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The Crystal Structure of the Arsenite Complex of Dithiothreitol

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Based on a three-dimensional crystal structure of the arsenite complex of dithiothreitol, the correct formula of this complex has been determined as $C_4H_7O_2S_2As$. The crystals are monoclinic, space group $P2_1/c$ with $a=8{\cdot}49$, $b=9{\cdot}02$, $c=9{\cdot}88$ Å, $\beta=93°48'$, and four formula units in the cell. The structure contains a pyramidal arsenic atom, common to three rings. The systematic name, 1-arsa-2,7-dithia-4-hydroxy-8-oxa[3:2:1]bicyclooctane, has been given to this novel cage structure.

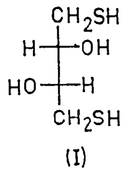
Introduction

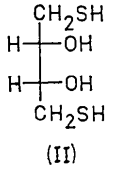
The dithiols, 1,4-dithiothreitol (I) and 1,4-dithioerythritol (II) (hereafter referred to as DTT and DTE respectively) are capable of reducing disulphides quantitatively to monothiols and of maintaining them in their reduced form (Cleland, 1964). Zahler & Cleland (1968) have used these reagents in the assay of disulphide in proteins by oxidizing them to the corresponding monothiols according to reactions (1) and (2).

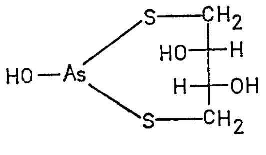
$$\mathrm{HSCH_2(CHOH)_2CH_2SH + RSSR'} \rightarrow \mathrm{HSCH_2(CHOH)_2CH_2SSR + R'SH} \quad (1)$$

$$\mathrm{HSCH_2(CHOH)_2CH_2SSR} \rightarrow \overline{\mathrm{SCH_2(CHOH)_2CH_2S}} + \mathrm{RSH} \quad (2)$$

Distinction between the monothiols so formed and excess dithiol used as reductant is accomplished by the addition of arsenite, which causes precipitation of stable arsenite complexes of DTT and DTE. Similar complexes also form with arsenite and 1,2-dithioglycerol or 1,3-dithioglycerol. The dissociation constants of the four arsenite complexes indicated the order of stability to be 1,2-dithioglycerol > DTT ~ DTE > 1,3-dithioglycerol.


(I)


(II)


(III)

Zahler & Cleland proposed a seven-membered ring structure (III) for the DTT- and DTE–arsenite complexes. They also inferred a five-membered ring for the arsenite complex of 1,2-dithioglycerol and a six-membered ring for the arsenite complex of 1,3-dithioglycerol. In order to account for the observed variation in stability of these compounds molecular models of these complexes were made. The arsenic and sulphur atoms in these complexes were given two extremes in bonding geometry: those of tetrahedral and octahedral coordination. Ring strain and close non-bonding interactions were not evident in these models. In order to test the correctness of the cyclic structures proposed by Zahler & Cleland, we decided to carry out a crystal-structure determination of the DTT-arsenite complex.

Experimental

The arsenite complex of DTT was prepared by the method of Zahler & Cleland (1968). It was recrystallized by slow evaporation of a 1:1 water-methanol solution to give tabular-shaped crystals, showing the pinacoidal form {010}. The other well-developed faces on the crystal were not identified.

Preliminary Weissenberg and precession photographs showed the systematic absences $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$, indicating the space group to be $P2_1/c$. Crystal data are given in Table 1. The cell dimensions were determined from 2θ values of the axial reflexions (Hornstra). The β angle was measured

Table 1. *Crystal data*

Formula	$C_4H_7O_2S_2As$
Morphology	$2/m$
Space group	$P2_1/c$
Cell dimensions	$a=8{\cdot}49\pm0{\cdot}01$ Å $b=9{\cdot}02\pm0{\cdot}01$ $c=9{\cdot}88\pm0{\cdot}01$ $\beta=93°48'\pm10'$
Density	$\varrho_{\text{obs}}=1{\cdot}96$ g.cm^{-3} $\varrho_{\text{calc}}=1{\cdot}99$ g.cm^{-3}
Absorption coefficient	$\bar{\mu}$(Mo $K\bar{\alpha}$)$=0{\cdot}518$ mm^{-1}
$F(000)$	448 e
Volume	755·25 Å^3

from a precession photograph of the *h*0*l* zone. The crystal density was measured by flotation in an aqueous solution of thallium malonate–thallium formate.

Intensity data were collected on a PAILRED diffractometer, using Si-monochromated Mo *Kα* radiation. A crystal of dimensions 0·08 × 0·10 × 0·10 mm was mounted with the *c* axis parallel to the rotation axis of the diffractometer. The layers *HK*0 to *HK*10 were collected. During this period, no appreciable decomposition was detected by the systematic monitoring of standard reflexions. In all, 1715 unique reflexions were measured, of which 870 satisfied our observed–unobserved criterion of $\Delta I/I<0{\cdot}40$, where $\Delta I/I=[(T+B+0{\cdot}03N^2)^{1/2}]/(T-B)$ and T = total count, N = net count, and B = total background. Reflexions with intensities greater than 2·5 σ were considered present. The term 0·03 N^2 is included to account for misalignment errors. The intensity data were collected using an ω scan mode of 1°. min^{-1} with an ω scan width of 1·2° for reflexions with $2\theta\le16°$, and a scan width of 0·7° for reflexions with $2\theta>16°$. These scan ranges were increased with higher layers to accommodate the increased spot width. Backgrounds were counted for 24 sec on each side of the reflexions. Reflexions at low 2θ whose spot extension exceeded the scan range were re-collected with a larger ω scan width. The axial reflexions 00*l* were too close to the primary beam or too extended to be measured accurately and so were omitted. No correction for absorption was made due to the small equidimensional crystal size and its low absorption coefficient.

Data reduction was performed with a locally modified University of British Columbia *DATAPREP* program (Trotter) which corrected for Lorentz and polarization effects. An estimation of an overall temperature factor of 2·9 and an overall scale of 2·10 was made using the method of Wilson (1942). Fourier maps and bond distances with estimated standard deviations were calculated using the NRC programs of Ahmed (1967). Refinement on *F* was done with a locally modified *ORFLS* full-matrix least-squares program (Busing, Martin & Levy, 1962). Form factors, corrected for the real component of anomalous dispersion (Cromer, 1965) were obtained from Cromer & Waber (1965). No corrections for the imaginary component of anomalous dispersion were made. The hydrogen curve was that of Mason & Robertson (1966).

Solution and refinement of the structure

Three unique As–As vectors were identified on a Patterson map computed with coefficients sharpened to point atoms at rest. These vectors gave the location of the arsenic atom at the position defined by the fractional coordinates $x/a=0{\cdot}119$, $y/b=0{\cdot}145$, $z/c=0{\cdot}120$. A heavy-atom Fourier map phased with this arsenic position revealed the locations of all the non-hydrogen atoms in the cell. Structure factors calculated from all non-hydrogen atom positions and an overall temperature factor of 2·89 resulted in a residual of $R=0{\cdot}21$ where $R=\sum||F_o|-|F_c||/\sum|F_o|$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively. These atomic positions were refined by full-matrix least-squares methods, using unit weights for four cycles. The residual dropped from $R=0{\cdot}21$ to $R=0{\cdot}10$. The thermal parameters of the non-hydrogen atoms were then refined anisotropically, using unit weights for two cycles, which reduced the residual to 0·069. A difference Fourier map was then calculated, showing the locations of all hydrogen atoms as peaks of 0·65 to 0·40 e.Å^{-3}.

When isotropic refinement of the hydrogen atoms was attempted, the parameters describing the thermal motion of H(11), H(21), H(31) and H(5) became negative. Therefore, the final isotropic temperature factors of the bound heavy atoms were assigned to their respective hydrogen atoms. Refinement was continued by minimizing the function $\sum W(|F_o|-k|F_c|)^2$, where the weight W was obtained from the expression $W=a^2/[a^2+(|F_o|/b)^2]$, with $a=8$e and $b=15$e. This weighting scheme satisfied Cruickshank's (1965) criterion that $\sum W||F_o|-|F_c||^2$ be constant over all ranges of the data. Convergence of the refinement at a residual of $R=0{\cdot}064$ occured after two more cycles, at which time all parameter shifts were less than one-tenth their e.s.d.s.

The final atomic fractional coordinates and thermal parameters for non-hydrogen atoms, with e.s.d.s in parentheses, are listed in Tables 2 and 3. Hydrogen-atom fractional coordinates and the assigned temperature factors are listed in Table 4. Observed and calculated structure factors, with unobserved reflexions marked with an asterisk, are listed in Table 5.

Table 2. *Final atomic fractional coordinates*

	x/*a*	*y*/*b*	*z*/*c*
As	0·1178 (2)*	0·1431 (1)	0·1250 (1)
S(1)	0·0048 (4)	−0·0049 (4)	0·2727 (4)
S(2)	0·2455 (4)	−0·0231 (5)	0·0030 (3)
O(1)	0·2786 (9)	0·1782 (8)	0·2534 (9)
O(2)	0·4734 (13)	−0·1652 (10)	0·3567 (10)
C(1)	0·1774 (18)	−0·0113 (16)	0·3944 (21)
C(2)	0·3233 (15)	0·0491 (14)	0·3354 (12)
C(3)	0·4183 (14)	−0·0602 (14)	0·2555 (13)
C(4)	0·3262 (17)	−0·1426 (16)	0·1407 (13)

* E.s.d's given in parentheses refer to the least significant digit of the position.

Description of the structure

The structure proposed by Zahler & Cleland for the complex formed from the reaction of arsenite with DTT is incorrect. The complex can now be given the systematic name 1-arsa-2,7-dithia-4-hydroxy-8-oxa-[3,2,1]bicyclooctane, and it contains a pyramidal arsenic atom common to three heterocyclic rings. The bond distances and interbond angles for this cage structure are listed in Tables 6 and 7, with the atomic designations of the stereoscopic pair drawn in Fig. 1.

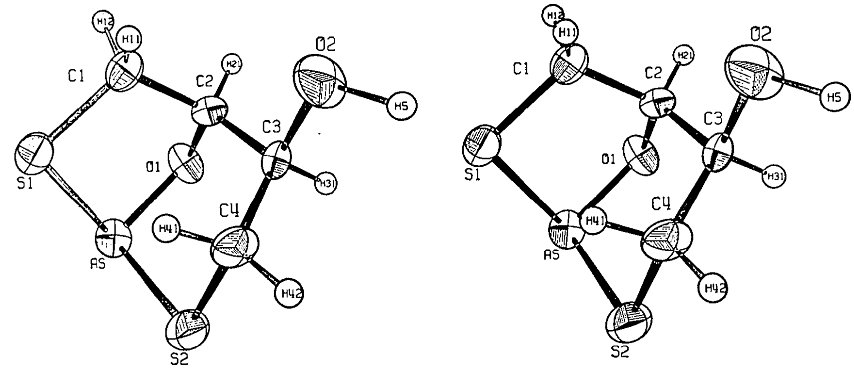


Fig. 1. Stereodiagram of the DTT-arsenite complex.

Table 3. *Thermal parameters of non-hydrogen atoms* (× 10^4)

The temperature factor is of the form $T_2=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$ for non-hydrogen atoms.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	111 (1)	64 (1)	92 (2)	9 (2)	4 (1)	23 (1)
S(1)	91 (5)	135 (5)	87 (4)	−4 (4)	21 (3)	15 (3)
S(2)	134 (6)	162 (6)	69 (4)	40 (4)	8 (3)	2 (3)
O(1)	99 (12)	59 (10)	100 (10)	−3 (8)	−20 (9)	2 (7)
O(2)	173 (17)	110 (14)	84 (11)	78 (13)	−15 (10)	2 (9)
C(1)	126 (21)	85 (16)	87 (17)	11 (16)	10 (14)	−5 (14)
C(2)	104 (17)	90 (16)	49 (13)	−22 (14)	−16 (11)	−11 (11)
C(3)	68 (15)	79 (16)	78 (14)	−4 (13)	17 (11)	1 (11)
C(4)	150 (21)	97 (15)	80 (15)	39 (19)	10 (13)	−30 (14)

E.s.d.'s in parentheses refer to the least significant digit of the parameter.

The two As–S bonds in the molecule are equal, with distances of 2·237 ± 0·004 and 2·247 ± 0·004 Å. These distances do not significantly differ from the previously reported As–S distances of 2·21 Å in realgar and 2·25 ± 0·02 Å in arsenic trisulphide (Lee & Donohue, 1944). Both of these latter compounds contain pyramidal arsenic atoms. The As–O(1) bond length of 1·83 ± 0·01 Å agrees with the value of 1·80 ± 0·02 Å in arsenic trioxide (Hampson & Stosick, 1938).

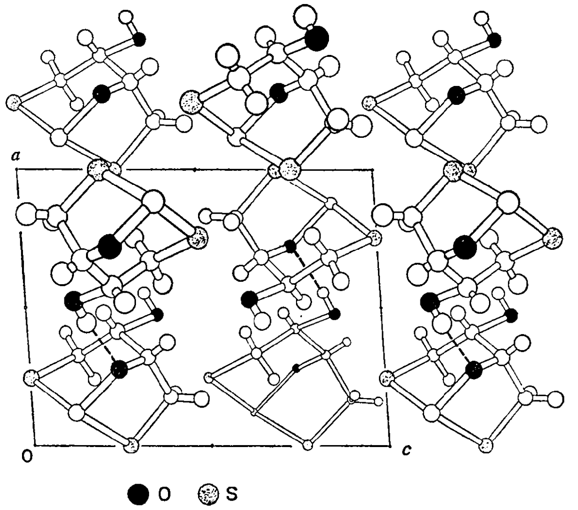


Fig. 2. Projection onto (010). The dashed line indicates the hydrogen bond from O(2) to O(1) of the twofold screw-related molecules.

Table 4. *Final positional parameters of hydrogen atoms with their assigned isotropic temperature factors**

	x/a	y/b	z/c	B(Å^2)
H(11)	0·191 (15)†	−0·080 (15)	0·407 (12)	2·5
H(12)	0·171 (13)	0·039 (13)	0·479 (12)	2·5
H(21)	0·375 (15)	0·073 (15)	0·396 (12)	3·0
H(31)	0·480 (12)	−0·013 (12)	0·218 (10)	1·8
H(41)	0·410 (12)	−0·196 (12)	0·109 (11)	2·3
H(42)	0·242 (12)	−0·190 (12)	0·182 (11)	2·3
H(5)	0·557 (17)	−0·190 (17)	0·336 (14)	4·0

* The temperature factor for the hydrogen atoms is in the form:

$$T_H=\exp[-B\sin^2\theta/\lambda^2].$$

† E.s.d.'s given in parentheses refer to the least significant digit of the parameter.

The bond angles about the arsenic atoms are intermediate between tetrahedral and octahedral values and are probably influenced by ring strain. The S(1)–As–O(1) angle of 89·3° in the five-membered ring is substantially less than the S(2)–As–O(1) and S(1)–As–S(2) angles of 97·1 ± 0·3 and 101·2 ± 0·1° in the six- and seven-membered rings respectively. In arsenic trioxide, which contains a trisubstituted arsenic in a six-membered ring in a chair conformation, the O–As–O angles are 100 ± 1·5°. In arsenic trisulphide, with a structure

Table 5. *Observed and calculated structure factors* (×10)

An asterisk (*) denotes an unobserved reflexion.

K	FO	FC
H= 0, L= 0		
2	986	937
4	300	-273
6	1042	1037
8	387	359
10	279	-284
H= 0, L= 1		
1	734	691
2	629	-552
3	495	-467
4	416	377
5	105	-78
6	370	355
7	493	465
8	225	-227
9	74*	-29
10	75*	-41
11	174	-199
H= 0, L= 2		
1	985	-914
2	109	86
3	344	-317
4	59*	6
5	866	821
6	172	-183
7	60*	-36
8	71*	80
9	355	-370
10	76*	-0
11	82*	113
H= 0, L= 3		
1	473	420
2	510	-466
3	1200	1076
4	145	-102
5	460	419
6	326	319
7	232	-266
8	204	-191
9	74*	101
10	79*	-149
11	86*	171
H= 0, L= 4		
1	34*	7
2	883	787
3	107	-97
4	1205	1115
5	62*	-62
6	179	-180
7	69*	48
8	245	-223
9	74*	-25
10	283	317
11	86*	-41
H= 0, L= 5		
1	185	-183
2	363	323
3	599	559
4	179	152
5	215	202
6	74*	-130
7	300	-282
8	233	210
9	79*	7
10	89*	90
11	92*	149
H= 0, L= 6		
1	553	552
2	48*	26
3	234	229
4	58*	20
5	487	-488
6	66*	49
7	73*	47
8	75*	-57
9	258	252
10	86*	-87
H= 0, L= 7		
1	633	612
2	344	340
3	63*	10
4	305	-287
5	191	170
6	204	-288
7	374	360
8	76*	101
9	79*	-5
10	86*	55
H= 0, L= 8		
1	38*	-15
2	149	144
3	63*	125
4	181	-187
5	135	101
6	393	360
7	80*	-31
8	194	171
9	90*	89
10	93*	-140
H= 0, L= 9		
1	40*	189
2	166	-156
3	201	-195
4	166	163
5	68*	-116
6	75*	108
7	80*	103
8	86*	-97
9	91*	-33
H= 0, L= 10		
2	69*	162
3	138	-130
4	84*	104
5	180	177
6	103*	-29
H= 1, L= 0		
0	706	825
1	623	-609
2	446	413
3	51*	-56
4	59*	-111
5	709	683
6	487	452
7	72*	38
8	435	435
9	156	-139
10	75*	-101
11	82*	131
H= 1, L= 1		
1	676	-652
2	1100	-1055
3	50*	-62
4	711	682
5	225	-223
6	736	711
7	69*	-26
8	280	-274
9	74*	39
10	73*	-43
11	82*	-48
H= -1, L= 1		
1	1338	1351
2	551	-556
3	1354	-1240
4	57*	-52
5	60*	-39
6	64*	-75
7	531	552
8	134	-135
9	265	-230
10	76*	-6
11	228	-228
H= 1, L= 2		
0	609	-674
1	263	-277
2	184	133
3	333	-304
4	375	370
5	515	501
6	479	-477
7	260	247
8	371	-365
9	213	-264
10	78*	129
11	79*	79
H= -1, L= 2		
0	437	473
1	800	-790
2	784	-744
3	496	-477
4	1023	-988
5	361	343
6	64*	82
7	177	-192
8	72*	68
9	324	-345
10	278	-293
11	80*	37
H= 1, L= 3		
1	653	-604
2	175	-150
3	936	844
4	283	256
5	252	238
6	197	201
7	504	-514
8	74*	38
9	75*	100
10	77*	-15
11	230	253
H= -1, L= 3		
1	145	120
2	1039	-951
3	536	502
4	407	361
5	58*	-7
6	369	369
7	70*	111
8	452	-450
9	154	193
10	160	-190
11	80*	-9
H= 1, L= 4		
0	264	-271
1	219	230
2	218	202
3	460	407
4	606	565
5	63*	-82
6	70*	7
7	128	89
8	75*	-91
9	261	289
10	156	211
11	85*	-70
H= -1, L= 4		
0	202	-208
1	379	-346
2	380	356
3	435	-419
4	668	600
5	156	156
6	131	-102
7	69*	-11
8	74*	-96
9	261	-280
10	197	212
11	82*	23
H= 1, L= 5		
1	193	-176
2	986	938
3	54*	-81
4	297	-292
5	69*	-98
6	256	-247
7	76*	-81
8	460	437
9	84*	-92
10	91*	150
H= -1, L= 5		
1	635	-627
2	51*	29
3	499	453
4	395	-370
5	66*	65
6	184	-177
7	547	-541
8	77*	8
9	63*	11
10	82*	-76
11	95*	193
H= 1, L= 6		
0	158	184
1	442	449
2	294	-315
3	179	223
4	506	-488
5	339	-343
6	68*	58
7	75*	24
8	77*	6
9	225	227
10	91*	-201
H= -1, L= 6		
1	209	205
2	46*	17
3	182	185
4	313	316
5	300	-280
6	276	-275
7	73*	-78
8	233	-243
9	82*	158
10	86*	112
H= 1, L= 7		
1	556	590
2	160	158
3	415	-383
4	216	211
5	125	108
6	68*	26
7	401	417
8	77*	32
9	81*	-29
10	83*	90
H= -1, L= 7		
1	180	189
2	408	399
3	178	165
4	286	-293
5	170	172
6	375	-372
7	71*	84
8	134	101
9	80*	-36
10	84*	15
H= 1, L= 8		
0	213	255
1	174	-180
2	58*	26
3	55*	33
4	165	-174
5	319	322
6	76*	81
7	81*	17
8	84*	187
9	92*	-46
10	97*	-79
H= -1, L= 8		
1	252	244
2	91	30
3	62*	1
4	127	-117
5	367	-353
6	251	252
7	78*	-72
8	167	148
9	90*	72
10	96*	-83
H= 1, L= 9		
2	364	-364
3	57*	-82
4	161	170
5	165	-202
6	201	227
7	79*	-78
8	87*	-133
9	90*	44
H= -1, L= 9		
1	122	122
2	119	-91
3	464	-464
4	110	38
5	143	-149
6	72*	-42
7	81*	156
8	86*	-69
9	93*	-107
10	97*	41
H= 1, L= 10		
0	55*	-138
1	62*	-106
2	73*	19
3	76*	-46
4	86*	101
5	207	220
6	107*	-87
H= -1, L= 10		
2	65*	11
3	71*	-97
4	192	-180
5	92*	91
6	100*	59
H= 2, L= 0		
0	51*	-130
1	922	-957
2	50*	-32
3	415	-405
4	57*	-68
5	845	831
6	66*	44
7	72*	42
8	76*	129
9	347	-366
10	76*	17
11	82*	144
H= 2, L= 1		
1	664	-659
2	513	-500
3	265	248
4	140	141
5	162	-139
6	554	541
7	535	-530
8	229	-197
9	74*	-17
10	195	-186
11	81*	111
H= -2, L= 1		
1	268	-260
2	1111	1105
3	648	-642
4	304	-291
5	294	-307
6	178	-199
7	357	353
8	313	332
9	75*	15
10	73*	56
11	80*	-151
H= 2, L= 2		
0	1529	-1758
1	352	-357
2	732	-703
3	97	-32
4	185	157
5	226	219
6	530	-548
7	68*	-30
8	361	-382
9	73*	-51
10	213	243
11	83*	-2
H= -2, L= 2		
0	121	113
1	360	-364
2	1225	-1231
3	180	-186
4	1318	-1292
5	61*	103
6	69*	107
7	69*	-86
8	71*	-1
9	75*	-54
10	326	-350
11	80*	66
H= 2, L= 3		
1	614	-601
2	519	493
3	64*	73
4	162	-161
5	62*	63
6	318	-317
7	328	-312
8	221	229
9	74*	43
10	79*	75
11	195	181
H= -2, L= 3		
1	333	332
2	1030	-969
3	862	-769
4	156	151
5	140	-125
6	237	201
7	385	336
8	367	-374
9	70*	-62
10	79*	-102
11	82*	-109
H= 2, L= 4		
0	58*	-126
1	902	872
2	287	272
3	261	255
4	240	218
5	768	-746
6	74*	-52
7	129	66
8	74*	1
9	310	311
10	81*	19
11	155	-111
H= -2, L= 4		
0	301	-320
1	605	-622
2	201	187
3	214	-184
4	118	92
5	771	730
6	73*	-121
7	71*	47
8	167	145
9	286	-312
10	81*	71
11	81*	79
H= 2, L= 5		
1	217	-244
2	611	587
3	811	-775
4	177	-145
5	317	-284
6	266	-262
7	78*	84
8	241	204
9	180	-175
10	89*	125
H= -2, L= 5		
1	784	-816
2	455	-437
3	55*	-16
4	62*	89
5	222	-216
6	283	284
7	433	-415
8	153	-146
9	80*	2
10	152	-118
11	92*	68
H= 2, L= 6		
0	196	213
1	55*	58
2	658	-630
3	110	137
4	740	-723
5	67*	7
6	179	186
7	74*	-72
8	79*	75
9	82*	45
10	166	-191
H= -2, L= 6		
0	839	-942
1	129	141
2	327	-351
3	104	-93
4	121	137
5	264	-248
6	354	-322
7	74*	41
8	236	-250
9	78*	19
10	169	184
H= 2, L= 7		
1	156	171
2	365	-376
3	187	-147
4	160	166
5	67*	-98
6	159	112
7	260	241
8	171	-199
9	83*	67
10	86*	2
H= -2, L= 7		
1	320	-311
2	341	329
3	269	278
4	133	-128
5	62*	56
6	245	-255
7	239	-239
8	162	161
9	80*	19
10	82*	56
H= 2, L= 8		
0	148	-143
1	387	-401
2	128	-103
3	229	-226
4	185	-166
5	339	304
6	77*	-111
7	79*	-41
8	85*	57
9	178	-194
10	92*	-5
H= -2, L= 8		
0	46*	-35
1	289	295
2	56*	-54
3	177	177
4	65*	-16
5	267	-294
6	74*	15
7	77*	-42
8	83*	-48
9	95*	165
10	90*	-32
H= 2, L= 9		
1	320	-325
2	146	-143
3	61*	-93
4	66*	72
5	76*	-117
6	236	225
7	195	-184
8	87*	-39
9	91*	14
H= -2, L= 9		
1	211	-210
2	246	252
3	463	-462
4	119	-108
5	185	-189
6	73*	-124
7	61*	79
8	80*	78
9	178	-75
10	96*	57
H= 2, L= 10		
0	307	-360
1	75*	-11
2	74*	-59
3	85*	-23
4	89*	104
5	98*	20
6	189	-156
H= -2, L= 10		
0	52*	61
1	59*	-71
2	218	-247
3	74*	-28
4	320	-320
5	95*	29
6	103*	60
H= 3, L= 0		
0	192	-186
1	378	-394
2	438	436
3	384	-375
4	624	607
5	390	388
6	68*	-105
7	70*	23
8	73*	-75
9	361	-389
10	169	198
11	80*	18
H= 3, L= 1		
1	554	-584
2	425	-439
3	454	444
4	58*	-29
5	212	227
6	70*	-117
7	397	-395
8	151	-153
9	76*	93
10	73*	-29
11	256	246
H= -3, L= 1		
1	242	229
2	614	605
3	113	-90
4	195	-172
5	63*	-66
6	378	-388
7	72*	116
8	411	411
9	74*	6
10	251	204
H= 3, L= 2		
0	1094	-1234
1	453	454
2	265	-285
3	144	123
4	268	244
5	591	-587
6	409	-407
7	71*	-72
8	311	-295
9	205	209
10	82*	151
H= -3, L= 2		
0	54*	75
1	939	965
2	500	-518
3	594	572
4	761	-778
5	295	-287
6	68*	58
7	256	266
8	144	158
9	278	290
10	204	-238
11	78*	-68
H= 3, L= 3		
1	56*	78
2	771	759
3	628	597
4	670	-653
5	65*	63
6	547	-528
7	71*	-101
8	174	215
9	73*	12
10	77*	6
H= -3, L= 3		
1	463	506
2	56*	-81
3	621	-608
4	107	131
5	60*	-4
6	130	82
7	462	441
8	71*	-38
9	71*	-60
10	76*	34
H= 3, L= 4		
0	720	787
1	414	411
2	56*	80
3	164	166
4	144	-118
5	533	-484
6	435	429
7	74*	-112
8	184	163
9	81*	161
10	81*	-80
H= -3, L= 4		
0	819	886
1	688	-622
2	54*	78
3	224	-221
4	143	-133
5	574	548
6	448	416
7	75*	-18
8	228	232
9	202	-164
10	82*	-38
H= 3, L= 5		
1	55*	70
2	50*	26
3	853	-834
4	67*	-18
5	180	-147
6	75*	-138
7	310	306
8	83*	-34
9	84*	-115
10	88*	52
H= -3, L= 5		
1	330	-367
2	472	-490
3	57*	13
4	476	440
5	287	-286
6	540	534
7	147	-187
8	82*	-144
9	78*	4
10	88*	-48
H= 3, L= 6		
0	291	320
1	417	-401
2	58*	-23
3	230	-234
4	378	-358
5	197	198
6	70*	48
7	244	-213
8	197	178
9	90*	-192
10	180	-191
H= -3, L= 6		
0	567	-635
1	209	-248
2	52*	-11
3	121	-107
4	214	205
5	394	382
6	298	-318
7	71*	128
8	78*	-156
9	167	-180
10	88*	113
H= 3, L= 7		
1	241	270
2	497	-492
3	58*	65
4	63*	52
5	67*	10
6	141	137
7	78*	133
8	270	-260
9	83*	69
10	87*	-103
H= -3, L= 7		
1	156	-166
2	124	121
3	330	345
4	53*	-64
5	237	232
6	69*	53
7	74*	-114
8	70*	111
9	81*	4
10	85*	-27
H= 3, L= 8		
0	136	-156
1	59*	-113
2	62*	58
3	159	-150
4	181	176
5	77*	131
6	76*	-63
7	82*	67
8	92*	-4
9	179	-173
H= -3, L= 8		
0	208	-222
1	267	261
2	62*	68
3	177	182
4	191	208
5	199	-192
6	75*	-63
7	81*	30
8	86*	-77
9	183	208
10	94*	76
H= 3, L= 9		
1	235	-239
2	61*	-87
3	178	190
4	70*	-39
5	75*	3
6	79*	3
7	174	-212
8	89*	-21
9	93*	22
H= -3, L= 9		
1	64*	-74
2	343	334
3	120	-108
4	65*	-4
5	69*	-77
6	167	-116
7	83*	-62
8	193	180
9	93*	-81
10	93*	108
H= 3, L= 10		
0	79*	-219
1	79*	61
2	83*	4
3	89*	-52
4	101*	133
5	107*	-221
6	114*	-75
H= -3, L= 10		
0	72*	60
1	137	180
2	78*	-159
3	80*	129
4	180	-199
5	94*	-93
6	106*	74
H= 4, L= 0		
0	56*	-15
1	305	-317
2	573	603
3	189	-193
4	971	960
5	66*	-24
6	70*	47
7	153	-133
8	75*	-127
9	74*	-30
10	240	305
H= 4, L= 1		
1	185	-179
2	513	496
3	907	919
4	184	-174
5	111	219
6	217	-223
7	388	-385
8	219	246
9	78*	75
10	81*	70
H= -4, L= 1		
1	59*	-2
2	474	515
3	535	541
4	169	-150
5	211	204
6	334	-327
7	194	-202
8	226	253
9	75*	54
10	100	136
H= 4, L= 2		
0	390	-399
1	506	633
2	136	128
3	250	274
4	127	142
5	473	-464
6	240	-248
7	73*	46
8	75*	-150
9	203	231
10	79*	-48
H= -4, L= 2		
0	145	174
1	358	386
2	55*	14
3	220	225
4	176	-172
5	505	-492
6	68*	9
7	71*	-55
8	72*	34
9	267	319
10	80*	-96
H= 4, L= 3		
1	730	724
2	479	477
3	186	-174
4	333	-307
5	289	301
6	375	-375
7	442	415
8	76*	137
9	76*	-38
10	77*	54
H= -4, L= 3		
1	663	755
2	677	680
3	268	-255
4	197	-173
5	65*	-19
6	141	-140
7	421	431
8	223	223
9	73*	-51
10	79*	9
H= 4, L= 4		
0	985	1064
1	58*	34
2	132	150
3	64*	65
4	203	-179
5	73*	-55
6	463	494
7	75*	-53
8	289	270
9	81*	40
10	149	-136
H= -4, L= 4		
0	1197	1302
1	55*	5
2	402	421
3	60*	52
4	63*	-54
5	72*	70
6	504	501
7	75*	1
8	282	313
9	76*	-18
10	142	-117
H= 4, L= 5		
1	414	443
2	425	-420
3	224	-241
4	233	233
5	157	-190
6	79*	110
7	228	223
8	189	-273
9	86*	-37
10	87*	27
H= -4, L= 5		
1	235	224
2	489	-508
3	294	-315
4	310	299
5	71*	9
6	251	247
7	231	206
8	182	-180
9	84*	-13
10	91*	26
H= 4, L= 6		
0	246	261
1	242	-265
2	65*	107
3	176	-178
4	68*	-64
5	277	262
6	75*	26
7	77*	-6
8	81*	94
9	213	-208
H= -4, L= 6		
1	342	-372
2	59*	95
3	174	-174
4	65*	68
5	386	382
6	178	-166
7	79*	17
8	78*	-45
9	88*	-190
10	88*	7
H= 4, L= 7		
1	58*	54
2	185	-211
3	393	395
4	69*	24
5	171	163
6	171	211
7	77*	-45
8	83*	-61
9	177	137
H= -4, L= 7		
1	169	184
2	235	-227
3	708	708
4	124	91
5	221	211
6	152	195
7	161	-144
8	81*	-43
9	85*	138
10	84*	-81
H= 4, L= 8		
0	64*	-77
1	130	-111
2	268	283
3	126	-68
4	428	390
5	77*	49
6	81*	-72
7	84*	2
8	92*	-86
9	91*	-27
H= -4, L= 8		
0	67*	-108
1	56*	65
2	184	181
3	64*	12
4	382	374
5	73*	4
6	76*	16
7	83*	84
8	89*	-76
9	93*	-1
H= 4, L= 9		
1	119	-119
2	122	102
3	196	198
4	74*	-102
5	77*	40
6	84*	-84
7	161	-178
8	93*	94
9	94*	-32
H= -4, L= 9		
1	55*	-90
2	246	239
3	66*	96
4	68*	-61
5	73*	46
6	79*	-70
7	82*	-84
8	198	157
9	90*	-28
H= 4, L= 10		
0	86*	-24
1	161	172
2	94*	73
3	97*	80
4	102*	116
5	111*	-134
6	115*	22
H= -4, L= 10		
0	139	159
1	80*	182
2	82*	98
3	88*	90
4	96*	35
5	105*	-166
6	107*	43
H= 5, L= 0		
0	393	-386
1	309	326
2	532	564
3	265	267
4	757	774
5	70*	-86
6	204	-190
7	155	141
8	75*	-89
9	196	180
10	269	244
H= 5, L= 1		
1	200	-187
2	673	704
3	143	129
4	68*	-55
5	72*	-63
6	147	-104
7	76*	-122
8	328	326
9	76*	-35
10	86*	114
H= -5, L= 1		
1	378	-392
2	214	240
3	403	409
4	66*	-77
5	135	161
6	67*	-48
7	427	-447
8	75*	23
9	75*	-17
10	80*	-29
H= 5, L= 2		
0	233	249
1	461	495
2	492	-472
3	219	206
4	520	-521
5	405	-435
6	130	147
7	73*	36
8	74*	-38
9	229	245
10	88*	-175
H= -5, L= 2		
0	477	-511
1	357	377
2	60*	-104
3	141	147
4	144	142
5	464	-489
6	230	-246
7	72*	-94
8	223	-203
9	199	171
10	82*	66
H= 5, L= 3		
1	549	575
2	143	138
3	344	-341
4	119	91
5	66*	23
6	71*	-52
7	368	395
8	75*	67
9	75*	-31
H= -5, L= 3		
1	100	54
2	270	281
3	69*	-19
4	293	-291
5	68*	16
6	452	-446
7	74*	118
8	73*	91
9	75*	22
10	80*	83
H= 5, L= 4		
0	635	641
1	238	-251
2	68*	138
3	69*	79
4	282	-275
5	391	393
6	202	169
7	73*	-13
8	184	189
9	80*	-28
H= -5, L= 4		
0	795	844
1	244	268
2	146	172
3	66*	15
4	245	-239
5	301	-319
6	316	312
7	72*	-26
8	226	197
9	81*	42
10	88*	-180
H= 5, L= 5		
1	70*	-88
2	219	-249
3	186	-174
4	148	153
5	80*	-161
6	297	288
7	81*	0
8	85*	-104
9	91*	18
H= -5, L= 5		
1	345	363
2	65*	-31
3	411	-440
4	70*	-14
5	160	-154
6	76*	10
7	198	234
8	82*	-44
9	89*	-94
10	93*	-35
H= 5, L= 6		
0	388	-406
1	191	-206
2	66*	-61
3	149	-111
4	71*	100
5	298	315
6	196	-183
7	82*	126
8	85*	-61
9	88*	-125
H= -5, L= 6		
0	62*	45
1	335	-368
2	280	-279
3	156	-180
4	326	-338
5	230	218
6	73*	26
7	77*	-129
8	79*	42
9	90*	-174
H= 5, L= 7		
1	64*	-13
2	125	-140
3	367	363
4	70*	89
5	73*	118
6	77*	93
7	172	-194
8	82*	-6
9	85*	16
H= -5, L= 7		
1	115	136
2	373	-378
3	262	264
4	67*	35
5	69*	82
6	74*	90
7	75*	27
8	162	-192
9	84*	44
H= 5, L= 8		
0	140	-198
1	140	128
2	72*	108
3	75*	73
4	254	231
5	81*	-68
6	85*	-96
7	91*	90
8	95*	-97
H= -5, L= 8		
0	140	-149
1	65*	-124
2	254	260
3	139	-128
4	322	328
5	74*	43
6	82*	-149
7	88*	-12
8	91*	-76
9	97*	-72
H= 5, L= 9		
1	178	-202
2	226	261
3	72*	-70
4	78*	-18
5	86*	-44
6	85*	-11
7	90*	-66
8	94*	160
H= -5, L= 9		
1	238	-267
2	64*	17
3	127	74
4	72*	-54
5	77*	-8
6	82*	-19
7	224	-226
8	90*	-2
9	93*	-37
H= 5, L= 10		
0	185	184
1	100*	126
2	90*	-47
3	104*	92
4	110*	-85
5	116*	-97
6	121*	103
H= -5, L= 10		
0	85*	-87
1	90*	114
2	89*	-1
3	93*	39
4	103*	86
5	109*	-136
6	110*	3
H= 6, L= 0		
0	64*	-41
1	451	470
2	66*	139
3	247	254
4	72*	170
5	339	-342
6	73*	66
7	74*	58
8	77*	58
9	208	223
H= 6, L= 1		
1	66*	-110
2	532	534
3	613	-612
4	254	-262
5	74*	-136
6	283	-285
7	76*	74
8	212	242
9	85*	-139
H= -6, L= 1		
1	597	-636
2	245	-259
3	312	312
4	67*	2
5	73*	-95
6	73*	52
7	322	-337
8	76*	-91
9	81*	87
H= 6, L= 2		
0	139	162
1	68*	57
2	391	-426
3	69*	145
4	613	-619
5	68*	-25
6	73*	45
7	71*	-63
8	77*	83
9	81*	93
H= -6, L= 2		
0	845	-868
1	68*	165
2	302	-317
3	66*	51
4	68*	75
5	71*	-142
6	401	-420
7	73*	3
8	329	-340
9	77*	41
H= 6, L= 3		
1	217	205
2	161	-178
3	332	-332
4	249	251
5	130	-123
6	156	115
7	279	269
8	78*	-111
9	82*	-15
H= -6, L= 3		
1	191	-196
2	435	439
3	135	128
4	187	-189
5	68*	40
6	280	-290
7	172	-173
8	173	153
9	75*	6
H= 6, L= 4		
0	69*	-57
1	244	-237
2	70*	-71
3	221	-193
4	73*	-95
5	265	242
6	75*	-10
7	74*	41
8	85*	97
9	179	-194
H= -6, L= 4		
0	70*	-90
1	219	236
2	68*	-72
3	70*	132
4	70*	-29
5	330	-347
6	74*	73
7	143	-101
8	160	97
9	88*	175
H= 6, L= 5		
1	358	-362
2	303	-344
3	77*	-42
4	146	135
5	163	-122
6	258	267
7	198	-185
8	88*	-115
9	87*	45
H= -6, L= 5		
1	69*	-2
2	184	146
3	478	-493
4	147	-104
5	204	-181
6	80*	-87
7	86*	150
8	86*	57
9	95*	-89
H= 6, L= 6		
0	397	-406
1	127	-115
2	72*	-105
3	73*	-20
4	74*	72
5	79*	132
6	209	-228
7	84*	30
8	175	-190
H= -6, L= 6		
0	151	184
1	65*	-49
2	320	-312
3	69*	-71
4	490	-502
5	71*	22
6	73*	4
7	79*	-2
8	84*	9
9	87*	-59
H= 6, L= 7		
1	170	-190
2	139	125
3	205	226
4	168	-98
5	74*	47
6	81*	-58
7	85*	-133
8	86*	74
H= -6, L= 7		
1	62*	58
2	303	-309
3	179	-188
4	68*	96
5	69*	-29
6	76*	80
7	168	130
8	199	-173
H= 6, L= 8		
0	195	-192
1	211	202
2	75*	-98
3	82*	105
4	84*	3
5	154	-138
6	87*	2
7	161	59
8	96*	-12
H= -6, L= 8		
0	69*	-88
1	196	-189
2	70*	4
3	73*	-101
4	75*	28
5	178	181
6	83*	-16
7	90*	3
8	95*	50
H= 6, L= 9		
1	75*	-54
2	166	189
3	225	-252
4	81*	-59
5	87*	-55
6	175	-113
7	91*	-6
H= -6, L= 9		
1	328	-326
2	71*	-95
3	71*	20
4	77*	-52
5	85*	-141
6	85*	24
7	215	-217
8	93*	-16
H= 6, L= 10		
0	108*	75
1	107*	19
2	111*	-69
3	111*	28
4	115*	-126
5	120*	-41
6	124*	36
H= -6, L= 10		
0	222	-269
1	96*	30
2	100*	-59
3	104*	-15
4	108*	70
5	111*	-88
6	119*	-122
H= 7, L= 0		
0	441	460
1	369	356

Table 5 (*cont.*)

K	FO	FC
H= 7, L= 0		
2	69*	90
3	73*	47
4	70*	13
5	437	-452
6	230	227
7	77*	-43
8	79*	55
9	171	150
H= 7, L= 1		
1	70*	105
2	69*	66
3	424	-435
4	71*	46
5	161	-118
6	75*	-113
7	206	210
8	78*	-10
H= -7, L= 1		
1	69*	-41
2	381	-390
3	67*	105
4	300	308
5	73*	67
6	334	343
7	73*	-17
8	79*	-131
9	80*	9
H= 7, L= 2		
0	186	185
1	171	-182
2	176	-183
3	69*	-73
4	356	-355
5	126	107
6	74*	93
7	135	-97
8	147	125
H= -7, L= 2		
0	760	-826
1	146	-111
2	189	-179
3	65*	-53
4	68*	90
5	165	145
6	307	-300
7	77*	51
8	80*	-102
H= 7, L= 3		
1	68*	85
2	406	-393
3	67*	0
4	69*	-53
5	71*	-19
6	74*	127
7	77*	97
8	211	-212
H= -7, L= 3		
1	149	-160
2	151	164
3	348	342
4	67*	-48
5	73*	122
6	76*	-29
7	200	-202
8	79*	93
H= 7, L= 4		
0	69*	20
1	316	-292
2	130	135
3	203	-195
4	198	159
5	202	224
6	76*	0
7	78*	-26
8	82*	29
H= -7, L= 4		
0	70*	83
1	308	321
2	145	176
3	233	206
4	235	222
5	217	-212
6	73*	28
7	75*	63
8	82*	-40
H= 7, L= 5		
1	210	-221
2	76*	-98
3	150	134
4	77*	55
5	78*	-3
6	79*	54
7	204	-207
8	87*	-29
H= -7, L= 5		
1	186	-152
2	332	347
3	138	-152
4	76*	-10
5	79*	-86
6	161	-146
7	85*	32
8	187	169
H= 7, L= 6		
0	418	-412
1	73*	81
2	73*	-13
3	76*	-46
4	79*	145
5	202	-188
6	87*	-157
7	85*	-18
H= -7, L= 6		
0	70*	50
1	69*	107
2	185	-201
3	139	106
4	257	-270
5	72*	-17
6	77*	62
7	85*	29
8	85*	64
H= 7, L= 7		
1	70*	20
2	178	189
3	76*	122
4	165	-157
5	156	127
6	86*	-157
7	83*	43
H= -7, L= 7		
1	240	241
2	69*	-85
3	162	-146
4	71*	1
5	72*	9
6	80*	43
7	184	174
8	84*	-37
H= 7, L= 8		
0	84*	168
1	212	147
2	82*	-14
3	87*	70
4	87*	-26
5	94*	-168
6	91*	87
7	93*	-24
H= -7, L= 8		
0	180	176
1	159	-162
2	75*	35
3	77*	-28
4	80*	-29
5	191	213
6	89*	84
7	92*	16
8	92*	73
H= 7, L= 9		
1	82*	10
2	82*	-3
3	153	-149
4	87*	-7
5	89*	-55
6	94*	-81
H= -7, L= 9		
1	203	-161
2	77*	-122
3	78*	-86
4	86*	149
5	85*	-77
6	94*	175
7	91*	-53
H= 7, L= 10		
0	114*	60
1	114*	-68
2	117*	-25
3	118*	-15
4	123*	-81
H= -7, L= 10		
0	107*	-194
1	104*	-24
2	108*	-20
3	111*	-46
4	114*	46
5	116*	19
6	124*	-85
H= 8, L= 0		
0	530	527
1	69*	19
2	151	124
3	71*	82
4	73*	-73
5	72*	-16
6	286	285
7	77*	-53
8	180	192
H= 8, L= 1		
1	269	258
2	136	-155
3	165	-163
4	72*	40
5	75*	-35
6	75*	41
7	211	211
H= -8, L= 1		
1	287	281
2	284	-291
3	71*	29
4	177	195
5	138	102
6	245	212
7	82*	83
8	82*	-92
H= 8, L= 2		
0	72*	114
1	243	-231
2	70*	12
3	208	-213
4	74*	-122
5	76*	152
6	75*	-33
H= -8, L= 2		
0	173	-142
1	288	-291
2	67*	-26
3	71*	-71
4	70*	40
5	337	356
6	77*	-105
7	76*	3
H= 8, L= 3		
1	151	136
2	267	-278
3	177	172
4	77*	105
5	76*	96
6	77*	139
7	79*	4
H= -8, L= 3		
1	121	-109
2	72*	-109
3	386	371
4	71*	44
5	74*	113
6	75*	84
7	80*	-87
H= 8, L= 4		
0	76*	-29
1	72*	-72
2	186	247
3	73*	-18
4	363	349
5	80*	70
7	82*	18
H= -8, L= 4		
0	70*	-1
1	73*	102
2	296	294
3	74*	54
4	399	411
5	75*	-54
6	75*	30
7	84*	48
H= 8, L= 5		
1	187	-200
2	77*	52
3	213	214
4	82*	-114
5	86*	0
6	88*	-67
7	92*	-166
H= -8, L= 5		
1	74*	34
2	264	245
3	79*	57
4	149	-89
5	80*	31
6	82*	-101
7	86*	-89
H= 8, L= 6		
0	77*	-29
1	150	167
2	78*	27
3	79*	39
4	83*	91
5	185	-203
6	83*	15
H= -8, L= 6		
0	70*	50
1	212	200
2	73*	-19
3	79*	150
4	77*	-31
5	83*	-139
6	81*	11
7	85*	15
H= 8, L= 7		
1	235	222
2	175	174
3	81*	96
4	83*	-52
5	84*	132
H= -8, L= 7		
1	235	220
2	140	118
3	75*	-1
4	76*	25
5	78*	60
6	83*	-34
7	216	169
H= 8, L= 8		
0	221	167
1	83*	-14
2	86*	14
3	88*	12
4	92*	-69
5	91*	-20
H= -8, L= 8		
0	345	333
1	79*	-41
2	83*	100
3	84*	-36
4	88*	-14
5	89*	31
6	95*	138
H= 8, L= 9		
1	86*	55
2	88*	-53
3	92*	-91
4	90*	35
5	90*	-33
H= -8, L= 9		
1	82*	38
2	154	-114
3	85*	-46
4	181	91
5	88*	-31
6	92*	95
H= 8, L= 10		
0	121*	105
1	125*	-45
H= -8, L= 10		
0	111*	-21
1	113*	-89
2	113*	22
3	116*	-9
4	119*	30
H= 9, L= 0		
0	390	383
1	72*	-63
2	75*	99
3	72*	-15
4	76*	-98
5	78*	93
6	84*	133
H= 9, L= 1		
1	148	101
2	175	-183
3	75*	-82
4	132	97
5	76*	-88
6	173	165
H= -9, L= 1		
1	144	162
2	72*	-68
3	248	-211
4	71*	-59
5	74*	-14
6	78*	42
H= 9, L= 2		
0	77*	-161
1	167	-152
2	141	-174
3	72*	-22
4	75*	-52
5	233	227
6	80*	-76
H= -9, L= 2		
0	71*	-2
1	193	-187
2	74*	-127
3	75*	-114
4	76*	-156
5	79*	130
6	75*	-31
H= 9, L= 3		
1	72*	-58
2	76*	-75
3	271	272
4	75*	51
5	79*	91
H= -9, L= 3		
1	70*	6
2	303	-288
3	77*	134
4	76*	70
5	75*	25
6	76*	54
H= 9, L= 4		
0	156	-157
1	75*	50
2	179	146
3	76*	-1
4	216	220
5	73*	-53
H= -9, L= 4		
0	73*	-99
1	76*	-66
2	180	204
3	77*	-45
4	258	282
5	77*	51
6	74*	-29
H= 9, L= 5		
1	146	-118
2	226	208
3	85*	-33
4	84*	-55
5	88*	-13
H= -9, L= 5		
1	236	-193
2	81*	81
3	85*	111
4	82*	-33
5	87*	3
6	80*	-34
H= 9, L= 6		
0	82*	82
1	87*	132
2	85*	-37
3	85*	101
4	90*	-40
H= -9, L= 6		
0	77*	-67
1	80*	92
2	81*	-64
3	80*	-5
4	84*	-14
5	189	-181
H= 9, L= 7		
1	82*	117
2	79*	12
3	85*	-76
H= -9, L= 7		
1	176	160
2	140	121
3	78*	18
4	81*	-85
5	80*	37
H= 9, L= 8		
0	91*	98
1	92*	-19
2	90*	-14
3	93*	14
H= -9, L= 8		
0	173	173
1	64*	53
2	88*	41
3	89*	44
4	90*	-51
5	96*	-36
H= 9, L= 9		
1	91*	23
2	91*	-34
H= -9, L= 9		
1	85*	19
2	89*	-37
3	156	-121
4	89*	-3
5	91*	-46
H= -9, L= 10		
0	123*	9
2	123*	-23
H= 10, L= 0		
0	81*	146
1	77*	-101
2	76*	36
3	79*	-39
4	80*	-44
H= 10, L= 1		
1	195	-163
2	144	-133
3	78*	-71
H= -10, L= 1		
1	74*	63
2	77*	28
3	172	-164
4	75*	-27
5	84*	-89
H= 10, L= 2		
0	361	-347
1	80*	-81
2	78*	-83
3	78*	-45
H= -10, L= 2		
0	74*	11
1	72*	-37
2	228	-221
3	79*	-49
4	247	-271
H= 10, L= 3		
1	79*	-75
2	79*	26
3	205	179
H= -10, L= 3		
1	76*	-36
2	147	-158
3	77*	-132
4	78*	16
H= 10, L= 4		
0	81*	-81
1	174	153
2	81*	-32
3	85*	86
H= -10, L= 4		
0	81*	-3
1	164	-160
3	84*	-108
4	84*	114
H= 10, L= 5		
1	89*	-66
2	95*	135
H= -10, L= 5		
1	217	-182
2	85*	-38
3	80*	67
4	87*	23
H= -10, L= 6		
0	323	-305
1	82*	62
2	87*	-110
3	83*	33
H= -10, L= 7		
1	79*	-12
2	80*	57
3	82*	37
H= -10, L= 8		
0	91*	62
1	87*	48
2	90*	-12
3	90*	4
H= -10, L= 9		
1	87*	-21
2	89*	36

similar to the As_2O_3 structure, the corresponding S–As–S angles are 114 ± 2°.

The As–S(1)–C(1) and As–S(2)–C(4) bond angles are 95·0 ± 0·5 and 99·5 ± 0·4° respectively. These angles agree with angles about apical sulphur atoms in five- and six-membered heterocyclic rings containing adjacent arsenic or carbon atoms. The two C–S distances are each 1·83 ± 0·02 Å compared to the value of 1·812 Å (Abrahams, 1956) for a pure, single carbon–sulphur bond.

None of the three carbon–carbon distances differ significantly from the accepted distance between two sp^3 carbon atoms of 1·541 Å (Sutton, 1958). The C(2)–O(1) and C(3)–O(2) bond distances of 1·45 ± 0·02 and 1·43 ± 0·02 Å respectively, agree with the accepted carbon–oxygen single bond length of 1·43 ± 0·01 Å (Sutton, 1958).

Table 6. *Interatomic distances**

Atom 1	Atom 2	Distance (Å)	E.s.d.
As	S(1)	2·237	0·004
As	S(2)	2·247	0·004
As	O(1)	1·83	0·01
S(1)	C(1)	1·83	0·01
S(2)	C(4)	1·83	0·01
O(1)	C(2)	1·45	0·02
O(2)	C(3)	1·43	0·02
C(1)	C(2)	1·50	0·02
C(2)	C(3)	1·53	0·02
C(3)	C(4)	1·53	0·02
C(1)	H(11)	0·64	0·13
C(1)	H(12)	0·89	0·12
C(2)	H(21)	0·76	0·13
C(3)	H(31)	0·72	0·12
C(4)	H(41)	0·93	0·11
C(4)	H(42)	0·94	0·11
O(2)	H(5)	0·74	0·15

* The calculation of bond distances and e.s.d.'s was performed using *NRC*-12 (Ahmed, 1967).

Table 7. *Interbond angles**

	Angle	E.s.d.
S(1)–As—S(2)	101·2°	0·1°
S(1)–As—O(1)	89·1	0·3
S(2)–As—O(1)	97·1	0·3
As—S(1)–C(1)	95·0	0·5
As—S(2)–C(4)	99·5	0·5
As—O(1)–C(2)	113·6	0·7
S(1)–C(1)–C(2)	112·1	1·0
O(1)–C(2)–C(1)	108·7	1·0
O(1)–C(2)–C(3)	110·9	1·0
C(1)–C(2)–C(3)	116·3	1·1
O(2)–C(3)–C(2)	103·3	1·0
O(2)–C(3)–C(4)	109·0	1·0
C(2)–C(3)–C(4)	115·8	1·1
S(2)–C(4)–C(3)	114·4	1·0

* The calculation of angles and e.s.d.'s was performed using NRC-12.

The As–O(1)–C(2) angle has a value of 103·3 ± 1·0° compared to the As–O–As angle of 126 ± 3° in arsenic trioxide, and the C–O–C angle of 109·5 ± 1·5° in 1,4-dioxan (Kimura & Aoki, 1951).

Two apparent anomalies occur in bond angles about carbon atoms. In the seven-membered ring, the bond angles S(1)–C(1)–C(2), C(1)–C(2)–C(3), C(2)–C(3)–C(4), and C(3)–C(4)–S(2) are larger than the tetrahedral value of 109·5°, and they fall in the range 112·1 to 116·3°. The angles O(1)–C(2)–C(3) and O(1)–C(2)–C(1) are approximately tetrahedral, since the oxygen atom is contained in both five- and six-membered rings. This suggests that the carbon chain is stretched open, because of ring expansion due to the longer As–S and S–C bonds. The second anomaly is the disagreement between the C(2)–C(3)–O(2) and C(4)–C(3)–O(2) angles: 103·3 ± 1·0 and 109·0 ± 1·0° respectively. The reason for this discrepancy is not apparent.

The bond distances to hydrogen atoms are included for completeness in Table 6. A Hamilton (1965) test showed that inclusion of the hydrogen atoms did improve the calculated model. Bond angles containing hydrogen atoms were approximately tetrahedral but were not considered meaningful because their e.s.d.'s were in general 10% of the calculated values.

An examination of the structure for intermolecular contacts revealed an intermolecular hydrogen bond between the hydroxyl oxygen atom and the bridging oxygen atom of the molecule related by the screw axis at $(\frac{1}{2}, 0, \frac{1}{4})$. The structure is held together in the **y** direction by an infinite chain of hydrogen bonds joining molecules related by the diad axis. This is shown in the projection diagrams in Figs. 2 and 3. The presence of this hydrogen bond was shown directly by the presence of a peak of 0·5 e.Å^{-3} in the difference Fourier, as well as indirectly by the short intermolecular contact of 2·81 ± 0·01 Å between O(2) and the bridging oxygen atom [O(1)] of the molecule related by the twofold screw axis.

Discussion

If the results of this structure determination are applied to the arsenite complexes of the other dithiol compounds examined by Zahler & Cleland, it is possible to propose a plausible bicyclic structure for each of them. These structures are shown in Fig. 4. The arsenite–DTT complex [Fig. 4(*c*)], as determined in this study, has a five-, six- and seven-membered bicyclic ring structure. The six-membered ring (containing As, S and O as heterocyclic atoms) has a chair conformation with an equatorial hydroxyl group on C(3). A consideration of the similarity of the dissociation constants of arsenite–DTT and arsenite–DTE indicates that a similar bicyclic structure is most probable for the arsenite–DTE complex. This has been shown in Fig. 4(*d*). The only difference is the epimerization at C(3), with the result that the hydroxyl group on this carbon atom is now axial.

In constructing models for the bicyclic arsenite complexes of 1,2-dithioglycerol and 1,3-dithioglycerol, Fig. 4(*a*) and (*b*) respectively, it was found that both of these complexes have a six-membered ring in a boat conformation with the As and C(2) of the carbon chain as the 'bow' and 'stern'. As is evident from the diagrams there is little difference between these two structures. There is one possible explanation for the difference in stabilities of these two compounds. In the 1,3-dithioglycerol complex, the bridging atom between the two five-membered rings is oxygen. The C(2)–O distance of 1·45 Å is considerably shorter than the C(2)–S distance of 1·83 Å. Owing to this large difference, the axial hydrogen atoms on C(1) and C(3) are in very close proximity (H···H ≃ 2·1 Å). This close approach is not evident in the 1,2-dithioglycerol complex, where the corresponding distance is approximately 2·5 Å. However, it is evident that, in order to derive a satisfactory explanation for the observed variation in stability amongst these several compounds, their three-dimensional structures should be determined.

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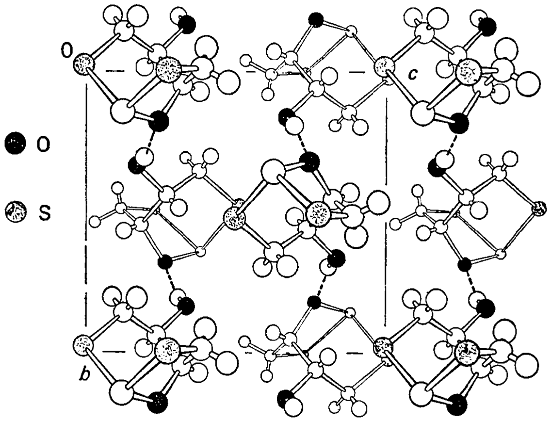

Fig. 3. Projection onto (100). Dashed line as for Fig. 2.

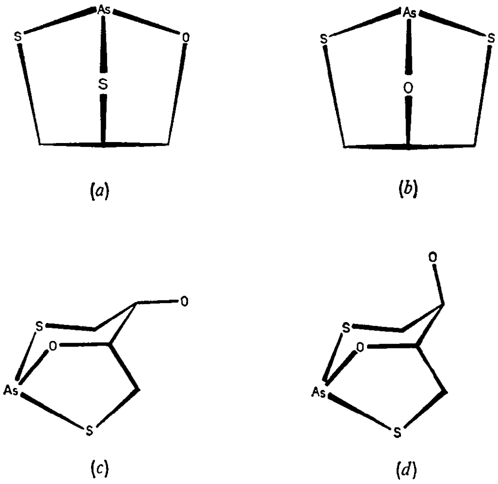

Fig. 4. Proposed arsenite dithiol structures; (*a*) 1,2-dithioglycerol, (*b*) 1,3-dithioglycerol, (*c*) dithiothreitol (by this work), (*d*) dithioerythritol.

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Refinement of the Crystal Structures of $(C_6H_5)_4AsI_3$ and CsI_3 at 20°C and at –160°C

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Three-dimensional intensity data have been collected both at room temperature and at -160°C for the triiodides CsI_3 and $(C_6H_5)_4AsI_3$. The present work confirms the conclusion of Tasman & Boswijk [*Acta Cryst.* (1955), **8**, 59] regarding the asymmetry and non-linearity of the I_3^- ion in CsI_3. The bond lengths in the symmetric I_3^- ions in $(C_6H_5)_4AsI_3$ [2·919 (1) Å] are somewhat longer than the values reported by Mooney-Slater [*Acta Cryst.* (1959), **12**, 187], but are still shorter than the average I–I bond lengths observed for $(C_2H_5)_4NI_3$(I) and $(C_2H_5)_4NI_3$(II), 2·935 and 2·936 Å respectively. The I–I bond lengths observed in different triiodides are compared, and the differences are discussed.

Introduction

The configurations of I_3^- ions in different crystals have aroused considerable interest (Brown & Nunn, 1966; Migchelsen & Vos, 1967; Wiebenga & Kracht, 1969). The bond lengths and angles known with reasonable accuracy at the beginning of the present study are given in Table 1(*a*). The Table shows that for $(C_2H_5)_4NI_7$ the I–I bond length is significantly shorter than the average I–I bond lengths observed for the compounds $(C_2H_5)_4NI_3$(I) and $(C_2H_5)_4NI_3$(II). This does not hold for $(C_6H_5)_4AsI_3$ for which the bonds had been reported to be relatively short (Mooney-Slater, 1959; Rundle, 1961). The presence of the short distances in $(C_2H_5)_4NI_7$ at -195°C cannot be attributed to the electrostatic crystal field as for all symmetric I_3^- ions the calculated bond orders are independent of this field (Wiebenga & Kracht, 1969). We have therefore tentatively assumed the presence of the short I–I bonds in $(C_2H_5)_4NI_7$ at -195°C to be due to either a shrinkage of the weak I–I bonds at low temperature or to complex formation (the I_3^- ions have strong interactions with neighbouring I_2 molecules). To get more insight in this problem we have refined the crystal structures of $(C_6H_5)_4AsI_3$, having symmetric I_3^- ions, and of CsI_3, having asymmetric I_3^- ions, both at room and at low temperature.

Discussion of the I–I bond lengths

Influence of the temperature

The I–I bond lengths and angles observed in $(C_6H_5)_4AsI_3$ and in CsI_3 at room temperature and at low temperature, are given in Table 1(*b*). We see that in both compounds the bond lengths at low temperature are equal to those at room temperature, so that it can be concluded that no shrinkage of the bonds occurs at low temperature.

Symmetric I_3^- ions

Comparison of the bond lengths in the different symmetric I_3^- ions in Table 1 shows that there are significant differences between the lengths of the bonds. Values increasing from 2·904 to 2·943 Å are observed when going from $(C_2H_5)_4NI_7$ *via* $(C_6H_5)_4AsI_3$ and $(C_2H_5)_4NI_3$(I) (ion *A*) to $(C_2H_5)_4NI_3$(I) (ion *B*). Consideration of the crystal structures shows that both for the I_3^- ion *B* in $(C_2H_5)_4NI_3$(I), having the longest I–I distance, and for the I_3^- ion in $(C_2H_5)_4NI_7$, having the