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The Crystal and Molecular Structure of α-Isosparteine Diperchlorate, $C_{15}H_{26}N_2.2HClO_4$*

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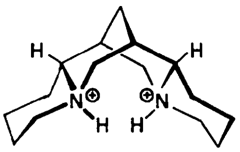
α-Isosparteine diperchlorate, $C_{15}H_{26}N_2.2HClO_4$, is orthorhombic, space group $C222_1$, with $a=9.902$ (3), $b=13.510$ (4) and $c=14.480$ (4) Å; $Z=4$. The molecule consists of four fused six-membered rings in the chair form; a twofold axis passes through the methylene bridge atom. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to $R=0.055$ for 879 observed reflexions. The α-isosparteine molecule straddles one of the ClO_4^- ions, to which it is hydrogen bonded.

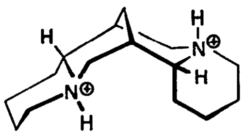
Introduction

The structure of α-isosparteine monohydrate, a lupin alkaloid, was solved by Przybylska & Barnes (1953). It was shown to consist of four chair rings with a twofold axis passing through the bridging atom. The diperchlorate of α-isosparteine was therefore expected to have the structure (I); however, because of the presence of considerable strain due to the repulsion between the N^+–H atoms, the structure (II) was considered as an alternative.



$2\,ClO_4^-$

(I)



$2\,ClO_4^-$

(II)

In (II), an inversion at one of the nitrogen atoms converts one of the inner rings to a boat form. Such inversion has indeed been shown to take place readily in solution in some derivatives of sparteine (Wiewiórowski, Edwards & Bratek-Wiewiórowska, 1967; Pellón, Mosquera, Castedo & Ribas, 1969).

The preliminary examination of the α-isosparteine diperchlorate crystals and the determination of the space group revealed twofold symmetry of the molecule. The structure (II) was therefore eliminated. However, because of the strain in the molecule it was important to obtain the structural details.

Experimental

Crystal data

$C_{15}H_{26}N_2.2HClO_4$, F.W. 435·30, m.p. 252–257 °C (dec. uncorr.), orthorhombic sphenoids, space group: $C222_1$;
$a=9.902$ (3), $b=13.510$ (4), $c=14.480$ (4) Å,
$V=1936.7$ Å^3, $Z=4$, $F(000)=920$.
$D_x=1.493$ g cm^{-3},
$D_m=1.485$ g cm^{-3} by flotation in carbon tetrachloride and toluene.
μ(Mo $K\alpha$) $=3.9$ cm^{-1}.

The crystals of α-isosparteine diperchlorate were prepared by Dr M. Wiewiórowski by adding concentrated aqueous perchloric acid to a methanolic solution of α-isosparteine monohydrate until the solution was acid to Congo red (Cockburn & Marion, 1951). Colourless crystals were obtained on slow cooling of a saturated solution in methanol.

Preliminary study of the crystals was carried out with precession films and the cell dimensions were measured on a diffractometer with Cu and Mo radiation. Since there are eight equivalent positions in the space group $C222_1$, each molecule must possess a twofold axis.

The crystal was cut into a sphere of 0·46 mm diameter and mounted with c along the φ axis. The data were collected at room temperature on a Picker four-circle automatic diffractometer with Mo radiation and a Nb filter. The $\theta/2\theta$ scanning method was used at a take-off angle of 5°. The scan was 2° in 2θ and the speed was 2° min^{-1}. Background measurements for 20 s were taken at each end of the scans. High intensities were remeasured with an extra thickness of Nb foil and, if necessary, attenuated with lower current settings. A standard reflexion was measured after every 30–50 reflexions.

The threshold was taken as a net count of 100 or 5% of the background, whichever was higher. 1266 reflexions were measured within $2\theta \sim 55°$ ($\sin^2\theta_{\max}=0.212$) but only 879 (69%) were observed above threshold.

The intensities were corrected for Lorentz and polarization factors but absorption corrections were considered unnecessary because the linear absorption coefficient was small and the crystal was spherical.

Solution of the structure and its refinement

The scale and overall isotropic temperature factors were evaluated by Wilson's method (1942).

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A sharpened Patterson synthesis revealed the position of the chlorine atoms, and the locations of the non-hydrogen atoms with the exception of the four oxygen atoms of one ClO_4 group were derived from the subsequent electron density maps.

The least-squares refinement began when R was 0·32 and continued until it decreased to 0·20. At this stage a difference map was computed in order to locate O(3), O(4), O(5) and O(6) of the ClO_4^- ion straddled by the isosparteine molecule. The distribution of peaks of $\frac{1}{2}$ oxygen height indicated the presence of positional disorder of that ClO_4 group. A thorough examination of the systematic absences of the space group $C222_1$ was then carried out with Cu radiation and a General Electric XRD-5 manual diffractometer, but the results were inconclusive. Two orientations of ClO_4 were therefore assumed to be present and the positions of the oxygen atoms were assigned by fitting a tetrahedral model as well as possible to the electron density map. In three more cycles R of 0·13 was obtained and the anisotropic refinement of the non-hydrogen atoms was undertaken. Four additional cycles brought R to 0·09. At this stage another difference map yielded the positions of all the hydrogen atoms. The final value of R was 0·055 and the maximum atomic shift was 0·4 of the e.s.d.'s.

The refinement was carried out by block-diagonal least-squares calculations, utilizing only the observed reflexions, and minimizing the quantity $\sum_w(|F_o|-|F_c|)^2$ where $w=1/\{|F_o|+10·24+0·01|F_o|^2\}$ and $4·5 \le |F_o| \le 213·2$.

The final parameters with their e.s.d.'s of the non-hydrogen atoms are presented in Table 1. The coordinates and the isotropic temperature factors of the hydrogen atoms are given in Table 2. The observed and calculated structure factors for all measured reflexions are listed in Table 3. Only two observed reflexions (020, 350) had their $|\Delta F|/|F_o| > 3R$. Their high observed values were probably due to multiple diffraction. All the unobserved reflexions have $|F_c| \le 1·5|F_{\text{threshold}}|$.

Table 2. *Fractional coordinates* (×10³) *with e.s.d.'s and temperature factors for the hydrogen atoms*

The number of the parent atom is obtained by omitting the last digit.

	x/a	y/b	z/c	B(Å²)
H(11)	391 (5)	369 (3)	235 (3)	1·9
H(21)	160 (6)	405 (4)	267 (4)	3·9
H(22)	144 (4)	312 (3)	217 (3)	1·0
H(31)	248 (12)	490 (9)	138 (8)	12·4
H(32)	110 (7)	440 (5)	125 (5)	5·5
H(41)	240 (5)	392 (4)	0 (3)	2·7
H(42)	169 (6)	292 (5)	045 (5)	5·6
H(51)	434 (7)	386 (6)	059 (5)	6·7
H(52)	405 (5)	279 (3)	9 (4)	2·4
H(61)	329 (6)	203 (4)	150 (4)	4·1
H(71)	539 (6)	155 (4)	112 (4)	3·5
H(81)	398 (6)	092 (4)	232 (4)	3·8
H(101)	351 (6)	323 (5)	370 (4)	4·6
H(102)	321 (5)	240 (4)	332 (4)	3·2

All calculations were carried out with the aid of the NRC crystallographic computer programs (Ahmed, Hall, Pippy & Huber, 1966). The scattering factors were those of Cromer & Waber (1965) for Cl^-, Hanson, Herman, Lea & Skillman (1964) for C, O & N, and Stewart, Davidson & Simpson (1965) for H.

An effort was made to determine the absolute configuration from all data, but owing to small anomalous dispersion corrections for Mo radiation (Cromer, 1965) and the fact that Cl atoms are situated on twofold axes, the application of Hamilton's (1965) test did not lead to any conclusive results.

Discussion

Molecular structure

A parallel projection of the α-isosparteine molecule is presented in Fig. 1. It was obtained with Johnson's (1965) *ORTEP* program and shows thermal ellipsoids enclosing the 50% probability level. The bond lengths and angles of the cation are shown in Fig. 2.

Table 1. *Final fractional coordinates and vibration tensor components for the expression* $T=\exp\{-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{12}a^*b^*hk)\}$ *and their e.s.d.'s* (*all quantities* ×10⁴)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	U_{12}
Cl(1)	1987 (2)	5000	5000	520 (10)	453 (9)	493 (10)	142 (20)	0	0
Cl(2)	5000	5860 (1)	2500	542 (11)	329 (8)	794 (14)	0	94 (24)	0
O(1)	2800 (11)	4185 (7)	4967 (6)	2800 (109)	1873 (84)	1129 (54)	−109 (129)	489 (179)	3184 (174)
O(2)	1346 (12)	4939 (9)	5826 (8)	2132 (94)	1917 (82)	1773 (85)	−35 (170)	2569 (163)	−117 (191)
O(3)	4751 (12)	4875 (6)	2849 (7)	755 (78)	283 (33)	1130 (96)	38 (81)	−445 (139)	−120 (92)
O(4)	6407 (12)	5867 (11)	2236 (10)	535 (60)	1322 (99)	1296 (104)	658 (183)	148 (130)	−255 (134)
O(5)	4182 (15)	6174 (10)	1827 (12)	1271 (122)	784 (72)	1932 (146)	793 (189)	−1849 (232)	419 (152)
O(6)	5107 (23)	6510 (7)	3286 (9)	2301 (161)	489 (50)	957 (81)	−392 (118)	259 (219)	−143 (210)
N(1)	3432 (4)	3181 (3)	2324 (3)	296 (19)	328 (18)	434 (24)	−117 (38)	−66 (34)	35 (32)
C(2)	1975 (6)	3572 (5)	2206 (5)	285 (25)	571 (33)	845 (45)	−322 (64)	−150 (61)	91 (54)
C(3)	1872 (7)	4165 (5)	1357 (6)	540 (39)	476 (32)	1006 (52)	−46 (73)	−745 (78)	316 (66)
C(4)	2333 (8)	3595 (6)	517 (5)	807 (53)	734 (45)	610 (38)	75 (78)	−632 (78)	−157 (83)
C(5)	3789 (8)	3209 (5)	642 (4)	687 (41)	592 (36)	459 (31)	131 (60)	−275 (60)	24 (71)
C(6)	3833 (6)	2566 (4)	1496 (3)	420 (29)	340 (24)	348 (24)	−206 (44)	−113 (45)	−50 (46)
C(7)	5163 (6)	2029 (3)	1669 (3)	513 (32)	358 (23)	304 (22)	−113 (43)	33 (47)	159 (54)
C(8)	5000	1351 (5)	2500	633 (49)	296 (31)	420 (36)	0	−103 (82)	0
C(10)	3579 (6)	2649 (4)	3231 (4)	404 (28)	539 (32)	348 (24)	−53 (51)	97 (47)	−152 (52)

Table 3. *Observed and calculated structure factors* (× 10)

Reflexions too weak to be measured are marked with an asterisk.

L	FO	FC
H= 0, K= 0		
2	1243	1250
4	1614	1550
6	304	288
8	527	536
10	292	315
12	513	535
14	93	91
16	133	143
18	136	140
H= 0, K= 2		
0	235	186
1	144	135
2	1241	1158
3	1085	992
4	1032	980
5	489	446
6	279	278
7	141	142
8	652	687
9	52	49
10	551	512
11	146	155
12	43*	18
13	287	310
14	126	147
15	70	72
16	119	128
17	54*	25
18	56*	19
H= 0, K= 4		
0	242	241
1	770	776
2	839	877
3	727	679
4	672	675
5	1324	1248
6	906	877
7	436	430
8	36*	44
9	110	135
10	343	318
11	151	156
12	206	203
13	46*	71
14	122	137
15	50*	56
16	57*	9
17	55*	44
18	84	71
H= 0, K= 6		
0	221	227
1	372	378
2	528	556
3	333	296
4	342	356
5	103	113
6	229	183
7	164	157
8	173	136
9	111	105
10	317	289
11	44*	14
12	46*	10
13	48*	44
14	154	145
15	52*	25
16	54*	66
17	83	91
H= 0, K= 8		
0	408	436
1	426	412
2	230	242
3	447	446
4	79	83
5	544	548
6	433	430
7	155	171
8	42*	41
9	125	134
10	217	176
11	116	102
12	92	80
13	50*	29
14	81	95
15	54*	8
16	56*	28
H= 0, K= 10		
0	447	400
1	81	85
2	78	56
3	199	183
4	389	384
5	65	65
6	43*	13
7	62	48
8	294	261
9	47*	12
10	122	98
11	50*	40
12	169	148
13	53*	53
14	55*	29
15	57*	16
H= 0, K= 12		
0	516	521
1	44*	17
2	45*	65
3	45*	71
4	256	238
5	124	140
6	47*	4
7	86	88
8	271	252
9	50*	20
10	52*	7
11	53*	7
12	85	96
13	56*	0
H= 0, K= 14		
0	150	171
1	49*	24
2	49*	59
3	131	129
4	140	149
5	227	216
6	67	80
7	167	151
8	109	102
9	54*	29
10	56*	71
11	57*	21
H= 0, K= 16		
0	99	98
1	144	143
2	87	87
3	77	81
4	55*	48
5	55*	6
6	90	89
7	57*	31
H= 1, K= 1		
0	567	569
1	891	851
2	1400	1299
3	1213	1173
4	673	722
5	594	590
6	421	410
7	492	529
8	170	176
9	387	383
10	306	303
11	476	463
12	331	348
13	130	141
14	57	63
15	98	98
16	51*	15
17	54*	61
18	56*	39
H= 1, K= 3		
0	565	569
1	2132	2170
2	712	672
3	653	649
4	201	186
5	626	590
6	73	93
7	364	358
8	90	87
9	397	392
10	63	51
11	270	278
12	73	65
13	266	272
14	33	104
15	53*	77
16	90	88
17	111	116
18	56*	34
H= 1, K= 5		
0	413	452
1	435	475
2	142	120
3	159	148
4	149	152
5	606	607
6	583	557
7	582	577
8	168	171
9	170	161
10	41*	50
11	223	230
12	215	212
13	47*	11
14	69	72
15	105	124
16	53*	82
17	55*	64
H= 1, K= 7		
0	223	267
1	462	459
2	76	75
3	255	285
4	481	518
5	402	385
6	465	434
7	414	425
8	367	367
9	199	175
10	44*	68
11	173	147
12	84	91
13	110	113
14	51*	19
15	85	99
16	115	129
17	57*	20
H= 1, K= 9		
0	73	87
1	454	424
2	193	210
3	332	334
4	82	95
5	306	295
6	41*	39
7	261	274
8	44*	40
9	279	252
10	47*	24
11	118	113
12	50*	75
13	127	115
14	53*	37
15	55*	36
16	57*	19
H= 1, K= 11		
0	206	218
1	287	251
2	352	347
3	295	282
4	331	317
5	202	178
6	404	407
7	143	133
8	122	116
9	129	115
10	175	154
11	95	80
12	82	52
13	55*	68
14	56*	55
H= 1, K= 13		
0	146	157
1	125	119
2	211	216
3	176	165
4	48*	32
5	188	192
6	40*	54
7	78	86
8	51*	13
9	100	112
10	54*	69
11	110	119
12	57*	83
H= 1, K= 15		
0	175	190
1	186	191
2	52*	62
3	121	128
4	53*	30
5	104	99
6	54*	57
7	107	121
8	56*	25
9	129	118
H= 1, K= 17		
0	56*	18
1	115	100
2	56*	45
3	57*	55
4	117	111
H= 2, K= 0		
0	509	518
1	809	719
2	1799	1841
3	679	591
4	345	353
5	223	236
6	424	472
7	86	93
8	241	257
9	77	78
10	443	440
11	41*	65
12	150	143
13	260	275
14	231	248
15	80	77
16	52*	50
17	54*	6
18	79	64
H= 2, K= 2		
0	390	420
1	1804	1777
2	1044	1002
3	641	572
4	401	389
5	472	446
6	804	823
7	113	101
8	249	256
9	336	317
10	242	244
11	444	432
12	208	202
13	126	137
14	102	116
15	89	89
16	52*	39
17	94	94
18	113	85
H= 2, K= 4		
0	140	133
1	525	562
2	383	372
3	258	297
4	216	218
5	255	249
6	63	77
7	425	411
8	335	326
9	280	286
10	81	72
11	43*	63
12	321	317
13	158	167
14	49*	47
15	96	103
16	123	120
17	98	95
18	57*	35
H= 2, K= 6		
0	265	263
1	550	615
2	135	134
3	198	230
4	544	541
5	296	316
6	318	323
7	134	119
8	342	325
9	135	111
10	43*	80
11	141	130
12	184	171
13	102	112
14	50*	48
15	52*	47
16	54*	58
17	154	139
H= 2, K= 8		
0	216	192
1	338	361
2	305	295
3	211	223
4	177	168
5	60	64
6	194	197
7	411	424
8	42*	46
9	143	137
10	110	102
11	148	142
12	120	116
13	94	93
14	53*	26
15	54*	77
16	56*	46
H= 2, K= 10		
0	45	68
1	252	249
2	383	357
3	263	268
4	42*	47
5	184	189
6	306	307
7	213	196
8	222	199
9	150	142
10	186	175
11	84	89
12	52*	43
13	54*	22
14	78	87
15	57*	27
H= 2, K= 12		
0	50	54
1	142	143
2	258	245
3	71	84
4	83	87
5	73	69
6	299	305
7	49*	52
8	70	67
9	51*	37
10	74	51
11	54*	10
12	55*	69
13	108	107
H= 2, K= 14		
0	50*	4
1	50*	61
2	204	206
3	152	154
4	51*	44
5	83	88
6	87	95
7	123	127
8	54*	18
9	55*	86
10	56*	90
H= 2, K= 16		
0	116	120
1	157	160
2	54*	45
3	55*	42
4	90	117
5	56*	61
6	56*	3
7	57*	44
H= 3, K= 1		
0	1154	1179
1	423	462
2	99	95
3	336	358
4	244	260
5	247	316
6	120	113
7	365	412
8	305	314
9	145	155
10	106	104
11	245	238
12	173	172
13	140	117
14	75	90
15	50*	55
16	110	108
17	55*	61
18	57*	27
H= 3, K= 3		
0	1103	1094
1	484	469
2	361	306
3	422	401
4	298	303
5	326	349
6	140	121
7	286	312
8	258	254
9	177	171
10	97	81
11	77	88
12	254	272
13	105	98
14	49*	47
15	51*	49
16	82	81
17	55*	22
H= 3, K= 5		
0	527	436
1	295	285
2	716	783
3	228	220
4	167	182
5	80	93
6	247	254
7	105	94
8	105	110
9	84	100
10	433	430
11	84	97
12	80	81
13	117	110
14	133	138
15	81	76
16	54*	39
17	56*	48
H= 3, K= 7		
0	532	545
1	98	105
2	221	284
3	99	98
4	126	134
5	224	219
6	500	528
7	221	205
8	149	158
9	123	128
10	264	256
11	146	141
12	106	105
13	119	116
14	107	110
15	54*	39
16	56*	28
H= 3, K= 9		
0	305	311
1	250	232
2	200	216
3	450	435
4	309	325
5	660	668
6	219	230
7	426	437
8	326	321
9	175	155
10	129	111
11	49*	58
12	51*	41
13	53*	49
14	98	114
15	56*	53
H= 3, K= 11		
0	275	291
1	282	281
2	79	75
3	200	187
4	174	179
5	144	126
6	95	88
7	116	106
8	236	240
9	50*	20
10	51*	37
11	94	87
12	121	123
13	90	82
H= 3, K= 13		
0	313	348
1	250	240
2	151	143
3	173	180
4	219	223
5	118	117
6	51*	64
7	136	132
8	159	156
9	87	90
10	55*	28
11	147	138
H= 3, K= 15		
0	53*	58
1	47	59
2	125	125
3	53*	71
4	54*	29
5	54*	75
6	78	79
7	56*	58
8	57*	10
H= 3, K= 17		
0	130	119
1	57*	59
H= 4, K= 0		
0	89	70
1	174	151
2	76	55
3	416	450
4	566	589
5	68	74
6	85	85
7	132	168
8	346	355
9	282	305
10	41*	21
11	201	201
12	95	83
13	118	126
14	136	140
15	51*	5
16	76	55
17	56*	57
H= 4, K= 2		
0	716	727
1	761	751
2	408	415
3	399	436
4	333	331
5	292	293
6	109	113
7	274	306
8	228	217
9	242	251
10	112	93
11	363	350
12	84	80
13	156	151
14	74	78
15	106	114
16	54*	52
17	56*	56
H= 4, K= 4		
0	682	663
1	689	664
2	78	52
3	113	130
4	61	65
5	332	335
6	149	172
7	239	242
8	61	47
9	292	276
10	234	232
11	110	88
12	111	103
13	125	124
14	104	87
15	53*	88
16	55*	19
17	80	62
H= 4, K= 6		
0	62	46
1	518	552
2	84	87
3	116	100
4	311	335
5	285	299
6	593	579
7	357	369
8	227	243
9	258	238
10	117	128
11	134	122
12	48*	74
13	135	132
14	57*	16
15	54*	45
16	56*	53
H= 4, K= 8		
0	60	73
1	369	345
2	184	179
3	383	388
4	316	302
5	126	116
6	204	212
7	263	257
8	102	106
9	225	211
10	71	55
11	155	164
12	82	82
13	53*	69
14	54*	63
15	118	99
H= 4, K= 10		
0	186	219
1	291	280
2	90	83
3	150	164
4	44*	40
5	378	391
6	204	196
7	129	127
8	129	121
9	112	112
10	51*	23
11	52*	81
12	140	135
13	92	104
14	57*	39
H= 4, K= 12		
0	47*	9
1	47*	74
2	82	71
3	146	159
4	244	232
5	179	193
6	155	159
7	51*	33
8	144	147
9	100	115
10	54*	87
11	55*	70
12	57*	33
H= 4, K= 14		
0	279	296
1	103	107
2	86	106
3	109	96
4	52*	62
5	53*	54
6	54*	50
7	117	126
8	56*	31
9	57*	42
H= 4, K= 16		
0	97	105
1	56*	67
2	109	100
3	80	87
4	57*	41
5	57*	65
H= 5, K= 1		
0	364	380
1	376	378
2	396	440
3	99	98
4	175	160
5	184	207
6	383	403
7	59	55
8	125	136
9	125	115
10	216	225
11	103	97
12	173	188
13	136	115
14	188	176
15	53*	29
16	55*	60
17	57*	27
H= 5, K= 3		
0	446	411
1	358	341
2	398	394
3	269	257
4	246	225
5	270	264
6	332	331
7	258	261
8	324	322
9	215	232
10	243	244
11	74	77
12	109	115
13	142	135
14	51*	44
15	53*	51
16	55*	38
17	57*	14
H= 5, K= 5		
0	390	393
1	120	123
2	225	224
3	92	81
4	343	356
5	137	148
6	221	210
7	278	278
8	254	255
9	223	215
10	46*	51
11	179	184
12	237	241
13	88	99
14	53*	37
15	55*	3
16	87	74
H= 5, K= 7		
0	355	375
1	321	311
2	90	86
3	199	202
4	651	643
5	116	134
6	229	247
7	93	91
8	324	315
9	142	145
10	107	94
11	101	95
12	118	124
13	53*	42
14	54*	44
15	56*	34
H= 5, K= 9		
0	236	243
1	101	68
2	199	195
3	171	162
4	100	111
5	246	245
6	313	307
7	246	257
8	133	136
9	103	101
10	90	104
11	52*	25
12	109	102
13	55*	42
14	57*	51
H= 5, K= 11		
0	128	116
1	300	291
2	391	388
3	87	58
4	143	146
5	124	127
6	281	270
7	50*	71
8	51*	43
9	52*	48
10	157	151
11	95	107
12	56*	28
H= 5, K= 13		
0	51*	26
1	136	130
2	171	160
3	51*	15
4	52*	22
5	52*	26
6	109	114
7	87	63
8	95	94
9	93	102
10	85	85
H= 5, K= 15		
0	153	130
1	107	99
2	55*	6
3	86	96
4	109	114
5	101	94
6	57*	39
H= 6, K= 0		
0	943	941
1	201	194
2	789	844
3	347	342
4	408	380
5	244	228
6	195	201
7	297	318
8	330	330
9	128	137
10	81	86
11	252	260
12	251	251
13	50*	59
14	52*	69
15	54*	17
16	56*	30
H= 6, K= 2		
0	45	43
1	296	285
2	296	277
3	202	177
4	132	123
5	282	282
6	159	167
7	212	226
8	231	238
9	143	145
10	89	88
11	99	108
12	138	141
13	183	192
14	53*	79
15	84	98
16	56*	23
H= 6, K= 4		
0	37*	60
1	343	335
2	316	332
3	497	470
4	170	177
5	435	444
6	287	298
7	308	294
8	167	178
9	205	197
10	171	165
11	106	114
12	50*	83
13	52*	47
14	53*	11
15	82	68
16	57*	26
H= 6, K= 6		
0	40*	6
1	183	173
2	137	141
3	227	223
4	105	107
5	234	231
6	139	123
7	464	459
8	46*	53
9	141	137
10	148	146
11	89	80
12	52*	31
13	53*	57
14	55*	79
15	88	81
H= 6, K= 8		
0	212	199
1	259	260
2	185	173
3	300	309
4	86	86
5	228	214
6	147	147
7	215	211
8	48*	27
9	88	93
10	130	142
11	136	142
12	54*	10
13	55*	55
14	57*	18
H= 6, K= 10		
0	242	225
1	131	124
2	104	112
3	143	137
4	71	63
5	97	93
6	49*	36
7	105	103
8	97	87
9	102	113
10	83	80
11	55*	13
12	56*	46
H= 6, K= 12		
0	178	165
1	50*	64
2	110	105
3	104	100
4	141	149
5	137	135
6	94	85
7	53*	60
8	81	96
9	56*	70
10	57*	38
H= 6, K= 14		
0	54*	68
1	54*	62
2	54*	32
3	92	108
4	55*	25
5	117	115
6	56*	62
7	112	102
H= 7, K= 1		
0	563	539
1	383	369
2	230	214
3	242	227
4	409	406
5	170	154
6	84	99
7	134	157
8	271	286
9	94	79
10	102	103
11	118	139
12	51*	52
13	52*	30
14	54*	57
15	56*	51
H= 7, K= 3		
0	39*	61
1	338	365
2	272	277
3	254	275
4	132	130
5	258	245
6	313	317
7	97	87
8	162	171
9	223	231
10	108	86
11	149	160
12	97	88
13	140	146
14	55*	12
15	57*	44
H= 7, K= 5		
0	41*	34
1	246	247
2	254	238
3	203	200
4	174	185
5	315	310
6	216	190
7	206	193
8	47*	51
9	101	109
10	129	115
11	51*	36
12	53*	56
13	54*	48
14	97	94
H= 7, K= 7		
0	44*	11
1	193	210
2	300	285
3	171	162
4	90	83
5	247	243
6	237	218
7	172	183
8	49*	71
9	71	77
10	120	128
11	53*	61
12	54*	57
13	56*	29
H= 7, K= 9		
0	47*	58
1	211	204
2	123	134
3	192	186
4	94	91
5	187	182
6	135	135
7	75	56
8	76	91
9	97	122
10	96	91
11	55*	42
12	57*	55
H= 7, K= 11		
0	174	180
1	50*	39
2	51*	66
3	88	87
4	230	228
5	52*	65
6	153	140
7	54*	10
8	186	188
9	56*	23
10	57*	22
H= 7, K= 13		
0	192	186
1	54*	74
2	54*	52
3	55*	74
4	55*	40
5	56*	65
6	56*	63
7	57*	54
H= 8, K= 0		
0	233	257
1	128	146
2	311	298
3	59	68
4	43*	22
5	159	176
6	203	195
7	183	193
8	133	124
9	110	115
10	260	252
11	132	134
12	82	87
13	54*	0
14	109	96
H= 8, K= 2		
0	263	264
1	296	317
2	217	215
3	331	338
4	85	109
5	141	145
6	355	347
7	195	195
8	106	104
9	201	195
10	50*	48
11	52*	61
12	103	95
13	92	87
14	56*	64
H= 8, K= 4		
0	43*	51
1	244	246
2	185	167
3	44*	21
4	328	333
5	213	199
6	75	89
7	70	74
8	159	165
9	80	68
10	51*	65
11	52*	45
12	80	81
13	56*	59
14	89	75
H= 8, K= 6		
0	237	263
1	113	106
2	108	133
3	192	200
4	251	254
5	79	72
6	86	85
7	122	113
8	167	165
9	51*	59
10	53*	26
11	54*	59
12	108	118
13	57*	40
H= 8, K= 8		
0	77	83
1	123	131
2	83	69
3	48*	39
4	139	143
5	113	122
6	50*	27
7	76	77
8	52*	27
9	110	114
10	85	91
11	56*	41
H= 8, K= 10		
0	51*	23
1	142	129
2	141	152
3	73	64
4	77	75
5	85	74
6	147	142
7	54*	38
8	55*	49
9	56*	65
10	57*	50
H= 8, K= 12		
0	54*	30
1	54*	35
2	124	130
3	55*	37
4	55*	45
5	56*	52
6	104	90
7	57*	51
H= 9, K= 1		
0	45*	23
1	117	111
2	140	129
3	271	271
4	127	124
5	207	197
6	48*	66
7	159	162
8	50*	56
9	51*	34
10	52*	67
11	87	86
12	55*	46
13	57*	55
H= 9, K= 3		
0	68	76
1	149	143
2	184	156
3	130	127
4	47*	68
5	126	129
6	75	76
7	104	112
8	75	64
9	122	121
10	106	106
11	97	94
12	83	74
13	57*	17
H= 9, K= 5		
0	204	192
1	157	170
2	149	184
3	48*	44
4	140	138
5	118	120
6	50*	20
7	101	95
8	113	104
9	53*	77
10	54*	55
11	55*	21
12	95	80
H= 9, K= 7		
0	146	136
1	79	116
2	49*	50
3	109	123
4	106	98
5	82	82
6	87	52
7	125	136
8	54*	68
9	55*	69
10	56*	55
11	57*	52
H= 9, K= 9		
0	52*	25
1	141	140
2	77	76
3	161	168
4	53*	46
5	104	91
6	87	88
7	146	165
8	115	102
9	95	102
H= 9, K= 11		
0	55*	60
1	78	61
2	55*	37
3	55*	41
4	56*	33
5	107	115
6	57*	48
H= 10, K= 0		
0	223	218
1	48*	2
2	48*	23
3	49*	14
4	125	120
5	102	90
6	51*	18
7	52*	48
8	171	170
9	54*	13
10	55*	6
11	56*	48
H= 10, K= 2		
0	191	191
1	99	85
2	49*	58
3	103	113
4	170	166
5	93	94
6	51*	42
7	52*	35
8	103	100
9	54*	64
10	55*	55
11	57*	77
H= 10, K= 4		
0	49*	26
1	49*	46
2	214	232
3	50*	31
4	51*	19
5	72	64
6	135	139
7	53*	26
8	54*	66
9	55*	24
10	56*	47
11	57*	27
H= 10, K= 6		
0	51*	19
1	105	88
2	141	149
3	86	84
4	52*	40
5	53*	20
6	141	154
7	54*	48
8	55*	73
9	56*	36
H= 10, K= 8		
0	53*	100
1	92	97
2	53*	54
3	99	109
4	126	133
5	55*	46
6	56*	24
7	56*	38
8	109	95
H= 10, K= 10		
0	56*	49
1	79	69
2	79	72
3	94	98
4	57*	43
H= 11, K= 1		
0	51*	46
1	113	107
2	52*	56
3	114	107
4	52*	25
5	53*	75
6	87	81
7	55*	63
8	56*	23
9	57*	33
H= 11, K= 3		
0	52*	34
1	109	108
2	96	86
3	53*	50
4	53*	15
5	99	82
6	54*	38
7	89	86
8	56*	50
9	57*	66
H= 11, K= 5		
0	101	94
1	53*	66
2	53*	42
3	54*	67
4	77	72
5	55*	74
6	56*	48
7	56*	36
8	57*	45
H= 11, K= 7		
0	55*	34
1	126	107
2	86	66
3	56*	30
4	137	134
5	57*	54
6	81	64
H= 11, K= 9		
0	57*	24
1	57*	49
H= 12, K= 0		
0	55*	19
1	55*	47
2	118	111
3	55*	68
4	86	62
5	56*	23
6	98	97
H= 12, K= 2		
0	55*	7
1	55*	68
2	55*	56
3	55*	71
4	56*	72
5	56*	59
6	57*	23
H= 12, K= 4		
0	83	97
1	56*	75
2	56*	52
3	56*	72
4	57*	39
5	89	83
H= 12, K= 6		
0	57*	38
1	57*	40
2	57*	40

The C–C bonds vary from 1·471 to 1·544 Å with a mean of 1·513 Å, which is in agreement with Sutton's (1965) value of 1·537 Å. The deviations from the average value are not chemically significant, but reflect the overall accuracy of this determination. The C–N bond lengths agree with values found in molecules in which a quaternary nitrogen atom is attached to three $C(sp^3)$ atoms (Birnbaum, 1967).

The angles given in Fig. 2, omitting the value of 117·7° for C(10′)–C(7)–C(6), give an acceptable mean of 110·9°. The large value of the excluded angle was expected on the basis of structural analyses of other lupine alkaloids (Przybylska & Barnes, 1953; Srivastava & Przybylska, 1969). A tetrahedral angle for C(10′)–C(7)–C(6) would bring the nitrogen atoms within the molecule too close to each other (2·5 Å). That distance in this structure is 3·147 Å and that between the hydrogen atoms of the NH groups is 2·21 Å. This H···H separation does not deviate significantly from the normal van der Waals contact.

The bond lengths and angles of the ClO_4 groups are listed in Table 4. The bonds range from 1·337 to 1·445, with a mean of 1·398 Å, and the O–Cl–O angles vary from 97·7° to 124·3° with a mean of 109·2°. Not too much significance should be attached to these values because of lack of correction for thermal motion and because of the disorder of one of the ClO_4 groups.

Table 4. *The bond lengths and angles of the perchlorate anions*

The e.s.d.'s for the angles are *ca.* 0·8°.

Cl(1)–O(1)	1·365 (11) Å	O(1)–Cl(1)–O(2)	104·9°
Cl(1)–O(2)	1·357 (12)	O(1)–Cl(1)–O(1′)	107·7
Cl(2)–O(3)	1·444 (8)	O(2)–Cl(2)–O(1′)	107·1
Cl(2)–O(4)	1·445 (12)	O(2)–Cl(1)–O(2′)	124·3
Cl(2)–O(5)	1·337 (16)	O(3)–Cl(2)–O(4)	105·3
Cl(2)–O(6)	1·442 (12)	O(3)–Cl(2)–O(5)	116·4
		O(3)–Cl(2)–O(6)	107·3
		O(4)–Cl(2)–O(5)	112·9
		O(4)–Cl(2)–O(6)	97·7
		O(5)–Cl(2)–O(6)	115·2

The C–H bond lengths are in the range 0·51–1·12 Å, and their mean is 0·96 Å. The H–C–H and C–C–H angles vary from 97·4 to 122·3° with a mean of 108·3°.

The results of the conformational analysis are presented in Table 5. The signs of the torsional angles are according to the convention of the IUPAC–IUB Commission on Biological Nomenclature (1970), and the e.s.d.'s were calculated according to Huber (1961). The two rings are of chair form, but owing to strain in the molecule the inner ring shows much greater deviations from the ideal conformation. Ring *A* is flattened at the nitrogen atom. The torsional angles of the C–N bonds are only 41·4 and 45·4° and the distance of N from the plane for C(7), C(9), C(6) and C(10) is 0·52 Å. The four atoms of ring *A* used for the calculation of the plane were found not coplanar, but those of the outer ring *B* were. The e.s.d.'s of *Δ* are 0·004 to 0·008 Å.

Crystal structure

The molecule of α-isosparteine is hydrogen bonded to O(3) of the perchlorate group, as shown in Fig. 3. The symmetry-related hydrogen bonds N(1)–H(11)···O(3′) and N(1′)–H(11′)···O(3′) are identical with those presented in Table 6. The hydrogen-bonding has probably contributed to the stability of the all chair conformation of the α-isosparteine molecule in spite of strong repulsion between the N^+–H groups. It had also reduced the vibration of O(3) leading to the lengthening of the Cl(2)–O(3) bond (1·44 Å).

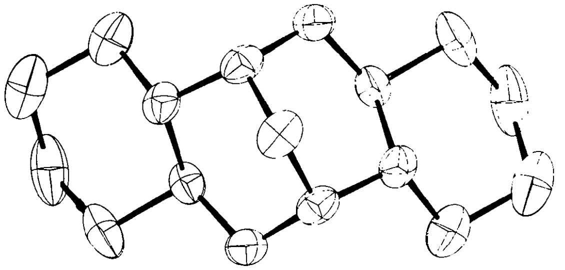

Fig. 1. A projection of the molecule down **b** showing thermal ellipsoids.

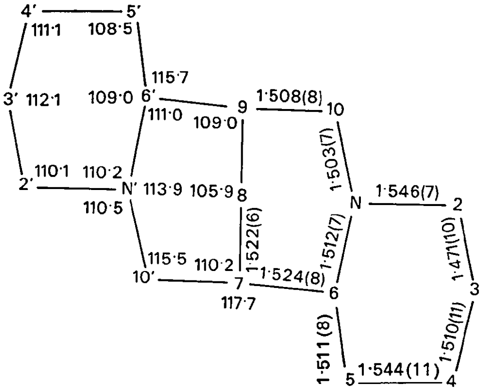

Fig. 2. Bond lengths and angles. The e.s.d.'s of angles vary from 0·4 to 0·6°.

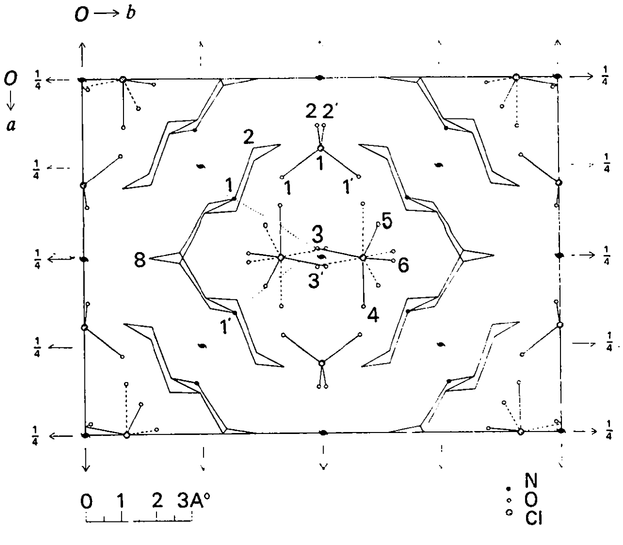

Fig. 3. Packing of the molecules projected along **c**.

Table 5. *Torsional angles with their e.s.d.'s and weighted least-squares planes*

Inner ring *A*

N(1)—C(6)—C(7)—C(8)	−60·0 (4)°
C(6)—C(7)—C(8)—C(9)	68·2 (5)
C(7)—C(8)—C(9)—C(10)	−62·4 (4)
C(8)—C(9)—C(10)-N(1)	50·3 (4)
C(9)—C(10)-N(1)—C(6)	−41·4 (5)
C(10)-N(1)—C(6)—C(7)	45·4 (4)

Outer ring *B*

N(1)-C(2)-C(3)-C(4)	−55·2 (7)
C(2)-C(3)-C(4)-C(5)	56·1 (6)
C(3)-C(4)-C(5)-C(6)	−57·8 (6)
C(4)-C(5)-C(6)-N(1)	60·5 (6)
C(5)-C(6)-N(1)-C(2)	−61·3 (5)
C(6)-N(1)-C(2)-C(3)	58·1 (5)

Ring *A*	Δ	Ring *B*	Δ
C(7)	−0·033	C(5)	−0·002
C(9)	0·034	N(1)	0·001
C(6)	0·032	C(2)	−0·002
C(10)	−0·038	C(4)	0·003
C(8)*	0·785	C(6)*	0·723
N(1)*	−0·524	C(3)*	−0·643
	$\chi^2=169$		$\chi^2=0·4$

Equations of the planes

$$A:\ -0·5140X-0·8568Y-0·0411Z=5·0425\ \text{Å}$$
$$B:\ -0·3357X-0·9399Y-0·0624Z=5·3903$$

* Atoms excluded from the calculation of the plane.

Table 6. *Distances and angles of the hydrogen bonds*

	Angle	$D\cdots A$	D–H	H$\cdots A$
N(1)–H(11)$\cdots$O(3)	159°	2·742 Å	0·84 Å	1·94 Å
N(1′)–H(11′)$\cdots$O(3)	169	2·922	0·84	2·09
C(2)—H(21)$\cdots$O(2′)	160	3·542	1·00	2·58

O(3) was placed at the beginning of refinement 0·40 Å from the twofold axis. The distance increased to a final value of 0·56 Å. The coordinates of O(3) in conjunction with those of O(4), O(5) and O(6) gave an arrangement of bonds considerably closer to tetrahedral geometry than those of O(3′).

It was not possible on the basis of the X-ray experiment, mentioned earlier, to decide unequivocally whether two orientations of that ClO_4 group are really present or whether one set of oxygen atoms was an artifact due to the symmetry of space group $C222_1$. Considering however the symmetrical environment of the ClO_4^- ion there does not seem to be any reason for the existence of only one of these orientations and the assumption that both are present is likely to be correct.

An additional very weak C–H$\cdots$O hydrogen bond may exist between C(2) and O(2′) attached to Cl(1). The details are also given in Table 6. The structure may therefore consist of spirals of hydrogen-bonded α-isosparteine and Cl(1)–O_4 molecules, parallel to **c**.

There is another short H(81)$\cdots$O(2) contact of 2·48 Å but the angle C(8)–H(81)$\cdots$O(2) is too small (122°) for it to be considered a hydrogen bond. There are no other intermolecular distances shorter than the sums of the appropriate van der Waals radii.

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