The Crystal and Molecular Structure

Of Meta-Aminobenzoic Acid Hydrochloride

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ABSTRACT

The structure of crystals of meta-aminobenzoic acid hydrochloride has been determined by two two-dimensional Patterson projections and refined by three-dimensional least-squares techniques. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions: a=4.562, b=5.823, c=14.724, $\alpha = 98^{\circ}39'$, $\beta = 91^{\circ}12'$, $\gamma = 95^{\circ}45'$. There are two molecules in the unit cell. The R index of the refined structure is 11.26% with 1507 reflections. Pairs of molecules are linked together to form dimers through two O-H··O hydrogen bonds arranged about a center of symmetry; and the amino and benzene ring fall in the same plane, with the oxygens in the carboxyl groups tilted out of the plane by 0.12 angstroms.

INTRODUCTION

Amino acids occur in certain biological processes which makes them of some interest to the investigation of molecular biology. As a continuing project regarding the structure of amino acids in this lab, we have undertaken the investigation of meta-aminobenzoic acid because of its biological interest and for the sake of comparing the meta- to the para- form which has previously been determined and reported in the literature. (Ref. 1)

Meta-aminobenzoic acid is a stable gray powder. Attempts to crystallize the pure compound from common inorganic and organic solvents proved to be unsuccessful; crystals of the hydrochloride form were, however, prepared and used for this investigation. The hydrochloride was formed by dissolving the compound in hot, concentrated hydrochloric acid. Then the solution was allowed to slowly cool, crystallizing out the hydrochloride. The crystals were then left to dry in the air. The crystals were long needles of a few millimeters in length with some twinning and cracking present. The crystals were found to be very soluble in water, but they were stable for long periods of time in air.

EXPERIMENTAL

Two crystals were used for the determination of the unit cell dimensions and for the collection of intensity data, one aligned with the a axis and the other with the b axis, parallel to the rotation axes. Unit cell dimensions were determined from zero-level precision Weissenberg photographs along the axes of both crystals. From these, the three reciprocal space lattice distances (a^*, b^*, c^*) and the two reciprocal space lattice angles (α^*, β^*) were determined. The third reciprocal space lattice angle (γ^*) was taken from an hk0 precession photograph. The cell dimensions were then calculated and are summarized in the subsequent table:

a = 4.562 A.	σ = 0.0004
b = 5.823 A.	σ = 0.0006
c = 14.724 A.	σ = 0.0011
α = 98°39'	σ = 0.7'
β = 91°12'	σ = 0.2'
γ = 95°45'	σ = 1'

The molecule forms a triclinic lattice, space group $P\bar{1}$, with two molecules in the unit cell being related by an inversion center.

Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs using CuK_α radiation. Films were taken of layers 0 to 3 about the a axis and layers 0 to 4 about the b axis. A standard deviation was assigned to each reflection according to an expression given by Sharma and McConnell (Ref. 2) and was used in obtaining film and pack factors for each set of photographs. These standard deviations were also used for determining an average intensity and assigning a standard deviation to the reflections. These and all subsequent calculations used the CRYRM system (Ref. 3) on an IBM 7094-7040 computer. Intensities were corrected for Lorentz-polarization but not for absorption. The resulting list of reflections (Table 4) was comprised of 1507 reflections, of which 248 were too weak to be observed above the background.

The heavy atom parameters were first determined from zero-layer data about the two axes. Two-dimensional Patterson maps were made, and the chlorine coordinates were taken from these Pattersons. The coordinates of the remaining heavy atoms were found using a Fourier map calculated from the phases based upon the chlorine coordinates.

These trial parameters were then used in a structure-factor and least-squares cycles for the complete three-dimensional data. The structure was refined to an R factor of 11.8% with the addition of the hydrogen atoms in their expected positions.

The intensities of 290 reflections whose observed and calculated structure factors showed marked disagreement were re-evaluated. Re-reading of intensities and changes in the weighting scheme were used to correct these reflections. Refinement of the structure then yielded an R factor of 11.26% with the hydrogen atoms not included in the refinement. Further evaluation of the data is still in progress.

Fourier (Fig. 1) and difference Fourier maps show the existence of no other heavy atoms in the unit cell. Tables 1, 2, and 3, demonstrate the results of the least-squares refinement.

CONCLUSIONS

An interesting feature of the structure arises from the chlorine to chlorine distance across the b and c axes. These distances are 3.82 and 3.60 angstroms respectively. This configuration is unfavorable by the chloride-chloride columb repulsion; however, this is balanced by the chloride-amine columb attractions. Another facet of the structure which is a common feature with carboxyl groups is the dimerization of the carboxyl groups with its associated hydrogen bonding. The difference between the C-O bond distances is 0.047 angstroms. (1.271 versus 1.224 angstroms) The conditions around the oxygen atoms are therefore quite similar. The question then arises of the possibility of tautomerism of the protons in the dimerized carboxyl groups. A difference Fourier map shows the presence of the electron in the position associated with the longer C-O bond length, but none in the second position. At the present level of refinement of the structure, we can say that probably no more than 20% tautomerism occurs.

The carboxyl groups are tilted out of the plane of the benzene ring with the oxygen atoms being 0.12 angstroms above and below the plane respectively. The amine group and the benzene ring are co-planar to within the accuracy of these calculations.

The carbon to carbon distance from the benzene to the carboxyl group compares favorably to the B structure of the para-aminobenzoic acid (Ref. 1) and to that of 2-amino-3-methylbenzoic acid. (Ref. 4) The carbon to nitrogen distance is larger than in the other two cases cited probably due to the absence of resonance forms resulting from the protonation of the amine group. It is also noted that several of the carbon to carbon bond distances are found to be smaller than would normally be expected for meta- substitution. The differences in the carbon to carbon bond distances in the benzene ring are about 0.04 angstroms; this difference exceeds the standard deviation in these values and is even greater than the differences found in the para- and the 2-amino-3-methyl-. Our knowledge of this effect is inconclusive.

REFERENCES

1 - Lai, T. F. and Marsh, R. E., Acta Crystallographica, 22, 885 (1967)

2 - Duchamp, D. J., Amer., Cryst. Assoc. Meeting, Bozeman, Montana, paper B-14, p. 29 (1964)

3 - Sharma, B. D. & McConnell, J. F., Acta Cryst., 19, 797 (1965)

4 - Brown, G. M. and Marsh, R. E., Acta Cryst., 16, 1191, (1963)

Fourier Map of Benzene Ring Fig. 1

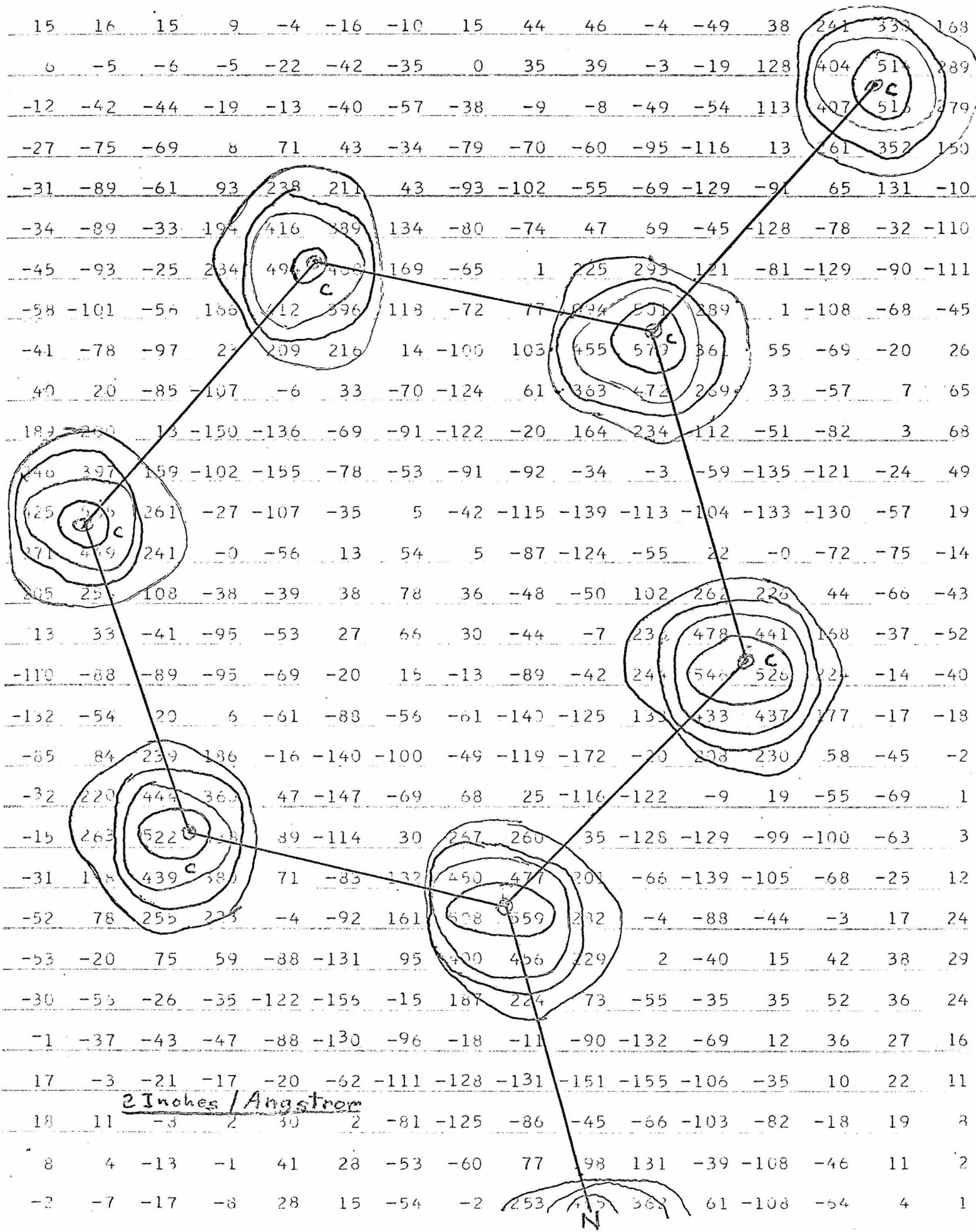

Fig. 2

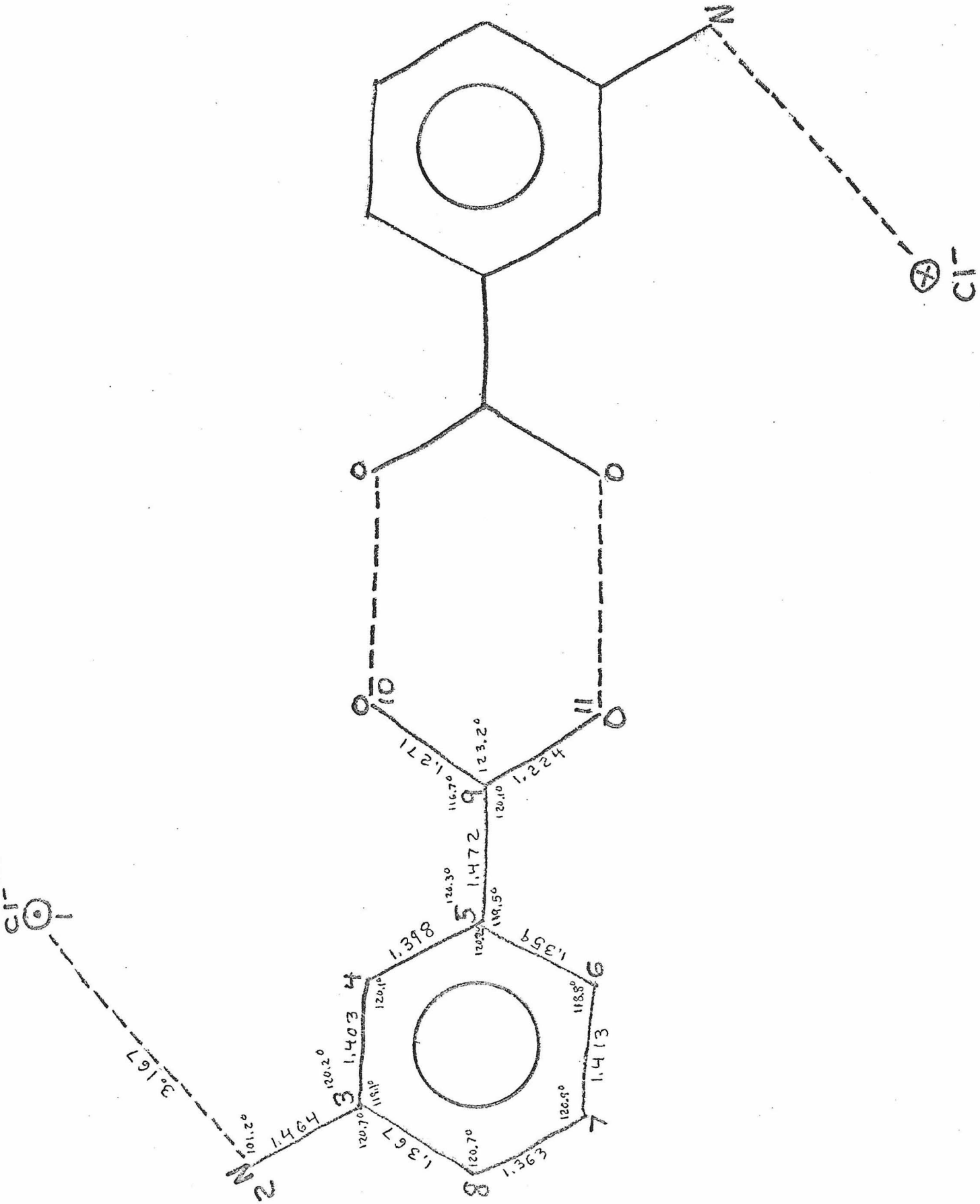
N
Cl⁻
O
O
O
O
1.271
1.224
116.7°
123.2°
120.1°
1.472
124.3°
119.5°
120.2°
1.398
1.354
5
4
6
120.1°
118.8°
1.403
1.413
3
120.2°
120.9°
119.1°
120.7°
1.367
1.363
120.7°
7
8
1.464
101.2°
2
3.167
Cl⁻

Table 1

BOND DISTANCES

Atom	Atom	Distance
1	2	3.167
2	3	1.464
3	4	1.403
3	8	1.367
4	5	1.398
5	6	1.359
5	9	1.472
6	7	1.413
7	8	1.363
9	10	1.271
9	11	1.224

Table 2

BOND ANGLES

Atom	Atom	Atom	Angle
1	2	3	101.2
2	3	4	120.2
2	3	8	120.7
8	3	4	119.1
3	4	5	120.1
4	5	6	120.2
4	5	9	120.3
6	5	9	119.5
5	6	7	118.8
6	7	8	120.9
7	8	3	120.7
5	9	10	116.7
5	9	11	120.1
10	9	11	123.2

Table 3

The Heavy-Atom Parameters

And Their Standard Deviations (in parentheses)

COORDINATES

Atom	x	y	z
Cl- (1)	.1436(4)	.2747(3)	.0668(1)
N (2)	.4077(13)	.8073(9)	.0923(4)
C (3)	.5529(15)	.8352(11)	.1835(5)
C (4)	.5038(15)	1.0240(11)	.2506(5)
C (5)	.6315(15)	1.0442(11)	.3389(5)
C (6)	.8154(15)	.8875(13)	.3590(5)
C (7)	.8646(16)	.6996(12)	.2904(5)
C (8)	.7328(17)	.6756(11)	.2050(5)
C (9)	.5749(17)	1.2391(12)	.4102(5)
O (10)	.3789(12)	1.3662(8)	.3907(3)
O (11)	.7176(12)	1.2750(8)	.4831(3)

Atoms are labeled on Fig. 2

ANISOTROPIC TEMPERATURE FACTOR

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl- (1)	567(13)	229(6)	39(1)	275(12)	-67(5)	-51(3)
N (2)	603(38)	248(19)	34(3)	273(43)	-36(17)	-34(11)
C (3)	513(49)	227(23)	34(4)	64(52)	38(21)	-33(14)
C (4)	486(44)	198(22)	41(4)	218(48)	-19(20)	24(14)
C (5)	405(42)	224(22)	36(4)	161(47)	-4(19)	-8(14)
C (6)	397(43)	342(26)	34(4)	190(55)	-19(19)	4(15)
C (7)	633(53)	313(28)	41(4)	358(61)	19(24)	3(17)
C (8)	611(50)	208(23)	46(4)	247(54)	35(24)	-25(15)
C (9)	508(50)	278(26)	31(4)	118(56)	13(21)	-33(16)
O (10)	737(38)	359(20)	43(3)	441(45)	-49(17)	-89(12)
O (11)	755(36)	404(21)	44(3)	391(45)	-129(17)	-94(13)

expressed in the form $\exp(-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl))$

all anisotropic temperature factors are multiplied by 10^4

Table 4

Observed and Calculated Structure Factors

Within each group are given the valmes of l, 100 F(obs.), and 100 F(calc.). Reflections indicated with an asterisk were omitted from the least-squares refinement. A minus sign preceding F(obs.) signifies 'less than'; these reflections have been omitted from the refinement unless the value F(calc.) exceeds the threshold value of F(obs.).

0	0	L
0	---*	8235

-5	2	L
0	409	259
1	533	489
2	355	210
3	529	555
4	-259	181
5	-247	-57
6	689	660
7	-209	-115
8	459	-404
9	276	-288

-5	3	L
0	330	186
1	206	167
2	-247	18
3	275	-144
4	344	-291
5	340	-364
6	318	-218

-5	4	L
0	560	-467
1	339	-276
2	379	-325
3	432	-427
4	410	-383

-4	2	L
0	678	573
1	729	667
2	834	697
3	-270	171
4	630	559
5	670	-600
6	1526	1416
7	443	338
8	486	-532

-4	3	L
0	-290	-203
1	-292	37
2	829	-531
3	1062	-953
4	661	490
5	851	-656
6	815	-713
7	726	-333
8	482	75
9	-247	356
10	394	282
11	238	377
12	283	149

-4	4	L
0	647	-592
1	763	-577
2	552	-392
3	-231	-60
4	-243*	237
5	687	625
6	614	603
7	407	310
8	510	412
9	182	-177

-3	1	L
0	-72	63
1	302	-176
2	1913	2193
3	649	807
4	1304	1414
5	254	302
6	458	525
7	407	-403
8	711	-793
9	763	-866
10	315	-294
11	665	-659
12	404	-433
13	-197	-99
14	268	187

-3	2	L
0	437	191
1	690	691
2	807	-861
3	542	-563
4	724	-811
5	-155	-17
6	493	-500
7	817	-899
8	-192	-123
9	-209	-273
10	252	211
11	453	489
12	-198	-79
13	-178	210
14	-150*	463
15	309	194

-3	3	L
0	529	-422
1	1240	1098
2	528	-379
3	1563	1294
4	2335	2209
5	1466	1244
6	-195	158
7	604	528
8	747	813
9	650	427
10	871	738
11	830	659

-3	4	L
0	527	-412
1	603	-596
2	1893	1719
3	220	195
4	352	205
5	386	384
6	792	639
7	663	643
8	-200	143
9	-186	30
10	-192*	-348
11	350	-333
12	167	-174

-3	5	L
0	683	555
1	922	881
2	733	708
3	785	721
4	519	406
5	458	-343
6	315	-320
7	1296	1108
8	170	-215
9	472	-472

-3	6	L
0	244	-177
1	-168	79
2	359	-271
3	434	-475
4	807	-753

-2	1	L
0	3941	4127
1	2303	2165
2	795	752
3	582	636
4	825	756
5	1755	1851
6	1841	1997
7	510	-302
8	1020	-992
9	706	-555
10	706	-649
11	-185	28
12	470	392
13	728	647
14	395	408
15	-189	81
16	-160	143
17	163	224

-2	2	L
0	1607	1713
1	1039	1109
2	185	-1
3	1543	1453
4	925	-671
5	1515	1348
6	1073	-924
7	817	-819
8	876	878
9	-181	24
10	779	635
11	798	782
12	966	905
13	403	446
14	312	283
15	189	49

-2	3	L
0	3069	2659
1	1659	1401
2	856	-762
3	1110	1113
4	851	777
5	506	472
6	1365	1261
7	1058	1033
8	814	787
9	750	743
10	585	-450
11	488	-419
12	-295	15
13	486	-481
14	452	-429
15	214	-283

-2	4	L
0	942	881
1	295	203
2	1031	-999
3	2683	2616
4	827	939
5	527	549
6	366	439
7	356	-310
8	345	-248
9	-274*	-181
10	901	1003
11	736	-594
12	800	-911
13	220	-217

-2	5	L
0	2046	2135
1	-186	61
2	395	-405
3	599	-588
4	511	-519
5	526	-507
6	676	-772
7	626	-640
8	544	-513
9	-168	-250
10	419	358
11	270	317

-2	6	L
0	438	-359
1	402	-433
2	452	-466
3	810	-846
4	449	-490
5	777	-809
6	432	339
7	340	364

-1	1	L
0	973	1059
1	624	552
2	2680	2474
3	477	-520
4	3491	3701
5	1999	1782
6	2457	2350
7	1495	1415
8	-149	40
9	698	-705
10	881	794
11	1216	1138
12	1030	1022
13	850	817
14	856	745
15	751	641
16	-180	186
17	-148	-130

-1	2	L
0	2433	2389
1	2601	2488
2	733	-674
3	3445	3711
4	2124	2223
5	927	897
6	594	533
7	1258	1311
8	920	890
9	1732	1510
10	1281	1261
11	861	798
12	-186	183
13	581	-581
14	617	-684
15	372	-360
16	537	-646

-1	3	L
0	373	405
1	-136	188
2	1289	1197
3	740	747
4	1354	1256
5	489	443
6	1895	1885
7	197	-117
8	244	184
9	131	-68
10	-186	-51
11	793	-680
12	657	-573
13	612	-607
14	141	-157
15	830	-922

-1	4	L
0	1217	1201
1	2568	2523
2	1253	1287
3	335	368
4	371	368
5	-181	-49
6	818	-785
7	759	-742
8	1375	1638
9	-250*	1189
10	-189	-134
11	161*	-252
12	-176*	71
13	623	456
14	561	639

-1	5	L
0	1420	1455
1	1002	1052
2	500	-391
3	872	-999
4	685	-753
5	773	-909
6	411	-425
7	172	210
8	293	-303
9	299	356
10	-162	42
11	553	582

-1	6	L
0	1038	1219
1	842	-889
2	326	-448
3	116	-30
4	-185	183
5	381	369
6	444	559
7	536	591

0	0	L
2	629	748
3	850	963
4	1176	1266
5	902	-786
6	2574	2111
7	3822	3284
8	1159	1116
9	1879	1828
10	789	414
11	-234*	224
12	911	659
13	-238	186
14	400	461
15	717	696
16	207	201
17	405	459

0	1	L
-17	328	350
-16	-235*	256
-15	223	-156
-14	867	-878
-13	428	-390
-12	1192	1173
-11	521	-576
-10	1634	1611
-9	1238	1077
-8	850	635
-7	986	-890
-6	1317	1336
-5	2182	2295
-4	728	742
-3	3719	5410
-2	2552	2977
-1	903	-907
0	1514	1402
1	1106	1053
2	401	-90
3	3305	3374
4	1070	-883
5	2761	2832
6	721	-614
7	280	-251
8	-188*	2
9	839	619
10	-210	-80
11	1496	1348
12	2768	2654
13	709	-625
14	594	609
15	-295*	-233
16	-228	-307
17	-239*	-212
18	488	-548

0	2	L
-17	263	-456
-16	-254*	-37
-15	-255*	-240
-14	603	-753
-13	542	-489
-12	-234*	100
-11	-225	149
-10	-213	-3
-9	-219*	1517
-8	1722	1768
-7	1771	1641
-6	402	249
-5	1434	1215
-4	-113*	48
-3	-104*	2300
-2	2079	2893
-1	2417	2252
0	4706	4501
1	855	-874
2	2582	2865
3	3689	4119
4	-141	291
5	1029	1216
6	2329	2538
7	1126	1115
8	1358	1445
9	1414	1416
10	2231	2033
11	-237	75
12	-244*	-358
13	-231	-297
14	656	-619
15	567	-687
16	227	-222

0 3 L		
-17	388	-325
-16	-238*	258
-15	-264*	234
-14	660	548
-13	684	596
-12	588	478
-11	-227	62
-10	640	482
-9	-202*	-79
-8	-186	94
-7	958	-919
-6	1203	1214
-5	1195	1294
-4	432	262
-3	1172	1298
-2	1073	1110
-1	716	-658
0	1789	1846
1	545	-554
2	702	566
3	2882	2523
4	1628	1333
5	1162	1037
6	-192	116
7	-207*	121
8	368	-156
9	1085	-859
10	1213	-990
11	1389	1269
12	1050	1011
13	-234	-80
14	313	-227
15	936	855

0 4 L		
-16	222	194
-15	-224	185
-14	-234	88
-13	577	546
-12	393	358
-11	1032	-994
-10	745	-744
-9	560	-379
-8	973	-937
-7	301	-333
-6	613	-545
-5	683	-644
-4	1436	1368
-3	1015	1057
-2	1690	1525
-1	1316	1257
0	1161	1018
1	-122	73
2	-143	53
3	1080	1042
4	-178	-209
5	2010	1600
6	1218	1142
7	774	-699
8	-237	-105
9	403	-293
10	306	299
11	356	319
12	958	900
13	369	-185
14	522	600

0 5 L		
-14	900	-747
-13	-225	-37
-12	-234	225
-11	427	-359
-10	-232	-108
-9	-233	73
-8	-237	77
-7	898	727
-6	527	360
-5	907	736
-4	290	205
-3	236	168
-2	236	128
-1	917	698
0	748	-548
1	1297	1260
2	978	-872
3	842	-647
4	769	-689
5	-234	-176
6	652	-441
7	-235	191
8	1049	985
9	796	803
10	591	637
11	636	688

0 6 L		
-11	440	269
-10	533	427
-9	540	463
-8	338	269
-7	-235	14
-6	266	146
-5	313	-214
-4	274	-202
-3	1069	-907
-2	1387	1427
-1	427	306
0	-235	-73
1	379	-297
2	343	298
3	373	303
4	728	632
5	938	915
6	315	302
7	393	371

0 7 L		
-8	284	-244
-7	275	-261
-6	296	-250
-5	391	-386
-4	270	249
-3	334	-260
-2	286	-253
-1	207	169
0	473	401
1	573	545
2	511	530
3	437	323

1 -6 L		
1	942	-992
2	391	432
3	425	-517
4	124	139
5	347	351
6	295	325
7	888	893
8	539	450

1 -5 L		
1	-185	-66
2	434	1022
3	1030	737
4	1066	1038
5	419	304
6	433	417
7	373	302
8	-185	-3
9	-183	-226
10	552	-435
11	573	-560
12	640	-665
13	270	-202

1 -4 L		
1	615	633
2	416	-418
3	281	296
4	1062	1172
5	157	-203
6	1223	1357
7	842	-858
8	620	-633
9	592	-587
10	606	674
11	627	598
12	685	-732
13	724	610
14	474	385
15	344	257
16	272	264

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2	198	129
3	3675	3278
4	1987	1781
5	299	-514
6	870	-869
7	607	626
8	500	279
9	123	-156
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11	1578	1426
12	425	338
13	-184	135
14	249	-119
15	-188	-95
16	-261*	-420
17	278	-244
18	173	-414
19	405	-137

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3	570	645
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7	305	390
8	895	920
9	434	-395
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12	227	-192
13	705	-669
14	-183	-78
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9	1720	1625
10	954	1007
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14	649	706
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16	599	612
17	412	416
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-9	1333	1298
-8	634	-712
-7	1610	1664
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5	3716	3434
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9	635	480
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13	871	752
14	718	685
15	658	612
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17	275	180

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9	1731	1699
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13	-185	-96
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-9	115	-159
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5	1608	1594
6	541	597
7	525	413
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11	2179	2001
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13	749	-766
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-8	905	-853
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-2	344	-339
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6	756	-728
7	353	-380
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9	400	-518
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12	-189	167
13	418	258
14	626	605
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-9	356	-334	
-8	384	-254	
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6	-186	-113	
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-6	801		701
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-9	198		165
-8	-181		-69
-7	156	-170	
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-5	545	-476	
-4	375	-362	
-3	313		230
-2	313	-232	
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3	524		518
4	264		125
6	470		394

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1	188		179

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4	572		482
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8	357		370
9	279		260
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9	640	-706	
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11	341	-431	
12	-191		74
13	357		264

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6	713	-651	
7	-199*	-201	
8	-215*	-199	
9	-202*		-88
10	-210*		-58
11	-248*		542
12	732		817
13	-212*		116
14	623		514

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3	273		150
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6	1059		988
7	1026		817
8	1942	1849	
9	1537	1530	
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12	-214*		-86
13	382	-364	
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6	825		657
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9	359		290
10	864	-868	
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13	-277*	-378	
14	546	-500	
15	-209		80
16	-180		-79
17	327		329

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3	524	-604	
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5	2105	2067	
6	1291	1358	
7	1996	2008	
8	1212	1068	
9	781	-724	
10	-283*		233
11	-199	-111	
12	958	1040	
13	-213	-197	
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16	-207*		170
17	356		392

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-12	132		-92
-11	917	1050	
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-9	-232*	-520	
-8	329	-337	
-7	2157	2267	
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9	721		635
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11	1201	1367	
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14	-250*		302
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16	201	-163	
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-13	227	-207
-12	-186	-65
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6	316	334
7	1590	1516
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9	607	505
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13	361	-303
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6	1022	965
7	-189	27
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13	-209	-184
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-8	890	-904
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3	285	-137
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7	-235*	-359
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9	1105	1035
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11	516	357
12	571	463
13	682	612
14	352	344

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-14	-161*	-266
-13	-183*	-44
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-2	182*	-228
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2	392	-372
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8	918	809
9	925	810
10	644	594
11	425	343
12	275	201

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-7	-204	19
-6	-220*	-145
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-4	-200	-178
-3	703	-722
-2	703	-716
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3	574	360
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5	386	404
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7	180	195

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-9	-131	-155
-8	-147	-24
-7	182	-93
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-5	198	-152
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-3	145	-247
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6	250	245
7	346	207
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9	-115*	-254
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7	226	-192
8	710	-700
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11	304	269

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3	594	-446
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9	487	429
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12	268	299

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8	-200	-37
9	-231*	270
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11	759	-706
12	-218*	-122
13	663	-546
14	432	-284

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6	642	490
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12	171	-150
13	174*	-156
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15	666	565
16	330	315

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7	-159	-82
8	604	-505
9	-293*	-123
10	-206	74
11	703	573
12	214*	343
13	675	658
14	213	188
15	341	334

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4	537	-535
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7	868	740
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-2	822	-857
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6	701	635
7	477	405
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11	823	-818
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13	557	-473
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2	949	984
3	1038	1095
4	543	-431
5	417	-173
6	801	-799
7	682	-717
8	927	-993
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10	413	-405
11	-189	118
12	246	-148
13	701	525

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-8	240	-174
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-2	-231*	217
-1	322	254
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2	-234*	-247
3	740	-722
4	180	-238
5	-215*	-286
6	-218*	-113
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11	527	452
12	264	301

	3 4	L
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9	419	299

	3 5	L
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	4 -4	L
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6	226	140
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8	655	701
9	500	517

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6	797	543
7	-306	90
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9	-279	-158
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4 -2		L
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12	-216	279
13	501	519

4 -1		L
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10	516	587
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12	-188	356
13	439	471

4 0		L
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2	-253	-3
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6	497	400
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12	408	-461
13	347	-276

4 1		L
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2	430	355
3	546	449
4	621	530
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7	261	-295
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4 2		L
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5	388	-377
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4 3		L
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2	368	-502
3	326	-293
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5	-237	-115
6	-213	-14
7	291	363
8	206	278

4 4		L
-8	434	479
-7	-187	-95
-6	257	-297
0	-214	-74
1	-208	-1
2	281	218
3	-186	312
4	-169	354
5	-142	-44
6	74	213

5 -4		L
1	-159	-15
2	-157	113
3	345	279
4	370	239
5	431	367
6	234	318

5 -3		L
1	-256	112
2	747	602
3	709	570
4	-240	64
5	-228	131
6	-211	59
7	-188	-168
8	-151	-590
9	549	-310

5 -2		L
1	531	-457
2	-277	19
3	460	-439
4	-263	-290
5	431	-360
6	274	-230

5 -1		L
1	-293	-326
2	466	-378
3	540	-431
4	338	-422
5	-279	230
6	510	477
7	-243	39
8	415	504
9	278	300

5 0		L
-9	202	303
-8	-201	-46
-7	-221	-92
-6	273	-196
-5	248	-218
-4	-245	-267
-3	-247	-100
-2	218	-304
-1	346	-275
0	-249	101
1	-248	31
2	532	442
3	666	585
4	604	-454
5	514	546
6	378	344

5 1		L
-4	289	-237
-3	187	315
-2	328	107
-1	-227	158
0	447	420
1	-225	11
2	628	582
3	337	278
4	-206	-187
5	248	-171
6	265	-290
7	191	-323

5 3		L
0	-142	-361
1	328	-123