ACTA CHEMICA SCANDINAVICA 26 (1972) 483–493

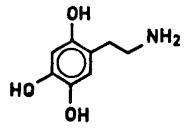
The Crystal Structure of 6-Hydroxydopamine Hydrochloride

M. KOLDERUP, ARVID MOSTAD and CHR. RØMMING

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal and molecular structure of 6-hydroxydopamine hydrochloride has been determined by X-ray methods using 1781 observed reflections obtained by counter methods. The crystals are monoclinic, space group Pc, with unit cell dimensions $a = 4.80_8$ Å; $b = 7.23_1$ Å; $c = 13.12_4$ Å; $\beta = 97.3_5°$. The refinements resulted in a conventional R-factor of 0.042. The estimated standard deviations in bond lengths are 0.002 – 0.003 Å and in bond angles 0.2°. The crystal structure is stabilized through a three-dimensional network of hydrogen bonds; each 6-hydroxydopamine ion is linked to four other organic ions and three chlorine ions by N – H···O, N – H···Cl^- and O – H···Cl^- hydrogen bonds.

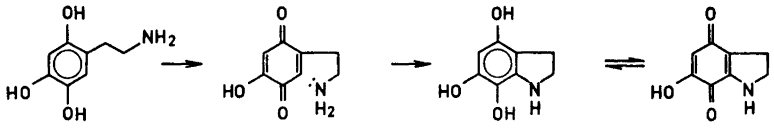
Quite a number of compounds interfering in the metabolism and functioning of neurons may be regarded as derivatives of L-tyrosine. The structural similarities of such molecules form an active field of structure-activity analysis in contemporary pharmacology. In this respect 6-hydroxydopamine (3,4,6-trihydroxyphenylethylamine) is an interesting compound from several points of view.



In 1959 this compound was reported to be an oxydation product of dopamine *in vitro* as well as *in vivo*.[1]

It was later realized that the pharmacological activity of the substance results in a prolonged depletion of peripheral noradrenaline [2] caused by an irreversible combination of 6-hydroxydopamine with tissue constituents followed by a degeneration of the nerve terminal. 6-Hydroxydopamine has therefore been suggested as a pharmacological tool for sympathectomy.[3,4] These observations have also led to a warning against possible long time effects on Parkinson patients using therapeutic doses of L-DOPA.[5]

Furthermore, it is likely that 6-hydroxydopamine plays a role in the melanine synthesis [6] as the following reactions with the formation of an aminochrome have been shown to occur:[7]



This is in accordance with our experience, as a solution of 6-hydroxydopamine hydrochloride in water gradually became pink, sometimes with precipitation of red crystals. The process was accompanied by changes in NMR and UV spectra consistent with the above reaction.

EXPERIMENTAL

Commercially obtained 6-hydroxydopamine hydrochloride was dissolved in a solution of HCl in ethanol. By slow diffusion of ethyl ether into the solution, colourless needle-formed crystals of the compound precipitated. Occasionally deep red crystals separated; these are probably a *p*-quinoid oxidation product.[7] The infra-red spectrum of the colourless crystals was identical with that of the original compound.

Oscillation and Weissenberg photographs indicated monoclinic symmetry. (*h*0*l*) reflections were systematically absent for *l* odd, indicating the space group *Pc* or *P*2/*c*. As the unit cell contains *two* molecules the latter space group may be disregarded for symmetry reasons, and this was found to be in accordance with the results of a Wilson plot.

Unit cell parameters were determined from angular measurements for 12 unique reflections and their symmetry equivalents on a Picker diffractometer using Cu$K\beta$ radiation ($\lambda = 1.3922$ Å). The take-off angle was 1°. The computer program employed in the least-squares treatment of the measurements as well as the programs used during the subsequent calculations are described in Ref. 8.

Three-dimensional intensity data were recorded on an automatic Picker diffractometer using graphite crystal monochromated Mo*K*-radiation. The take-off angle was 4°, and the temperature was kept constant at 18°C during the data collection. A crystal with dimensions $0.12 \times 0.15 \times 0.21$ mm^3 was mounted with a^* along the diffractometer ϕ axis. The $\omega - 2\theta$ scan technique was used, the 2θ scan speed being 1° min^{-1} through the scan range from 0.5° below $2\theta(\alpha_1)$ to 0.5° above $2\theta(\alpha_2)$. Background counts were taken for 20 sec at each of the scan range limits. The intensities of three standard reflections measured for every 50 reflections of the data set showed no decrease in intensity during the measurements. The data were adjusted according to the fluctuations in the intensities of the standard reflections. The estimated standard deviations in the intensities were taken as the square root of the total counts with a 2 % addition for the uncertainty in the adjustments.

The measurements included 2323 unique reflections with $\sin\theta/\lambda$ less than 0.85. Of these, 1781 had net intensity larger than $2\sigma(I)$ and were regarded as "observed" reflections whereas the remaining reflections were excluded from the further calculations.

The intensity data were corrected for Lorentz, polarization, and absorption effects, later also for secondary extinction.

Atomic form factors used were those of Hanson *et al.*[9] for nitrogen, oxygen, and carbon, and of Stewart *et al.*[10] for hydrogen. For the chloride ion the values listed in *International Tables* (1962) were employed.

CRYSTAL DATA

6-Hydroxydopamine hydrochloride, $C_8H_{12}O_3NCl$, monoclinic, $a = 4.808(0.002)$ Å; $b = 7.231(0.003)$ Å; $c = 13.124(0.002)$ Å; $\beta = 97.35(0.01)°$. Figures in parentheses are estimated standard deviations.

$V = 452.5$ Å^3; $M = 205.64$; $F(000) = 216$; $\mu = 0.38$ mm^{-1}; $Z = 2$.

σ_{obs} (flotation) $= 1.50$ g cm^{-3}, $\sigma_{calc} = 1.509$ g cm^{-3}.

Absent reflections: (*h*0*l*) for *l* odd; space group *Pc*.

Table 1. Observed and calculated structure factors. The columns are h, k, l, $10|F_o|$, $10|F_c|$.

0	0	2	243	225
0	0	4	259	253
0	0	6	337	339
0	0	8	183	179
0	0	10	48	47
0	0	12	153	153
0	0	14	124	123
0	0	16	69	72
0	0	18	50	49
0	1	18	22	25
0	1	17	34	38
0	1	16	89	90
0	1	15	64	65
0	1	14	69	70
0	1	13	191	196
0	1	12	131	134
0	1	11	50	52
0	1	10	173	173
0	1	9	246	249
0	1	8	61	65
0	1	7	30	32
0	1	6	181	178
0	1	5	298	294
0	1	4	267	262
0	1	3	174	170
0	1	2	263	263
0	1	1	112	106
0	1	0	131	120
0	2	0	185	187
0	2	1	216	212
0	2	2	146	146
0	2	3	542	562
0	2	4	187	187
0	2	5	59	63
0	2	6	169	166
0	2	7	200	192
0	2	8	39	41
0	2	9	187	185
0	2	10	41	43
0	2	11	118	119
0	2	12	26	28
0	2	13	27	20
0	2	14	52	53
0	2	15	56	57
0	2	16	40	43
0	2	17	60	61
0	3	17	36	36
0	3	16	65	63
0	3	15	79	80
0	3	14	112	113
0	3	13	67	68
0	3	12	80	82
0	3	11	54	57
0	3	10	59	58
0	3	9	33	38
0	3	8	139	137
0	3	7	122	126
0	3	6	183	176
0	3	5	107	107
0	3	4	64	65
0	3	3	36	35
0	3	2	194	194
0	3	1	328	333
0	3	0	181	181
0	4	0	56	53
0	4	1	133	131
0	4	2	287	281
0	4	3	127	126
0	4	4	204	195
0	4	5	80	79
0	4	6	119	118
0	4	7	47	43
0	4	8	147	152
0	4	10	141	140
0	4	11	60	64
0	4	12	57	61
0	4	13	45	46
0	4	14	41	41
0	4	15	20	21
0	4	16	23	25
0	5	15	59	60
0	5	14	44	48
0	5	13	84	82
0	5	12	87	85
0	5	11	163	165
0	5	10	125	127
0	5	9	17	19
0	5	8	73	71
0	5	7	74	73
0	5	6	19	19
0	5	5	100	98
0	5	4	96	93
0	5	3	200	199
0	5	2	158	164
0	5	1	62	58
0	6	1	229	232
0	6	2	134	135

0	6	3	122	130
0	6	4	63	66
0	6	5	155	158
0	6	6	84	87
0	6	7	104	105
0	6	8	51	49
0	6	9	82	82
0	6	10	40	42
0	6	11	69	70
0	6	12	26	31
0	6	13	39	42
0	6	14	22	18
0	7	12	58	59
0	7	11	24	27
0	7	10	61	60
0	7	9	51	51
0	7	8	41	43
0	7	7	79	80
0	7	6	68	68
0	7	5	81	84
0	7	4	129	131
0	7	3	60	58
0	7	2	48	49
0	7	1	49	48
0	7	0	71	71
0	8	0	34	34
0	8	1	37	37
0	8	2	78	81
0	8	3	30	31
0	8	4	72	71
0	8	5	43	41
0	8	6	79	79
0	8	7	19	15
0	8	8	75	78
0	8	9	51	49
0	8	10	30	32
0	9	8	17	11
0	9	7	67	67
0	9	6	49	50
0	9	5	53	52
0	9	3	39	38
0	9	2	18	22
0	9	1	51	52
0	9	0	73	71
0	10	0	38	39
0	10	1	60	57
1	9	-7	25	29
1	9	-6	39	39
1	9	-4	31	31
1	9	-3	51	50
1	9	-2	37	38
1	9	-1	88	84
1	9	0	17	6
1	9	1	20	23
1	9	2	53	51
1	9	3	68	68
1	9	4	34	34
1	9	5	55	57
1	9	6	37	36
1	9	7	40	46
1	8	10	85	84
1	8	9	22	25
1	8	8	33	31
1	8	7	34	35
1	8	6	50	50
1	8	5	45	47
1	8	4	49	47
1	8	3	29	31
1	8	2	65	66
1	8	1	21	17
1	8	0	25	25
1	8	-1	53	57
1	8	-2	53	55
1	8	-3	22	21
1	8	-4	110	112
1	8	-5	45	41
1	8	-6	74	73
1	8	-7	59	58
1	8	-8	57	59
1	8	-9	29	27
1	8	-10	67	66
1	7	-13	55	55
1	7	-12	76	76
1	7	-11	21	25
1	7	-10	64	63
1	7	-9	38	43
1	7	-8	39	38
1	7	-6	112	115
1	7	-5	31	38
1	7	-4	41	36
1	7	-3	99	103
1	7	-2	74	79
1	7	-1	43	42
1	7	0	173	175
1	7	1	99	99
1	7	2	49	46
1	7	3	59	57

1	7	4	56	56
1	7	5	54	58
1	7	6	32	32
1	7	7	68	68
1	7	8	107	107
1	7	9	78	76
1	7	10	30	34
1	7	12	26	22
1	6	13	119	119
1	6	12	44	46
1	6	11	22	20
1	6	10	22	17
1	6	9	40	39
1	6	8	36	36
1	6	7	121	123
1	6	5	106	105
1	6	4	126	128
1	6	3	167	167
1	6	2	72	70
1	6	1	97	97
1	6	0	124	126
1	6	-1	152	150
1	6	-2	101	104
1	6	-3	103	102
1	6	-4	64	70
1	6	-5	140	145
1	6	-6	44	46
1	6	-7	46	43
1	6	-8	51	55
1	6	-9	112	116
1	6	-10	33	34
1	6	-11	52	53
1	6	-12	15	7
1	6	-13	61	58
1	6	-14	46	42
1	5	-15	35	40
1	5	-14	41	41
1	5	-13	40	42
1	5	-12	42	44
1	5	-11	24	22
1	5	-10	86	87
1	5	-9	226	231
1	5	-8	69	70
1	5	-7	92	94
1	5	-6	113	116
1	5	-5	77	72
1	5	-4	39	37
1	5	-3	204	204
1	5	-2	56	57
1	5	-1	7-	79
1	5	0	126	127
1	5	1	117	118
1	5	2	21	20
1	5	3	181	186
1	5	4	192	193
1	5	5	134	136
1	5	6	100	103
1	5	7	125	128
1	5	8	67	69
1	5	9	73	72
1	5	10	50	51
1	5	11	62	62
1	5	12	65	66
1	5	13	77	79
1	5	14	41	45
1	5	15	59	61
1	4	16	72	73
1	4	14	42	41
1	4	13	63	64
1	4	11	36	39
1	4	10	116	117
1	4	9	34	34
1	4	8	36	33
1	4	7	41	44
1	4	6	156	152
1	4	5	62	63
1	4	4	184	180
1	4	3	112	111
1	4	2	182	180
1	4	1	204	206
1	4	0	227	223
1	4	-1	156	155
1	4	-2	72	72
1	4	-3	73	72
1	4	-4	142	137
1	4	-5	95	95
1	4	-6	134	134
1	4	-7	42	41
1	4	-8	158	158
1	4	-9	135	140
1	4	-10	31	29
1	4	-11	76	79
1	4	-12	130	135
1	4	-13	32	30
1	4	-14	64	64
1	4	-15	58	55
1	4	-16	74	76

1	3	-17	63	67
1	3	-16	54	54
1	3	-15	46	43
1	3	-14	49	48
1	3	-13	59	61
1	3	-12	116	119
1	3	-11	68	67
1	3	-10	110	110
1	3	-9	69	69
1	3	-8	156	158
1	3	-7	191	192
1	3	-6	146	144
1	3	-5	36	36
1	3	-4	71	69
1	3	-3	204	195
1	3	-2	341	334
1	3	-1	197	193
1	3	0	189	180
1	3	1	182	179
1	3	2	33	32
1	3	3	48	49
1	3	4	85	81
1	3	5	162	160
1	3	6	134	134
1	3	7	117	116
1	3	8	71	70
1	3	9	63	60
1	3	10	43	41
1	3	11	71	72
1	3	12	59	60
1	3	13	73	76
1	3	14	76	75
1	3	15	26	28
1	3	16	31	29
1	2	17	43	40
1	2	15	70	72
1	2	14	29	30
1	2	13	27	32
1	2	12	31	34
1	2	11	167	167
1	2	10	70	72
1	2	9	132	128
1	2	8	31	32
1	2	7	157	154
1	2	6	50	47
1	2	5	264	267
1	2	4	124	121
1	2	3	331	325
1	2	2	171	172
1	2	1	258	256
1	2	0	93	92
1	2	-1	241	241
1	2	-2	391	390
1	2	-3	194	192
1	2	-4	215	211
1	2	-5	242	233
1	2	-6	102	100
1	2	-7	105	101
1	2	-8	79	78
1	2	-9	78	77
1	2	-10	38	35
1	2	-11	136	136
1	2	-12	164	171
1	2	-13	98	99
1	2	-14	72	75
1	2	-15	78	80
1	2	-16	22	19
1	2	-17	40	36
1	1	-18	18	21
1	1	-17	47	46
1	1	-16	51	50
1	1	-15	63	63
1	1	-14	113	116
1	1	-13	51	52
1	1	-12	79	79
1	1	-11	244	252
1	1	-10	181	185
1	1	-9	59	61
1	1	-8	242	238
1	1	-7	151	145
1	1	-6	111	102
1	1	-5	329	330
1	1	-4	241	241
1	1	-3	41	42
1	1	-2	301	298
1	1	-1	371	368
1	1	0	322	314
1	1	1	588	602
1	1	2	500	505
1	1	3	374	369
1	1	4	22	20
1	1	5	129	130
1	1	6	169	169
1	1	7	98	97
1	1	8	153	149
1	1	9	112	107
1	1	10	63	63

1	1	11	70	71
1	1	12	52	51
1	1	13	55	54
1	1	14	53	55
1	1	15	70	71
1	1	16	79	78
1	1	17	84	83
1	0	16	108	105
1	0	14	149	151
1	0	12	169	172
1	0	10	79	80
1	0	8	230	229
1	0	6	234	226
1	0	4	594	599
1	0	2	780	787
1	0	0	20	16
1	0	-2	300	306
1	0	-4	271	265
1	0	-6	434	435
1	0	-8	227	220
1	0	-10	113	109
1	0	-12	101	99
1	0	-14	88	88
1	0	-16	51	50
1	0	-18	56	55
2	0	-16	81	79
2	0	-14	63	66
2	0	-12	180	186
2	0	-10	130	131
2	0	-8	65	67
2	0	-6	339	339
2	0	-4	220	214
2	0	-2	394	393
2	0	0	244	245
2	0	2	233	226
2	0	4	156	155
2	0	6	188	187
2	0	8	145	146
2	0	10	59	60
2	0	12	66	65
2	0	14	22	21
2	0	16	117	117
2	1	16	27	22
2	1	15	39	37
2	1	13	57	59
2	1	12	36	36
2	1	11	71	71
2	1	10	113	113
2	1	9	31	32
2	1	8	33	32
2	1	7	208	207
2	1	6	90	91
2	1	5	212	214
2	1	4	382	387
2	1	3	233	226
2	1	2	47	49
2	1	1	200	194
2	1	0	93	92
2	1	-1	228	230
2	1	-2	250	246
2	1	-3	92	91
2	1	-4	216	209
2	1	-5	284	279
2	1	-6	50	49
2	1	-7	238	237
2	1	-8	157	157
2	1	-9	41	37
2	1	-10	119	120
2	1	-11	26	17
2	1	-12	43	40
2	1	-13	39	40
2	1	-14	58	56
2	1	-15	57	59
2	1	-16	19	18
2	1	-17	48	48
2	2	-17	61	64
2	2	-16	51	51
2	2	-15	85	84
2	2	-14	51	53
2	2	-13	92	92
2	2	-12	111	117
2	2	-11	56	56
2	2	-10	218	231
2	2	-9	241	245
2	2	-8	158	167
2	2	-7	49	46
2	2	-6	75	74
2	2	-5	112	112
2	2	-4	152	152
2	2	-3	144	141
2	2	-2	70	69
2	2	-1	178	171
2	2	0	68	68
2	2	1	79	78
2	2	2	108	107
2	2	3	77	65
2	2	4	191	191

2	2	5	187	187
2	2	6	90	91
2	2	7	98	97
2	2	8	38	38
2	2	9	128	126
2	2	10	24	23
2	2	11	33	33
2	2	12	49	51
2	2	13	90	92
2	2	14	41	44
2	2	15	58	59
2	2	16	26	27
2	3	14	17	12
2	3	13	29	27
2	3	12	42	44
2	3	11	43	43
2	3	10	47	50
2	3	9	24	24
2	3	8	42	41
2	3	7	62	61
2	3	6	97	97
2	3	5	114	112
2	3	4	58	57
2	3	3	14	17
2	3	2	266	259
2	3	1	321	319
2	3	0	229	224
2	3	-1	92	91
2	3	-3	149	148
2	3	-4	225	219
2	3	-5	54	49
2	3	-6	141	142
2	3	-7	103	103
2	3	-8	101	104
2	3	-9	56	59
2	3	-10	66	68
2	3	-11	114	115
2	3	-12	63	64
2	3	-13	78	80
2	3	-14	38	37
2	3	-15	37	37
2	3	-16	51	51
2	3	-17	61	60
2	4	-16	71	69
2	4	-15	20	14
2	4	-14	23	25
2	4	-13	94	95
2	4	-12	72	69
2	4	-11	28	25
2	4	-10	102	102
2	4	-9	63	64
2	4	-8	210	214
2	4	-7	198	208
2	4	-6	88	88
2	4	-5	123	127
2	4	-4	210	211
2	4	-3	24	27
2	4	-2	121	115
2	4	-1	86	82
2	4	0	107	107
2	4	1	87	87
2	4	2	78	73
2	4	3	94	95
2	4	4	24	21
2	4	5	68	69
2	4	6	127	125
2	4	7	126	123
2	4	8	75	77
2	4	9	36	37
2	4	10	76	77
2	4	12	59	59
2	4	13	21	22
2	4	14	78	79
2	4	15	60	55
2	5	14	45	45
2	5	13	23	18
2	5	12	38	34
2	5	11	28	28
2	5	10	15	16
2	5	9	98	102
2	5	8	131	131
2	5	7	80	77
2	5	6	71	73
2	5	5	192	194
2	5	4	87	86
2	5	3	132	133
2	5	2	66	67
2	5	1	81	81
2	5	0	66	68
2	5	-1	100	99
2	5	-2	54	50
2	5	-3	119	122
2	5	-4	32	33
2	5	-5	44	47
2	5	-6	60	56
2	5	-7	121	123
2	5	-8	81	85

Table 1. Continued.

2	5	-9	64	68
2	5	-10	47	47
2	5	-11	41	42
2	5	-13	58	59
2	5	-14	98	97
2	5	-15	61	57
2	6	-13	41	45
2	6	-12	16	12
2	6	-11	92	92
2	6	-10	29	26
2	6	-9	31	35
2	6	-8	69	75
2	6	-7	111	116
2	6	-6	28	29
2	6	-5	108	109
2	6	-4	40	43
2	6	-3	123	128
2	6	-2	79	83
2	6	-1	128	135
2	6	0	50	54
2	6	1	82	78
2	6	2	82	82
2	6	3	80	80
2	6	4	52	48
2	6	5	64	64
2	6	6	51	51
2	6	7	65	68
2	6	8	30	33
2	6	9	51	54
2	6	10	49	47
2	6	11	31	31
2	7	11	77	75
2	7	10	38	40
2	7	9	18	21
2	7	8	53	55
2	7	6	50	51
2	7	5	42	43
2	7	4	60	60
2	7	3	58	58
2	7	2	147	148
2	7	1	93	93
2	7	0	29	30
2	7	-1	61	60
2	7	-2	73	74
2	7	-3	42	40
2	7	-4	47	52
2	7	-5	43	44
2	7	-6	99	101
2	7	-7	31	33
2	7	-8	57	55
2	7	-9	54	55
2	7	-10	23	26
2	7	-11	73	74
2	7	-12	58	58
2	8	-10	52	55
2	8	-9	58	52
2	8	-8	47	47
2	8	-7	44	42
2	8	-6	43	44
2	8	-4	29	29
2	8	-3	39	37
2	8	-2	81	81
2	8	-1	38	41
2	8	0	81	82
2	8	1	22	21
2	8	2	68	70
2	8	3	41	41
2	8	4	69	68
2	8	5	49	47
2	8	6	38	39
2	8	7	29	23
2	8	8	42	43
2	9	5	43	41
2	9	4	37	30
2	9	3	50	44
2	9	2	34	31
2	9	1	50	46
2	9	0	26	24
2	9	-1	50	50
2	9	-2	50	47
2	9	-4	36	33
2	9	-5	90	86
2	9	-6	49	47
3	8	6	33	32
3	8	5	62	58
3	8	4	59	60
3	8	3	66	65
3	8	2	19	29
3	8	1	41	40
3	8	0	48	48
3	8	-2	72	69
3	8	-3	20	20
3	8	-4	40	39
3	8	-6	23	23
3	8	-7	71	66
3	8	-8	51	50
3	7	-11	44	43
3	7	-10	71	69
3	7	-9	21	22
3	7	-8	18	17
3	7	-7	58	54
3	7	-6	68	70
3	7	-5	62	65
3	7	-4	26	28
3	7	-3	40	38
3	7	-2	63	67
3	7	-1	37	39
3	7	0	53	58
3	7	1	41	41
3	7	2	43	42
3	7	3	84	81
3	7	4	36	37
3	7	6	84	81
3	7	7	19	19
3	7	8	23	24
3	6	10	27	34
3	6	9	31	28
3	6	8	38	37
3	6	7	70	70
3	6	6	37	32
3	6	5	23	27
3	6	4	24	27
3	6	3	62	62
3	6	2	26	27
3	6	1	117	123
3	6	0	16	20
3	6	-3	64	66
3	6	-4	35	37
3	6	-5	104	109
3	6	-6	52	55
3	6	-7	58	58
3	6	-8	39	39
3	6	-9	18	17
3	6	-10	44	46
3	6	-11	73	72
3	6	-12	38	40
3	6	-13	49	50
3	5	-14	18	14
3	5	-13	48	42
3	5	-12	58	59
3	5	-11	41	40
3	5	-10	80	78
3	5	-9	57	59
3	5	-8	70	72
3	5	-7	50	48
3	5	-6	37	36
3	5	-5	58	56
3	5	-4	47	48
3	5	-3	64	63
3	5	-2	118	118
3	5	-1	154	162
3	5	0	61	63
3	5	1	24	28
3	5	3	55	56
3	5	4	63	62
3	5	5	49	51
3	5	6	58	59
3	5	7	67	70
3	5	8	35	37
3	5	9	80	79
3	5	10	38	37
3	5	11	35	35
3	5	12	20	26
3	4	13	17	17
3	4	12	24	20
3	4	11	32	33
3	4	10	58	59
3	4	9	107	106
3	4	8	107	108
3	4	7	33	35
3	4	6	36	40
3	4	5	42	45
3	4	4	105	107
3	4	3	74	74
3	4	2	99	98
3	4	1	65	65
3	4	0	82	84
3	4	-1	67	66
3	4	-2	77	79
3	4	-3	90	94
3	4	-4	55	59
3	4	-5	125	128
3	4	-6	134	139
3	4	-7	28	25
3	4	-8	95	98
3	4	-9	45	48
3	4	-10	88	87
3	4	-11	53	54
3	4	-12	62	62
3	4	-13	21	17
3	4	-14	129	125
3	4	-15	30	26
3	3	-16	29	26
3	3	-15	24	23
3	3	-14	29	31
3	3	-13	57	54
3	3	-12	68	70
3	3	-11	17	17
3	3	-10	90	88
3	3	-9	86	86
3	3	-8	95	99
3	3	-7	199	209
3	3	-6	40	43
3	3	-5	206	211
3	3	-4	220	226
3	3	-3	80	77
3	3	-2	59	99
3	3	-1	56	55
3	3	0	74	74
3	3	1	73	72
3	3	2	114	112
3	3	3	119	117
3	3	4	122	123
3	3	5	53	54
3	3	6	67	67
3	3	7	71	70
3	3	8	79	78
3	3	9	38	35
3	3	10	39	40
3	3	11	29	30
3	3	12	20	23
3	3	13	33	33
3	3	14	50	48
3	2	14	20	19
3	2	13	34	37
3	2	12	16	18
3	2	11	40	43
3	2	10	15	11
3	2	9	68	70
3	2	8	68	71
3	2	7	76	75
3	2	6	149	149
3	2	5	99	100
3	2	4	112	113
3	2	3	96	94
3	2	2	106	103
3	2	1	88	82
3	2	0	84	85
3	2	-1	115	112
3	2	-2	95	97
3	2	-3	133	128
3	2	-4	49	51
3	2	-5	119	126
3	2	-6	125	132
3	2	-7	194	198
3	2	-8	148	151
3	2	-9	114	118
3	2	-10	94	99
3	2	-11	38	35
3	2	-12	19	24
3	2	-13	80	82
3	2	-15	81	82
3	2	-16	76	74
3	1	-17	73	71
3	1	-16	72	70
3	1	-15	54	56
3	1	-14	28	26
3	1	-13	38	31
3	1	-12	57	59
3	1	-11	96	103
3	1	-10	68	71
3	1	-9	29	31
3	1	-8	77	77
3	1	-7	98	100
3	1	-6	60	58
3	1	-5	34	37
3	1	-4	108	108
3	1	-3	95	94
3	1	-2	132	131
3	1	-1	170	172
3	1	0	124	124
3	1	1	87	90
3	1	2	59	58
3	1	3	69	71
3	1	4	70	71
3	1	5	165	163
3	1	6	115	117
3	1	7	118	117
3	1	8	94	91
3	1	9	57	57
3	1	10	45	45
3	1	11	48	47
3	1	12	31	28
3	1	14	28	30
3	1	15	23	19
3	0	12	91	89
3	0	10	92	91
3	0	8	73	73
3	0	6	55	54
3	0	4	50	48
3	0	2	185	177
3	0	0	86	86
3	0	-2	109	106
3	0	-4	296	290
3	0	-6	242	243
3	0	-8	70	76
3	0	-10	115	116
3	0	-12	107	105
3	0	-14	49	50
3	0	-16	77	78
4	0	-14	40	39
4	0	-12	89	86
4	0	-10	61	59
4	0	-8	54	54
4	0	-6	112	116
4	0	-4	117	117
4	0	-2	36	35
4	0	0	129	130
4	0	2	93	95
4	0	4	49	45
4	0	6	84	84
4	0	8	65	69
4	0	10	21	26
4	0	12	43	40
4	1	12	29	33
4	1	11	45	41
4	1	10	35	35
4	1	9	50	48
4	1	7	32	34
4	1	6	61	62
4	1	5	43	44
4	1	4	25	29
4	1	3	28	27
4	1	2	63	65
4	1	1	90	91
4	1	0	42	42
4	1	-1	57	57
4	1	-2	108	108
4	1	-3	94	97
4	1	-4	19	16
4	1	-5	51	52
4	1	-6	33	34
4	1	-7	87	92
4	1	-8	124	130
4	1	-9	51	56
4	1	-10	26	26
4	1	-11	57	57
4	1	-12	19	20
4	1	-13	25	21
4	1	-14	57	57
4	1	-15	56	54
4	2	-15	34	31
4	2	-14	69	64
4	2	-13	27	30
4	2	-12	73	70
4	2	-11	66	66
4	2	-10	21	21
4	2	-9	64	61
4	2	-8	38	38
4	2	-7	59	59
4	2	-6	95	98
4	2	-5	53	54
4	2	-4	62	62
4	2	-3	169	169
4	2	-2	53	56
4	2	-1	74	72
4	2	0	16	17
4	2	1	41	43
4	2	2	25	22
4	2	3	58	58
4	2	4	25	25
4	2	5	77	79
4	2	6	110	114
4	2	7	43	44
4	2	8	57	57
4	2	9	52	47
4	2	10	52	51
4	2	11	35	44
4	3	11	34	31
4	3	10	51	54
4	3	9	76	78
4	3	8	76	77
4	3	7	33	33
4	3	5	44	45
4	3	4	28	29
4	3	3	46	46
4	3	2	34	39
4	3	1	54	54
4	3	0	99	101
4	3	-1	105	106
4	3	-2	97	100
4	3	-3	139	146
4	3	-4	88	88
4	3	-5	151	154
4	3	-6	142	143
4	3	-7	71	72
4	3	-9	41	41
4	3	-10	25	27
4	3	-11	39	43
4	3	-12	47	49
4	3	-13	61	58
4	3	-14	60	58
4	4	-13	41	39
4	4	-12	60	59
4	4	-11	52	47
4	4	-10	84	84
4	4	-9	59	61
4	4	-8	19	20
4	4	-7	61	59
4	4	-6	27	27
4	4	-5	77	80
4	4	-4	116	119
4	4	-3	59	63
4	4	-2	84	88
4	4	0	81	81
4	4	2	18	20
4	4	3	45	49
4	4	4	82	82
4	4	5	15	13
4	4	6	15	17
4	4	7	16	21
4	4	8	54	54
4	4	9	38	38
4	4	11	46	43
4	5	9	35	32
4	5	8	22	22
4	5	7	52	54
4	5	6	27	28
4	5	5	34	34
4	5	4	23	27
4	5	3	64	66
4	5	2	95	95
4	5	1	42	45
4	5	0	25	25
4	5	-1	20	21
4	5	-2	50	48
4	5	-4	62	63
4	5	-5	27	22
4	5	-6	24	22
4	5	-7	38	43
4	5	-8	51	46
4	5	-9	93	96
4	5	-10	17	15
4	5	-12	41	42
4	6	-11	50	49
4	6	-10	27	27
4	6	-8	21	21
4	6	-7	48	51
4	6	-6	39	38
4	6	-5	54	54
4	6	-4	35	34
4	6	-2	59	60
4	6	-1	41	43
4	6	0	30	32
4	6	1	53	53
4	6	2	28	29
4	6	3	36	36
4	6	5	25	25
4	6	7	41	40
4	7	5	22	21
4	7	4	31	36
4	7	3	21	22
4	7	2	37	38
4	7	1	28	28
4	7	0	33	33
4	7	-1	49	47
4	7	-2	20	17
4	7	-3	80	80
4	7	-4	67	68
4	7	-5	36	30
4	7	-6	48	44
4	7	-7	45	42
4	7	-8	47	47
4	8	-3	33	35
4	8	-2	40	38
4	8	-1	39	43
4	8	0	22	14
5	6	1	26	21
5	6	0	17	20
5	6	-1	21	25
5	6	-2	46	41
5	6	-3	50	50
5	6	-4	43	42
5	6	-6	40	42
5	6	-7	52	50
5	5	-9	28	26
5	5	-8	31	31
5	5	-7	48	47
5	5	-6	16	12
5	5	-5	26	27
5	5	-4	26	22
5	5	-3	52	55
5	5	-1	41	39
5	5	0	19	16
5	5	1	19	22
5	5	2	20	24
5	5	3	16	20
5	5	4	39	43
5	5	5	30	30
5	5	6	35	37
5	4	6	33	33
5	4	4	52	49
5	4	3	55	55
5	4	2	45	45
5	4	0	34	36
5	4	-2	48	48
5	4	-3	112	111
5	4	-4	20	20
5	4	-5	35	34
5	4	-6	45	47
5	4	-8	59	57
5	4	-9	56	55
5	4	-10	18	19
5	4	-11	30	30
5	3	-12	31	33
5	3	-11	45	42
5	3	-10	79	80
5	3	-9	41	39
5	3	-8	27	31
5	3	-5	44	41
5	3	-4	59	61
5	3	-3	87	88
5	3	-2	86	87
5	3	-1	51	51
5	3	0	30	31
5	3	1	59	62
5	3	2	26	28
5	3	3	19	18
5	3	4	19	14
5	3	6	20	17
5	3	8	17	12
5	2	9	27	31
5	2	8	30	28
5	2	7	30	33
5	2	5	21	17
5	2	4	18	22
5	2	3	48	49
5	2	2	32	32
5	2	1	44	45
5	2	0	133	134
5	2	-1	90	94
5	2	-2	50	48
5	2	-3	16	18
5	2	-4	15	17
5	2	-5	46	45
5	2	-6	48	48
5	2	-7	29	30
5	2	-8	27	25
5	2	-9	31	26
5	2	-10	27	26
5	2	-12	86	81
5	1	-13	74	73
5	1	-11	68	65
5	1	-10	35	32
5	1	-9	48	46
5	1	-8	26	26
5	1	-7	19	19
5	1	-6	67	70
5	1	-5	80	81
5	1	-4	44	42
5	1	-3	25	24
5	1	-2	43	46
5	1	-1	33	33
5	1	0	46	45
5	1	1	48	46
5	1	2	30	29
5	1	3	20	20
5	1	4	25	25
5	1	5	30	31
5	1	6	25	23
5	1	7	32	30
5	1	8	25	27
5	1	9	34	34
5	1	10	23	18
5	0	10	20	18
5	0	8	28	32
5	0	6	29	29
5	0	4	31	29
5	0	2	59	64
5	0	0	68	69
5	0	-2	56	56
5	0	-4	60	63
5	0	-6	70	72
5	0	-8	56	60
5	0	-10	18	13
6	0	-10	19	24
6	0	-8	18	10
6	0	-6	29	28
6	0	-4	73	73
6	0	-2	58	55
6	0	0	24	23
6	0	4	24	18
6	1	4	24	27
6	1	2	27	24
6	1	1	70	71
6	1	0	40	40
6	1	-1	25	21
6	1	-2	33	30
6	1	-3	34	35
6	1	-6	17	17
6	1	-7	18	17
6	1	-9	24	22
6	2	-9	38	33
6	2	-8	25	20
6	2	-5	20	21
6	2	-2	38	36
6	2	-1	32	37
6	2	1	39	42
6	2	2	69	68
6	2	3	19	24
6	2	4	48	44
6	3	2	38	33
6	3	1	25	25
6	3	0	29	29
6	3	-1	28	30
6	3	-2	36	39
6	3	-3	33	25
6	3	-6	33	34
6	3	-7	40	41
6	4	-2	54	51
6	4	-1	56	53
6	4	1	37	38
0	0	22	70	70
0	1	22	32	28
0	1	21	25	25
0	1	20	26	28
0	1	19	40	37
0	2	18	21	19
0	2	19	39	36
0	3	20	50	50
0	3	19	56	51
0	4	17	22	23
0	4	18	44	43
0	4	20	24	21
0	5	19	23	29
0	5	18	25	19
0	5	17	54	48
0	6	15	79	81
0	6	16	46	42
0	6	17	27	26
0	6	18	27	28
0	6	19	32	28
0	7	18	57	52
0	7	17	35	35
0	7	16	27	28

Table 1. Continued.

0	7	15	41	41
0	7	14	60	61
0	7	13	35	35
0	8	12	49	47
0	8	13	20	20
0	8	14	26	28
0	8	16	50	46
0	9	15	35	27
0	9	13	24	28
0	9	12	41	35
0	9	9	35	37
0	10	2	19	18
0	10	3	52	54
0	10	5	22	23
0	10	7	28	26
0	10	9	38	38
0	10	10	28	29
0	10	11	23	28
0	11	9	46	43
0	11	8	43	42
0	11	7	23	25
0	11	6	24	20
0	11	4	48	49
0	11	3	39	38
0	11	2	27	33
0	11	0	31	28
0	12	0	37	35
0	12	3	32	29
0	12	4	24	22
1	12	1	29	23
1	12	-1	32	26
1	12	-2	44	40
1	12	-3	66	57
1	11	-9	24	18
1	11	-8	47	45
1	11	-5	40	38
1	11	-4	38	41
1	11	-2	31	28
1	11	0	21	22
1	11	2	51	52
1	11	5	34	31
1	11	6	65	62
1	11	7	53	46
1	11	8	30	26
1	11	9	25	21
1	10	12	28	24
1	10	10	28	20
1	10	9	27	19
1	10	5	36	40
1	10	3	20	10
1	10	2	34	33
1	10	1	76	73
1	10	-1	31	32
1	10	-3	31	35
1	10	-5	38	36
1	10	-6	77	72
1	10	-7	79	79
1	10	-11	39	40
1	10	-12	26	23
1	9	-15	32	26
1	9	-13	27	29
1	9	-12	31	25
1	9	-11	40	39
1	9	-10	30	17
1	9	-9	32	31
1	9	8	33	29
1	9	9	29	21
1	9	11	25	29
1	9	13	27	23
1	9	14	30	24
1	8	16	30	30
1	8	12	22	26
1	8	11	24	20
1	8	-11	37	34
1	8	-12	43	45
1	8	-13	51	49
1	8	-14	35	34
1	8	-15	44	44
1	7	-17	34	34
1	7	-16	40	40
1	7	-15	68	68
1	7	-14	68	63
1	7	13	38	38
1	7	14	28	31
1	7	15	33	25
1	7	16	44	44
1	7	17	37	33
1	6	18	31	30
1	6	17	44	41
1	6	16	29	28
1	6	15	24	26
1	6	14	30	24
1	6	-15	48	55
1	6	-18	27	29
1	6	-19	46	41
1	5	-20	21	16
1	5	-18	52	50
1	5	-17	36	34
1	5	-16	29	30
1	5	16	53	53
1	5	17	30	29
1	4	20	34	33
1	4	-17	35	34
1	4	-18	33	32
1	4	-19	21	21
1	4	-20	25	32
1	4	-21	41	41
1	3	-21	40	44
1	3	-18	53	53
1	3	17	24	13
1	3	18	47	47
1	3	19	40	41
1	3	20	31	31
1	2	21	34	37
1	2	19	23	19
1	2	18	22	21
1	2	-18	25	17
1	2	-19	45	47
1	2	-20	26	25
1	2	-21	47	44
1	1	-22	22	24
1	1	-21	36	34
1	1	-19	52	54
1	1	19	23	21
1	0	20	21	18
1	0	18	75	77
1	0	-20	86	83
2	0	-20	28	25
2	0	-18	104	104
2	0	18	81	78
2	0	20	54	53
2	1	18	48	51
2	1	17	48	48
2	1	-18	53	52
2	1	-19	39	37
2	1	-21	32	34
2	2	-21	57	58
2	2	-19	53	47
2	2	-18	36	40
2	2	17	33	36
2	2	19	26	21
2	3	19	27	21
2	3	17	35	36
2	3	-18	30	23
2	3	-20	66	64
2	3	-21	57	58
2	4	-20	62	61
2	4	-19	47	46
2	4	-18	36	35
2	4	-17	20	20
2	4	18	27	28
2	5	15	30	25
2	5	-16	31	36
2	5	-17	45	45
2	5	-18	26	11
2	5	-20	31	33
2	6	-19	33	27
2	6	-18	21	20
2	6	-17	55	49
2	6	14	57	59
2	6	15	36	40
2	6	17	53	55
2	7	16	28	28
2	7	15	27	32
2	7	12	57	58
2	7	-14	42	44
2	7	-16	25	16
2	8	-15	35	33
2	8	-14	57	57
2	8	-13	50	50
2	8	-12	25	25
2	8	-11	102	98
2	8	10	28	26
2	8	11	49	43
2	8	15	23	9
2	9	13	23	22
2	9	12	25	23
2	9	11	44	42
2	9	10	24	12
2	9	9	25	31
2	9	7	27	32
2	9	6	41	40
2	9	-7	32	29
2	9	-8	28	18
2	9	-9	37	41
2	9	-11	29	28
2	9	-12	38	40
2	9	-13	26	26
2	10	-12	26	28
2	10	-11	24	15
2	10	-9	33	37
2	10	-8	32	27
2	10	-7	28	26
2	10	-5	69	67
2	10	-4	77	74
2	10	-3	67	63
2	10	-2	48	43
2	10	0	26	21
2	10	1	42	45
2	10	2	40	40
2	10	3	31	34
2	10	5	25	29
2	10	6	31	26
2	10	7	43	40
2	10	8	39	39
2	10	10	32	29
2	11	7	23	27
2	11	6	29	22
2	11	4	45	42
2	11	1	27	23
2	11	-2	22	24
2	11	-7	21	8
3	11	-6	29	23
3	11	-5	27	21
3	11	-3	27	19
3	11	-2	24	26
3	11	-1	30	28
3	11	0	29	27
3	11	1	29	24
3	11	3	28	14
3	11	4	33	27
3	10	5	25	31
3	10	3	25	27
3	10	0	50	54
3	10	-1	38	38
3	10	-2	45	42
3	10	-4	34	35
3	10	-5	30	27
3	10	-6	30	24
3	10	-8	22	19
3	9	-13	51	45
3	9	-12	35	34
3	9	-11	48	47
3	9	-10	34	38
3	9	-9	43	46
3	9	-8	59	58
3	9	-4	74	68
3	9	-3	82	82
3	9	-2	53	49
3	9	-1	60	56
3	9	0	44	44
3	9	1	26	28
3	9	2	23	23
3	9	3	32	33
3	9	5	45	43
3	9	6	28	20
3	9	8	22	17
3	9	9	25	29
3	9	11	24	25
3	8	12	37	40
3	8	10	28	28
3	8	8	32	33
3	8	7	43	47
3	8	-9	77	73
3	8	-10	61	59
3	8	-11	22	21
3	8	-15	41	39
3	7	-16	23	23
3	7	-15	44	43
3	7	-14	23	17
3	7	-12	33	30
3	7	12	26	18
3	7	14	32	31
3	6	16	25	24
3	6	13	36	36
3	6	12	37	35
3	6	-14	24	29
3	6	-16	21	14
3	6	-17	28	34
3	6	-18	23	16
3	5	-17	23	24
3	5	-16	46	45
3	5	-15	40	40
3	5	13	41	39
3	5	14	22	22
3	5	15	22	22
3	4	18	34	24
3	4	-16	29	30
3	4	-17	30	28
3	4	-20	25	27
3	3	-20	54	54
3	3	-19	98	92
3	3	-18	89	87
3	3	-17	23	13
3	3	15	35	42
3	3	17	27	25
3	2	19	24	27
3	2	18	29	25
3	2	17	33	30
3	2	15	26	27
3	2	-17	50	50
3	2	-18	42	48
3	2	-19	37	32
3	2	-20	51	49
3	2	-21	41	41
3	1	-21	26	22
3	1	-20	38	37
3	1	-19	22	25
3	1	17	43	37
3	1	18	24	26
3	0	18	53	53
3	0	16	44	44
3	0	-18	70	63
3	0	-20	49	43
4	0	-20	49	45
4	0	14	44	44
4	1	14	21	15
4	1	-16	60	57
4	1	-17	72	72
4	1	-18	25	21
4	1	-19	42	42
4	1	-20	32	35
4	2	-19	38	36
4	2	-18	58	54
4	2	-17	44	45
4	2	-16	115	110
4	2	17	21	2
4	3	16	23	26
4	3	14	20	19
4	3	-15	33	34
4	3	-16	53	54
4	3	-17	26	27
4	3	-18	34	36
4	3	-19	28	27
4	4	-19	71	62
4	4	-18	63	62
4	4	-17	40	34
4	4	-15	56	53
4	4	12	56	58
4	4	13	35	33
4	4	15	21	15
4	5	11	39	41
4	5	10	27	34
4	5	-13	61	60
4	5	-15	45	46
4	5	-16	26	24
4	5	-17	31	27
4	6	-15	22	22
4	6	-14	33	33
4	6	-13	40	42
4	6	-12	22	25
4	6	9	45	41
4	6	11	28	15
4	7	10	23	15
4	7	9	20	20
4	7	8	32	32
4	7	7	41	37
4	7	-9	28	30
4	7	-10	38	33
4	7	-11	21	21
4	7	-13	32	28
4	7	-14	24	23
4	8	-14	36	38
4	8	-13	69	68
4	8	-12	47	45
4	8	-8	52	54
4	8	-7	28	32
4	8	-5	36	32
4	8	1	27	25
4	8	2	34	36
4	8	3	21	14
4	8	4	22	25
4	8	5	55	51
4	8	6	48	45
4	8	7	44	36
4	8	9	40	38
4	8	10	26	26
4	9	6	41	39
4	9	4	27	24
4	9	1	60	59
4	9	0	74	68
4	9	-1	59	60
4	9	-2	39	30
4	9	-4	25	27
4	9	-5	32	37
4	9	-6	49	47
4	9	-7	63	60
4	9	-8	39	33
4	9	-10	32	26
4	10	-6	32	30
4	10	-5	32	24
5	9	-6	34	29
5	9	-5	49	44
5	9	2	37	30
5	9	3	33	28
5	8	7	24	24
5	8	5	26	17
5	8	4	27	27
5	8	3	26	24
5	8	2	25	21
5	8	1	61	59
5	8	0	41	40
5	8	-1	42	39
5	8	-4	36	36
5	8	-5	25	21
5	8	-8	25	21
5	8	-9	23	25
5	8	-10	25	25
5	8	-11	49	41
5	7	-13	37	36
5	7	-12	69	66
5	7	-11	35	37
5	7	-9	21	24
5	7	-8	24	18
5	7	-6	26	25
5	7	-4	44	41
5	7	-3	24	19
5	7	-1	23	21
5	7	0	24	28
5	7	2	30	25
5	7	3	30	23
5	7	4	30	23
5	7	5	39	35
5	7	9	23	24
5	6	6	27	25
5	6	-9	46	41
5	6	-10	20	20
5	6	-11	21	30
5	5	-16	42	40
5	5	-15	58	53
5	5	-13	38	42
5	5	-12	29	22
5	5	10	23	18
5	4	10	36	40
5	4	9	26	21
5	4	8	40	35
5	4	-12	32	31
5	4	-14	46	44
5	4	-15	50	46
5	4	-16	29	29
5	4	-17	53	49
5	3	-17	37	32
5	3	-16	32	34
5	3	-15	32	35
5	3	-14	25	28
5	3	-13	27	28
5	3	9	42	37
5	3	10	34	33
5	3	12	39	42
5	3	13	49	47
5	3	14	23	20
5	2	11	43	39
5	2	10	47	42
5	2	-14	70	68
5	2	-15	62	59
5	2	-16	22	15
5	2	-18	26	16
5	1	-17	36	39
5	1	-15	51	45
5	1	-14	82	80
5	1	11	30	31
5	1	13	26	17
5	0	14	31	26
5	0	12	28	27
5	0	-14	23	17
5	0	-16	53	55
5	0	-18	71	67
6	0	-16	36	31
6	0	-14	28	24
6	0	-12	104	101
6	0	10	38	41
6	1	11	23	18
6	1	-10	42	40
6	1	-11	71	67
6	1	-12	61	60
6	1	-13	22	17
6	1	-14	30	34
6	1	-15	30	33
6	2	-15	30	30
6	2	-14	22	12
6	2	-13	47	44
6	2	-10	36	30
6	3	11	27	25
6	3	10	24	13
6	3	5	20	11
6	3	-8	65	61
6	3	-9	32	33
6	3	-10	25	20
6	3	-11	62	58
6	3	-13	27	18
6	3	-14	33	25
6	4	-15	26	31
6	4	-13	24	24
6	4	-8	25	17
6	4	2	35	35
6	4	5	26	23
6	4	6	28	24
6	4	7	22	18
6	5	8	23	22
6	5	7	24	17
6	5	5	28	11
6	5	3	22	10
6	5	-1	46	43
6	5	-2	26	31
6	5	-3	29	22
6	5	-6	22	20
6	5	-7	39	37
6	5	-9	30	28
6	5	-10	22	13
6	5	-11	25	25
6	5	-12	22	11
6	5	-13	34	30
6	5	-14	52	49
6	6	-11	32	32
6	6	-10	27	21
6	6	-8	29	30
6	6	-5	45	42
6	6	-1	30	20
6	6	0	34	32
6	6	1	27	19
6	7	5	26	18
6	7	4	23	13
6	7	2	23	26
6	7	-4	29	24
6	7	-8	31	33
6	7	-9	47	42
6	7	-10	51	44
6	8	-6	31	29
6	8	1	26	21
7	6	0	23	6
7	6	-3	22	16
7	5	-7	23	16
7	5	0	25	22
7	5	1	35	36
7	5	3	24	21
7	4	4	24	6
7	4	3	24	18
7	4	1	27	25
7	4	0	22	14
7	4	-5	22	5
7	4	-6	21	22
7	3	-7	28	26
7	3	-5	21	17
7	3	-4	25	27
7	2	6	25	25
7	2	4	22	15
7	2	3	29	21
7	2	2	24	24
7	2	-3	24	10
7	2	-4	24	18
7	2	-5	27	19
7	2	-7	31	32
7	2	-9	24	21
7	2	-13	31	27
7	1	-13	24	21
7	1	-12	22	24
7	1	-11	34	32
7	1	-10	42	39
7	1	-7	25	24
7	1	-2	23	12
7	1	-1	35	36
7	1	2	27	29
7	1	4	24	25
7	1	5	32	31
7	0	4	29	32
7	0	2	31	26
7	0	0	32	28
7	0	-2	29	23
7	0	-8	41	38
7	0	-10	93	90
7	0	-12	24	19
8	0	-6	48	47
8	2	-4	27	16
8	2	-3	24	21

STRUCTURE DETERMINATION

The observed structure factors were brought on an approximately absolute scale by Wilson's statistical methods. These methods also demonstrated uniquely the lack of a centre of symmetry in the crystals.

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms ($\times 10^5$). The temperature factor is given by exp $-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl^-	0	13188	97	5641	1094	305	2005	639	77
	0	7	0	29	8	2	31	13	9
O1	82763	72243	27806	4247	914	280	−1141	926	−161
	33	19	10	75	24	7	71	37	22
O2	93919	44484	15655	3666	963	328	−370	1344	−140
	32	19	10	67	24	7	70	37	22
O3	36222	3232	32136	4712	946	278	−1519	1440	−312
	34	19	11	81	26	8	75	42	23
N	23581	20284	64188	3189	1106	220	280	634	64
	38	23	12	77	30	8	81	38	25
C1	41390	35160	38085	2191	962	180	97	378	−33
	40	24	12	73	30	8	83	38	27
C2	53410	52300	36735	2604	820	209	34	497	−115
	40	24	13	81	29	8	81	41	26
C3	71049	55259	29350	2413	703	218	−331	364	3
	39	23	13	78	27	8	78	41	26
C4	76651	40735	22934	2264	831	196	−92	477	7
	38	24	13	78	30	8	78	40	25
C5	64675	23461	24049	2984	838	246	−340	695	−190
	43	25	14	87	30	8	85	43	27
C6	47238	20717	31629	2541	796	222	−577	422	−99
	41	25	13	81	29	8	83	41	26
C7	23435	32386	46569	2203	974	224	−42	600	57
	39	25	13	77	31	8	81	40	27
C8	41203	24703	56002	2189	1257	220	−116	355	−67
	40	27	14	78	35	8	89	40	29

Table 3. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms.

Atom	x	y	z	B
HO1	8570	7689	3307	3.89
	59	38	22	0.61
HO2	9637	3587	1246	2.41
	51	31	19	0.49
HO3	2812	213	3689	3.53
	54	37	20	0.57
H1N	1462	2959	6588	2.64
	51	35	20	0.49
H2N	3433	1743	6999	3.17
	57	34	21	0.54
H3N	1125	1120	6149	3.22
	52	35	21	0.55
HC2	4767	6266	4056	2.60
	49	32	20	0.50
HC5	6818	1349	1942	1.64
	47	29	16	0.41
H1C7	748	2458	4457	0.97
	37	26	14	0.38
H2C7	1512	4476	4792	1.74
	44	30	17	0.41
H1C8	5447	3394	5841	4.12
	58	36	23	0.64
H2C8	5043	1288	5447	2.56
	52	33	18	0.49

Table 4. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and B values (Å^2) along the principal axes of vibration given by the components of a unit vector e in fractional coordinates ($\times 10^3$).

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
Cl^-	0.269	5.70	194	52	11
	0.159	2.00	17	38	74
	0.147	1.70	−77	123	18
O1	0.234	4.32	191	−44	28
	0.144	1.64	57	130	18
	0.138	1.51	64	16	−69
O2	0.228	4.10	179	−22	46
	0.158	1.97	38	136	2
	0.121	1.16	−102	12	61
O3	0.258	5.27	180	−45	39
	0.144	1.64	−51	59	64
	0.141	1.57	96	117	−17
N	0.197	3.07	195	37	28
	0.169	2.26	57	−133	5
	0.126	1.25	50	6	−72
C1	0.162	2.08	164	84	18
	0.159	1.99	120	−109	22
	0.117	1.09	−50	13	71
C2	0.177	2.46	201	−6	31
	0.151	1.80	30	129	−25
	0.120	1.14	−51	51	66
C3	0.170	2.29	199	−36	23
	0.137	1.48	16	102	52
	0.129	1.32	64	86	−52
C4	0.166	2.18	197	−17	34
	0.148	1.73	20	137	9
	0.119	1.11	70	9	−68
C5	0.195	3.00	187	−37	37
	0.150	1.77	82	119	−21
	0.124	1.21	−49	60	64
C6	0.180	2.57	184	−59	26
	0.137	1.48	99	118	−12
	0.131	1.37	−22	41	71
C7	0.170	2.28	181	18	46
	0.161	2.05	−36	136	1
	0.118	1.10	100	16	−62
C8	0.183	2.65	32	−136	10
	0.160	2.03	199	25	29
	0.132	1.37	−58	10	70

The Patterson function was calculated and the y parameter of the chlorine ion readily obtained. The x and z parameters were arbitrarily chosen to be zero. A weighted Fourier synthesis [11] contained an extra two-fold axis of symmetry; the pattern of a benzene ring with four attached atoms could be recognized, however, and a Fourier map based on the positions of these atoms revealed the locations of the remaining non-hydrogen atoms. The R-factor at this stage was 0.20; a few cycles least-squares calculation and inclusion of the hydrogen atoms bonded to carbon in calculated positions gave an R-factor of 0.14. Further refinements after introduction of anisotropic thermal param-

eters lowered R to 0.055. A difference Fourier map revealed the positions of the remaining hydrogen atoms, and after correction for secondary extinction effects the final refinement of all parameters yielded an R-value of 0.042 for all observed reflections. The weighted R was 0.036. A total difference Fourier map showed no electron density larger than 0.4 eÅ^{-3}.

A comparison of observed and calculated structure factors is given in Table 1. Final parameters for non-hydrogen atoms are listed in Table 2 and for hydrogen atoms in Table 3.

Magnitudes and directions of the principal axes of the vibrational ellipsoids are given in Table 4. The r.m.s. discrepancy between the atomic vibration tensor components obtained in the structure determination and those calculated from a rigid-body analysis of the cation was 0.0019 Å^2. The low value indicates that the molecule may be regarded as a rigid unit, and the atomic coordinates were accordingly adjusted. The translational r.m.s. amplitudes of vibration are 0.15, 0.14, and 0.12 Å along the principal axes, and the r.m.s. librational amplitudes 4.8°, 2.0°, and 1.1°. The major axis of libration coincides with the axis of the lowest moment of inertia in the ion.

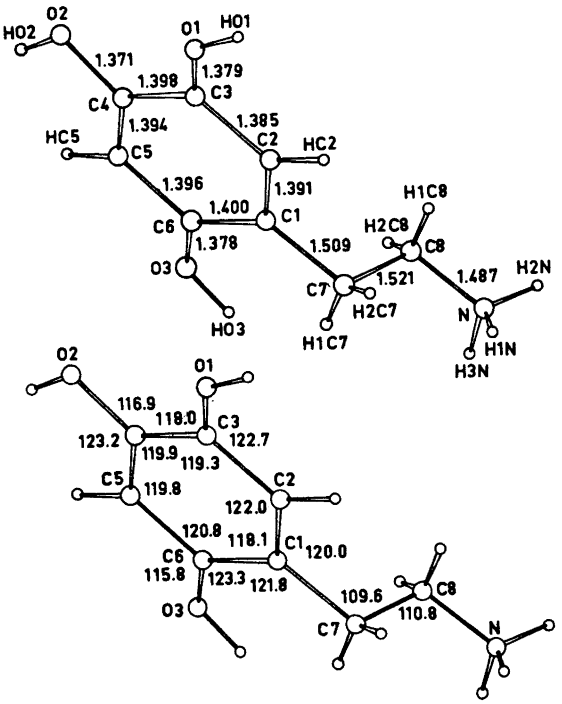


Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects) and angles in the cation of 6-hydroxydopamine hydrochloride.

DISCUSSION

Bond lengths and angles are presented in Table 5 and also in Fig. 1, where the numbering of the atoms is indicated. The estimated standard deviations listed are calculated from the correlation matrix ignoring standard deviations in cell parameters.

Table 5. Bond lengths (Å) and bond angles (°). Estimated standard deviations (in parentheses) apply to the least significant digits.

Bond length		Corrected	Bond angle	
C1 – C2	1.388(3)	1.391	C1 – C2 – C3	122.0(2)
C2 – C3	1.384(2)	1.385	C2 – C3 – C4	119.3(2)
C3 – C4	1.394(2)	1.398	C3 – C4 – C5	119.9(2)
C4 – C5	1.391(3)	1.394	C4 – C5 – C6	119.8(2)
C5 – C6	1.395(2)	1.396		
C6 – C1	1.396(2)	1.400	C5 – C6 – C1	120.8(2)
C1 – C7	1.507(2)	1.509	C6 – C1 – C2	118.1(2)
C7 – C8	1.517(3)	1.521	C2 – C3 – O1	122.7(2)
C8 – N	1.486(2)	1.487	C4 – C3 – O1	118.0(2)
C3 – O1	1.377(2)	1.379	C3 – C4 – O2	116.9(2)
C4 – O2	1.371(2)	1.371	C5 – C4 – O2	123.2(2)
C6 – O3	1.376(2)	1.378	C5 – C6 – O3	115.8(2)
C2 – HC2	0.96(2)		C1 – C6 – O3	123.3(2)
C5 – HC5	0.97(2)		C2 – C1 – C7	120.0(2)
C7 – H1C7	0.96(2)		C6 – C1 – C7	121.8(2)
C7 – H2C7	1.01(2)		C1 – C7 – C8	109.6(2)
C8 – H1C8	0.95(3)		C7 – C8 – N	110.8(2)
C8 – H2C8	1.00(2)			
O1 – HO1	0.77(3)		C3 – O1 – HO1	107(2)
O2 – HO2	0.77(2)		O4 – O2 – HO2	112(2)
O3 – HO3	0.78(3)		C6 – O3 – HO3	112(2)
N – H1N	0.84(3)		C8 – N – H1N	112(2)
N – H2N	0.89(3)		C8 – N – H2N	110(2)
N – H3N	0.92(3)		C8 – N – H3N	106(2)

Hydrogen bond lengths		Other short contacts	
O1 – Cl $(1+x, 1-y, \frac{1}{2}+z)$	3.120	Cl – H1C7$(x, -y, -\frac{1}{2}+z)$	2.860
O2 – Cl $(1+x, y, z)$	3.087	Cl – C8 $(x, -y, -\frac{1}{2}+z)$	3.412
O3 – Cl $(x, -y, \frac{1}{2}+z)$	3.324	O1 – H2N $(x, 1-y, -\frac{1}{2}+z)$	2.534
N – O1$(-1+x, 1-y, \frac{1}{2}+z)$	2.870	O2 – H1C8 $(x, 1-y, -\frac{1}{2}+z)$	2.544
N – O2$(-1+x, 1-y, \frac{1}{2}+z)$	2.938	Distance between benzene planes	3.43
N – O3$(x, -y, \frac{1}{2}+z)$	2.905		
N – Cl$(x, -y, \frac{1}{2}+z)$	3.167		

The C1 – C7 bond length corresponds to the normal value for a single bond between sp^2 and sp^3 hybridized carbon atoms. The C7 – C8 bond of 1.521 Å is slightly shorter than the aliphatic carbon-carbon single bond. This, however, is also found for the corresponding bond in 5-hydroxydopamine hydrochloride.[12] The C – NH_3^+ bond length has the value of 1.487 Å, which is given as the average value for α-aminoacids by Marsh and Donohue.[13] The valence angles in the side chain are tetrahedral, and the dihedral angle C1 – C7 – C8 – N is 175.1°.

The hydroxyhydroquinone part of the molecule is nearly planar. The carbon atoms in the benzene ring deviate less than 0.006 Å from a least-squares plane defined by these atoms, whereas the oxygen atoms are situated 0.026 Å(01), 0.009 Å(02) and 0.010 Å(03), and C7 0.058 Å out of this plane. None of the carbon-carbon bond lengths in the benzene ring deviates significantly from the normal value, and the mean C–O value of 1.375 Å agrees well with that usually found in phenols. The distortions of the external angles from 120° at the C3, C4, and C6 atoms are analogous to what has been observed in other phenols where the oxygen atoms are hydrogen donors in an arrangement roughly coplanar with the benzene ring. The larger external angles are *cis* to the hydrogen atoms.

The angle between the plane of the benzene ring and the one defined by C1–C7–C8 is 84.9°. As the dihedral angle about the C7–C8 bond deviates by 5° from 180°, the plane through C1, C7, and N forms an angle of about 80° with the benzene plane.

The arrangement of the ions is shown in Fig. 2. There are a few van der Waals contacts as listed in Table 5; the crystal structure is, however, stabilized mainly by interionic hydrogen bonds.

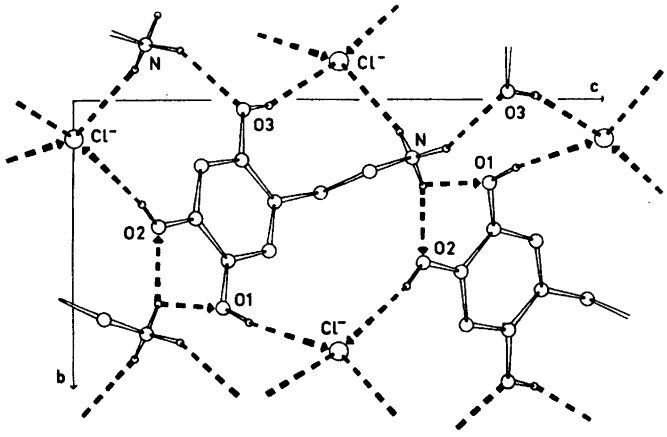


Fig. 2. The crystal structure as seen down the *a*-axis.

The phenol oxygen atoms act as hydrogen donors in hydrogen bonds to chlorine ions with lengths 3.120 Å, 3.087 Å, and 3.324 Å, respectively. The O–H···Cl- arrangements are nearly linear, the angles being larger than 160°. The H–Cl- separations are in the range 2.33 to 2.58 Å. The three oxygen atoms are acceptors in hydrogen bonds from nitrogen atoms in neighbouring ions. The N–H···O3 bond is normal, 2.905 Å. O1 and O2 are both close to the same hydrogen atom, the separations being 2.33 Å and 2.12 Å. This might possibly be an asymmetric bifurcated hydrogen bond with N–O distances of 2.870 Å(01) and 2.938 Å(02). The N–H···O angles are 122° and 163°, respectively, and the combination of a shorter H–O distance and a more linear N–N···O arrangement indicates the N–H···O2 to be the stronger

of the two hydrogen bonds. The third of the hydrogen atoms attached to nitrogen is engaged in a hydrogen bond of 3.167 Å to the chlorine ion; the H3N – C*l* distance is 2.33 Å.

In the three-dimensional network of hydrogen bonds each organic ion is bonded to four other 6-hydroxydopamine ions and three chlorine ions. Each of the chlorine ions is coordinated to three organic ions by four hydrogen bonds. Two of these are thus directed to the same organic ion (to O3 and N), and the chlorine ion is also situated fairly close to H1C7 and C8.

REFERENCES

1. Senoh, S., Witkop, B., Creveling, C. R. and Udenfriend, S. *J. Am. Chem. Soc.* **81** (1959) 1768.
2. Malmfors, T. and Sachs, C. *Eur. J. Pharmacol.* **3** (1968) 89.
3. Ong, H. H., Creveling, C. R. and Daly, J. W. *J. Med. Chem.* **12** (1969) 458.
4. Bloom, F. E., Algeri, S., Groppetti, A., Revuelta, A. and Costa, E. *Science* **166** (1969) 1284.
5. Calne, D. B. and Sandler, M. *Nature* **226** (1970) 21.
6. Nicolaus, R. A. *Chem. Nat. Prod. 6*, Hermann, Paris 1968.
7. Senoh, S. and Witkop, B. *J. Am. Chem. Soc.* **81** (1959) 6231.
8. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
9. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
11. Sim, G. A. *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon, Oxford 1961, p. 227.
12. Andersen, A. M., Mostad, A. and Römming, C. *Acta Chem. Scand. To be published.*
13. March, R. E. and Donohue, J. *Advan. Protein Chem.* **22** (1967) 235.

Received May 3, 1971.