517 (3)	1·507
C(17)–O(18)	1·425 (2)	1·416

* The estimated standard deviations in bond lengths range from 0·002 to 0·004 Å.

The resonance in thiochrome which imparts thiazolium character to the five-membered ring results characteristically in placing approximately half of the residual positive charge in the ring on the sulfur (Sax, Pulsinelli & Pletcher, 1974). Indeed in many crystal structures negative ions or neighboring oxygen atoms are located closer to the thiazolium sulfur atom than would be predicted from the van der Waals separation. In thiochrome dihydrate a similar close contact occurs between S(1) and O(18) which is 0·3 Å shorter (Table 7) than the normal van der Waals distance. The angles, C(17)–O(18)···S(1) at 85° and S(1)···O(18)···H(192) at 80°, indicate that the lone-pair electrons on O(18) are favorably disposed geometrically for coulombic interaction with sulfur and for hydrogen bonding with H(192). This S···O interaction involving O(18), the *β*-hydroxy oxygen, has not been observed in any of the other thiamine structures (Kraut & Reed, 1962; Karle & Britts, 1966; Carlisle & Cook, 1969; Pletcher & Sax, 1972; Pletcher, Sax, Sengupta, Chu & Yoo, 1972; Sax, Pulsinelli & Pletcher, 1974) although it is a characteristic feature of the *α*-hydroxy oxygen in the 2-(*α*-hydroxyethyl)thiamine derivatives (Sax, Pulsinelli & Pletcher, 1974). In thiamine compounds the torsion angle defined by S(1)–C(5)–C(16)–C(17) is characteristically observed near 90° which prevents any intramolecular interaction with the ring sulfur regardless of the torsion angle for C(5)–C(16)–C(17)–O(18). In this structure (Table 5) the C(16)–C(17) bond is nearly synperiplanar with the S(1)–C(5) bond and the torsion angle about the C(16)–C(17) bond places O(18) within 0·15 Å of the plane of the thiazole ring (Table 4). The extent to which the conformation of the 5-(*β*-hydroxyethyl) side chain in thiochrome is constrained by the packing of the planar tricyclic ring system cannot be fully determined from the structural data available.

The molecular packing and hydrogen bonding for the structure are given in Table 7 and Figs. 3 and 4. In the crystal the molecules are held together in the **a** and **b** directions by an extensive network of hydrogen bonds all of which are mediated through the water molecules except for O(18)H···N(13). Both water molecules are tightly bonded into the structure which undoubtedly accounts for crystallization of the dihydrate structure even from solutions of anhydrous solvents which are evaporated at room temperature. The water

Table 7. *Hydrogen bonding and close contact distances and angles*

Symmetry code

None	x	y	z				
i	x	$y+1$	z	iv	$\bar{x}$	$\bar{y}+1$	$\bar{z}$
ii	$\bar{x}$	$\bar{y}$	$\bar{z}+1$	v	x	y	$z-1$
iii	$\bar{x}+1$	$\bar{y}$	$\bar{z}+1$	vi	$\bar{x}+1$	$\bar{y}+1$	$\bar{z}+1$

A. Hydrogen bonds

a	*b*	*c*	Distance *a*–*b* (Å)	Distance *a*–*c* (Å)	∠*abc*(°)
N(9)····	H(201) —	O(20)	2·13 (4)	2·935 (2)	163·5 (10)
N(11)···	H(191^{i}) –	O(19^{i})	2·12 (3)	2·880 (3)	174·4 (8)
N(13)···	H(181^{ii}) –	O(18^{ii})	1·98 (3)	2·904 (2)	160·8 (10)
O(18)···	H(192^{iii}) –	O(19^{iii})	2·22 (3)	2·918 (3)	160·4 (9)
O(19)···	H(202) —	O(20)	1·99 (4)	2·847 (3)	176·0 (11)

B. Close contacts

a	*b*	*c*	Distance *a*–*b* (Å)	Distance *a*–*c* (Å)	∠*abc*(°)
S(1)····	O(18) ——	C(17)	2·937 (2)	—	85·22 (11)
S(1)····	O(18) ——	H(181)	—	—	117·7 (9)
S(1)····	O(18) ···	H(192^{iii})	—	—	80·0 (9)
O(18)···	S(1) ——	C(2)	—	—	167·03 (7)
O(18)···	S(1) ——	C(5)	—	—	75·70 (7)
O(20)	H(141^{iv})		2·70 (5)		
O(20)	H(152^{v})		2·59 (3)		
O(20)	H(153^{vi})		2·66 (3)		
O(20)	H(161^{v})		2·52 (3)		
O(20)	H(172^{ii})		2·62 (3)		

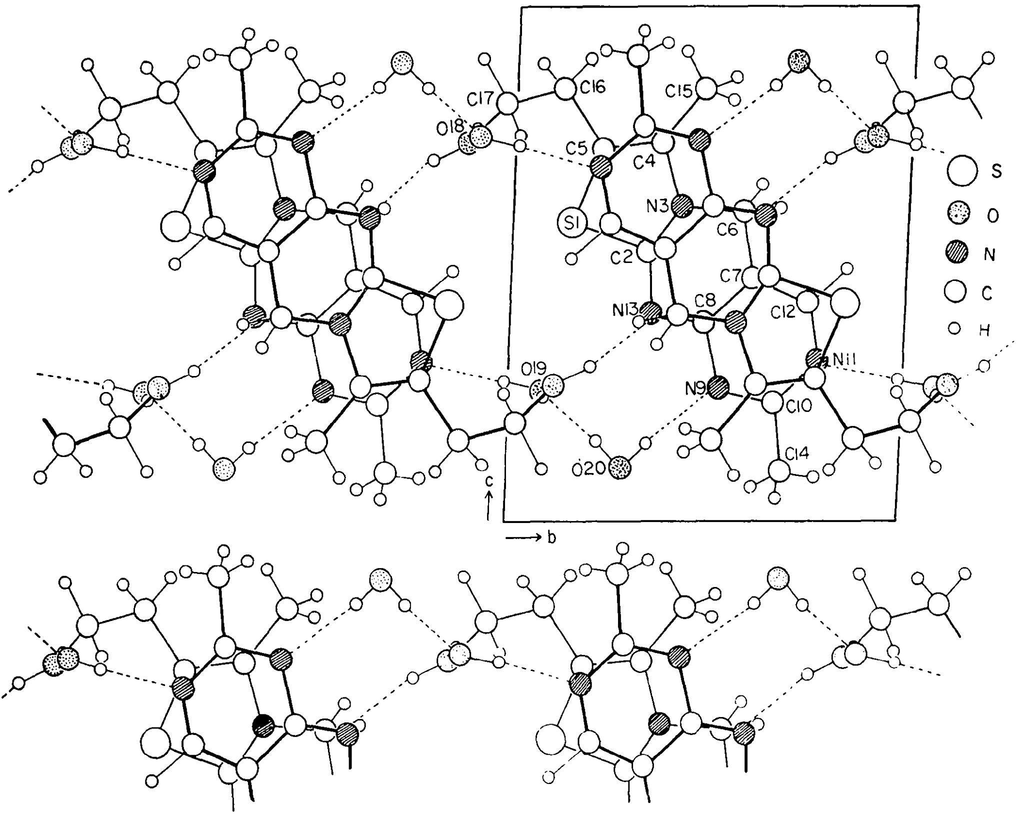

Fig. 3. A projection of the crystal structure down the *a* axis. Hydrogen bonding is depicted by dashed lines. The absence of hydrogen bonding in the direction of the *c* axis is apparent.

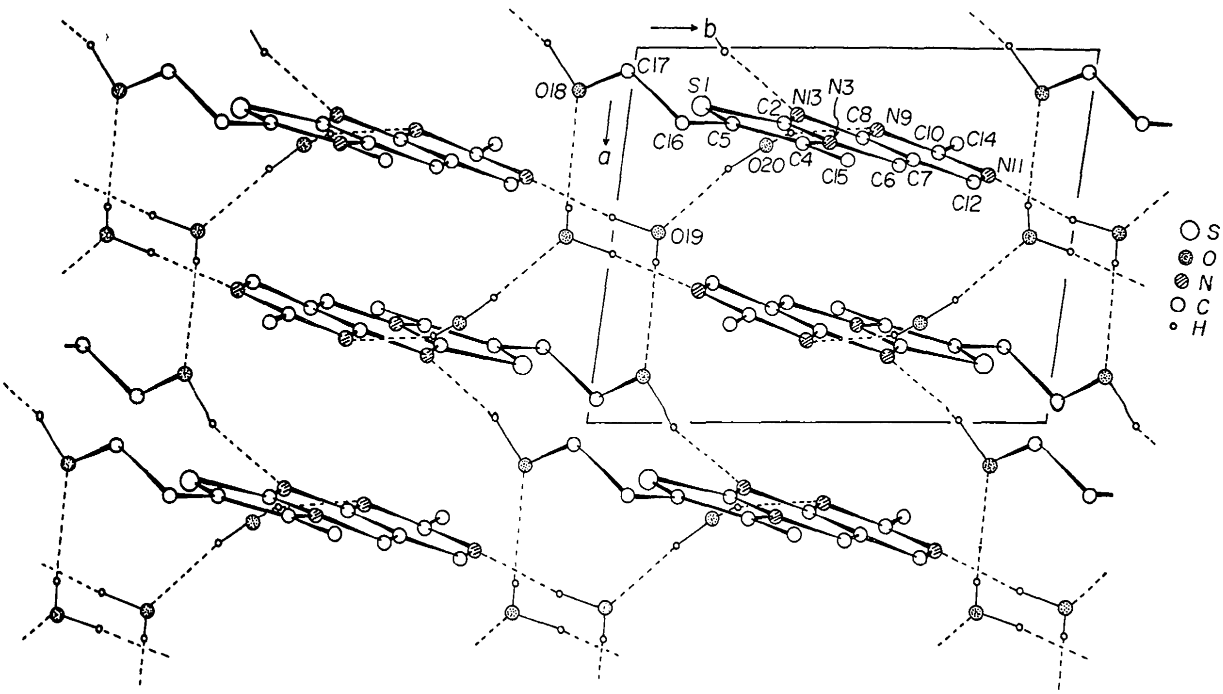

Fig. 4. Crystal structure projected down the *c* axis. Dashed lines indicate hydrogen bonds.

Table 8. *Comparison of bonds to the methylene bridging atom in thiamine compounds*

Structure	C(2)–N(3)	N(3)–C(6)	N(3)–C(4)	C(6)–C(7)
N-Benzylthiazolium bromide[a]	1·308 (5)	1·481 (5)	1·398 (5)	1·499 (6)
Thiamine chloride[b]	1·311 (3)	1·496 (3)	1·392 (2)	1·490 (3)
Thiamine pyrophosphate . HCl[c]	1·324 (4)	1·498 (4)	1·391 (4)	1·500 (4)
2-(α-Hydroxyethyl)thiamine . Cl.HCl[d]	1·331 (3)	1·480 (4)	1·392 (3)	1·507 (3)
Thiamine chloride . HCl[e]	1·332 (7)	1·476 (7)	1·401 (7)	1·496 (8)
Thiochrome	1·351 (2)	1·471 (2)	1·404 (2)	1·497 (2)
Average	1·326	1·484	1·396	1·498

a (Power, Pletcher & Sax, 1970); *b* (Pletcher, Sax, Sengupta, Chu & Yoo, 1972); *c* (Pletcher & Sax, 1972); *d* (Sax, Pulsinelli & Pletcher, 1973); *e* (Kraut & Reed, 1962).

molecule containing O(19) is the donor in two hydrogen bonds and the acceptor in a third bond. The environment of the other water molecule, which contains O(20), is especially interesting, for while it is the donor in two strong hydrogen bonds, it accepts none. Instead five CH bonds are pointed in the general direction of its lone-pair electrons (Fig. 4) from distances that are close to the sum of their van der Waals radii (Table 7). Three of these, O(20) to H(141), H(152) and H(161), may constitute the predominant force to maintain the crystal structure in the **c** direction since they provide the closest intermolecular contacts. With the exception of N(3), all of the nitrogen atoms in the molecule are hydrogen-bond acceptors.

In the various thiamine structures which have been determined, there is a small but significant variation in the length of the bond between the nitrogen in the five-membered ring and the methylene bridging carbon. From the data assembled in Table 8 it is apparent that the N(3)–C(6) bond increases (even to values significantly greater than that for a C–N single bond) as the C(2)–N(3) bond shortens or assumes increased double-bond character. At the same time the C(6)–C(7) and the N(3)–C(4) bonds do not exhibit variations which are as significant nor do their variations show the systematic trend which is seen for C(6)–N(3). Whether this effect has any significant influence on the properties of thiamine compounds is not presently known, but it is of interest that it does occur even in thiamine-related compounds which are chemically different such as *N*-benzylthiazolium bromide (Power, Pletcher & Sax, 1970) and thiochrome.

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