Acta Cryst. (1970). B**26**, 373

The Crystal Structure of *N*-Methylrhoeagenine Iodide

BY CAROL SAUNDERSON HUBER

Biochemistry Laboratory, National Research Council of Canada, Ottawa 7, Canada

(*Received* 12 *May* 1969)

The structure and stereochemistry of *N*-methylrhoeagenine iodide have been determined by three-dimensional Fourier and least-squares methods using visually estimated intensity data. The crystals have orthorhombic symmetry, space group $C222_1$, with $a=8{\cdot}54$, $b=18{\cdot}52$, $c=26{\cdot}19$ Å, $Z=8$. The two 1,3-benzodioxole systems, which are linked by *cis*-fused azacycloheptene and dihydropyran rings, are nearly mutually perpendicular. The hydroxyl group and the hydrogen atoms at the junction of the two heterocyclic rings lie on the same side of the dihydropyran ring. Infinite chains of alternating iodide ions and organic cations are arranged parallel to the [110] direction.

Introduction

The structures of the alkaloid rhoeagenine and the closely related alkaloid rhoeadine have been under investigation by chemical methods for several decades. A structure (Fig. 1) was proposed for rhoeagenine by Santavy, Kaul, Hruban, Dolejs, Hanus, Blaha & Cross (1965). However, the authors noted that the product of one of the oxidation reactions was still not explained, and since the proposed structure represented a new type of alkaloid skeleton, an X-ray analysis of the methiodide derivative was undertaken. The structure found by X-ray diffraction agrees with the structure proposed on chemical grounds, and also establishes the stereochemistry of the molecule.

Experimental

The crystals used for the structure determination were kindly provided by Dr Danuta Rozwadowska, then of Carleton University. Crystal data are as follows:

N-Methylrhoeagenine iodide, $[C_{21}H_{22}NO_6]^+I^-$
M.W. 511·3

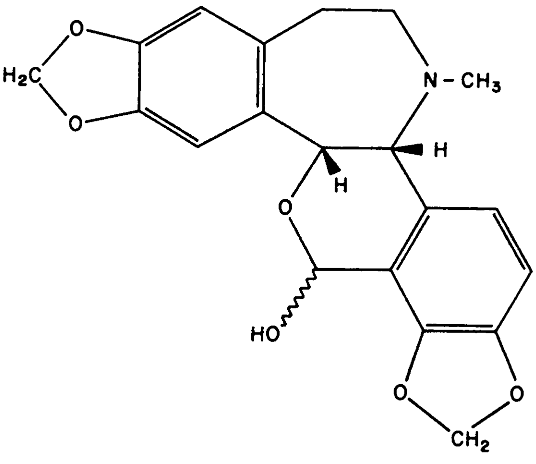

Fig. 1. Structure proposed for rhoeagenine.

Orthorhombic, space group $C222_1$
$a=8{\cdot}54\pm0{\cdot}02$, $b=18{\cdot}52\pm0{\cdot}04$, $c=26{\cdot}19\pm0{\cdot}06$ Å.
D_m (by flotation) $=1{\cdot}65$ g.cm^{-3}, $Z=8$, $D_x=1{\cdot}64$ g.cm^{-3}.
μ (Cu $K\alpha$) $=128{\cdot}1$ cm^{-1}.

Unit-cell dimensions were determined from precession photographs obtained with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). Systematic absences hkl when $h+k$ is odd and $00l$ when l is odd were deduced from Weissenberg and precession photographs, and led uniquely to space group $C222_1$.

Intensity data were collected from equi-inclination multiple-film Weissenberg photographs obtained with Cu $K\alpha$ radiation for the $0kl\cdots7kl$, $h0l\cdots h4l$, and $hk0$ layers. The crystals deteriorated noticeably with exposure to X-rays, and consequently fresh crystals were mounted at intervals during the data collection. Altogether, seven different crystals were used, each of which was ground to an approximately spherical shape in order to simplify the application of absorption corrections.

Intensities were estimated by visual comparison with a calibrated intensity scale, and corrected for Lorentz and polarization factors. Absorption corrections appropriate for spherical crystals (*International Tables for X-ray Crystallography*, 1959) were applied to the various sets of data collected with different crystals. The F^2 values from various layers were placed on a common relative scale using the Hamilton, Rollett & Sparks (1965) method. Of the 2643 independent reflexions accessible with Cu $K\alpha$ radiation, 2137 were observed, and another 316 reflexions were recorded as having intensities too weak to be measured. The latter were excluded from the structure determination and refinement, but were included in the final structure factor calculation; the value given in place of $|F_o|$ was two thirds of the minimum observable amplitude.

Structure determination and refinement

The coordinates of the iodide ion were deduced from two-dimensional Patterson syntheses, and the first three-dimensional heavy-atom-phased Fourier synthesis revealed all twenty-eight atoms of the organic cation. A subsequent structure-factor calculation in which all non-hydrogen atoms were included gave an R value $(=\sum|K|F_o|-|F_c||/\sum K|F_o|$ for all observed reflexions) of 0·24.

The structure was refined by block-diagonal least-squares calculations. The quantity minimized was $\sum w(K|F_o|-|F_c|)^2$, and the form of the weighting scheme used throughout the refinement was

$$w=1/[1+\{(K|F_o|-g)/f\}^2]\,.$$

Table 1. *Fractional coordinates, vibration tensor components* (Å^2) *for the expression* $T=\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{23}b^*c^*kl+\cdots)]$, *and their e.s.d.'s (all quantities* × 10^4)

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
I	1808 (1)	2254 (1)	1211 (1)	725 (6)	528 (4)	907 (7)	−337 (10)	−303 (11)	196 (10)
N	6966 (15)	3340 (7)	1193 (5)	541 (65)	643 (61)	719 (63)	−5 (111)	86 (129)	−5 (106)
O(1)	8101 (13)	4891 (5)	1050 (3)	691 (55)	544 (43)	483 (38)	39 (66)	150 (86)	138 (95)
O(2)	8967 (17)	5758 (7)	1605 (4)	861 (75)	735 (64)	671 (56)	312 (98)	51 (114)	−93 (123)
O(3)	13932 (15)	4198 (7)	48 (4)	674 (57)	1166 (87)	417 (42)	25 (103)	139 (92)	−146 (135)
O(4)	12647 (14)	3804 (8)	−656 (4)	678 (64)	1079 (87)	542 (49)	−460 (108)	116 (96)	210 (134)
O(5)	6956 (16)	5746 (5)	2551 (4)	857 (77)	679 (52)	542 (45)	−74 (84)	263 (110)	66 (119)
O(6)	6715 (17)	5037 (7)	3268 (4)	995 (81)	834 (63)	521 (45)	−66 (91)	405 (119)	−296 (151)
C(1)	7213 (21)	3116 (11)	620 (8)	588 (89)	879 (111)	893 (104)	−499 (182)	71 (162)	−231 (169)
C(2)	7571 (20)	3680 (13)	250 (6)	480 (77)	1265 (148)	632 (76)	−632 (184)	−210 (137)	309 (197)
C(3)	9210 (17)	3891 (8)	197 (5)	522 (72)	627 (71)	497 (59)	22 (106)	7 (109)	127 (124)
C(4)	9992 (18)	4154 (9)	627 (5)	520 (71)	759 (82)	438 (56)	−69 (116)	−122 (108)	30 (137)
C(5)	9203 (15)	4307 (7)	1139 (5)	446 (64)	530 (59)	549 (66)	32 (101)	−334 (108)	113 (102)
C(6)	8436 (17)	3703 (7)	1424 (5)	519 (72)	533 (61)	546 (59)	76 (98)	−80 (112)	−68 (119)
C(7)	7973 (19)	4029 (7)	1943 (5)	668 (89)	473 (57)	539 (59)	179 (96)	−218 (127)	1 (123)
C(8)	7674 (18)	4777 (8)	1967 (5)	565 (74)	619 (75)	487 (59)	−17 (108)	2 (112)	113 (124)
C(9)	7798 (19)	5274 (7)	1509 (4)	708 (89)	533 (63)	410 (52)	22 (93)	71 (112)	164 (123)
C(10)	11602 (18)	4273 (7)	6142 (5)	561 (74)	565 (64)	483 (56)	−192 (96)	187 (116)	67 (123)
C(11)	12412 (17)	4125 (8)	159 (5)	473 (66)	648 (73)	542 (63)	160 (113)	13 (110)	280 (127)
C(12)	11570 (25)	3897 (9)	−264 (5)	1014 (130)	706 (83)	427 (59)	98 (111)	−90 (151)	416 (188)
C(13)	9995 (23)	3759 (10)	−273 (6)	735 (99)	805 (92)	553 (73)	−147 (140)	126 (142)	225 (177)
C(14)	14015 (29)	4074 (13)	−481 (6)	1002 (133)	1100 (136)	525 (73)	−312 (170)	105 (179)	47 (248)
C(15)	7293 (18)	5036 (8)	2422 (5)	604 (80)	582 (63)	563 (70)	143 (116)	96 (121)	45 (131)
C(16)	7257 (19)	4626 (9)	2871 (4)	676 (86)	818 (87)	327 (45)	125 (108)	32 (107)	−80 (150)
C(17)	7568 (21)	3912 (9)	2865 (5)	781 (96)	834 (96)	330 (49)	238 (113)	78 (118)	99 (166)
C(18)	7968 (18)	3610 (8)	2382 (5)	519 (84)	737 (78)	553 (70)	253 (116)	−19 (120)	161 (137)
C(19)	6909 (23)	5783 (8)	3090 (6)	706 (95)	659 (78)	702 (76)	−7 (128)	203 (167)	−230 (169)
C(20)	6628 (30)	2660 (11)	1462 (11)	906 (134)	688 (106)	1442 (177)	−140 (209)	−62 (256)	−672 (216)
C(21)	5500 (18)	3784 (11)	1196 (7)	460 (74)	935 (104)	796 (90)	34 (179)	68 (151)	58 (156)

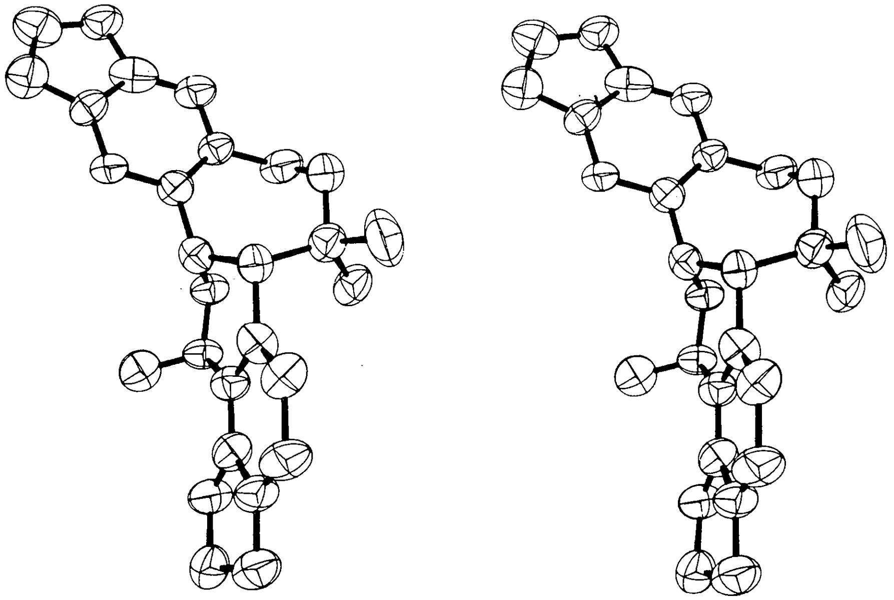

Fig. 2. Stereoscopic view of the organic cation in *N*-methylrhoeagenine iodide. The ellipsoids are scaled to include 50% probability.

Table 2. *Observed and calculated structure amplitudes* (× 10)

* Indicates an unobserved reflexion, with $^2/_3F_{\min}$ given in place of F_o.

L	FO	FC
H= 0, K= 0		
4	2542	2715
6	189	281
8	3443	3528
10	267	142
12	1864	2103
14	1038	786
16	2161	1993
18	696	685
20	539	592
22	1168	1185
24	175	121
26	74*	38
28	108	116
30	157	169
32	136	186
H= 0, K= 2		
0	831	810
1	666	671
2	1200	1371
3	302	68
4	3257	4317
5	551	542
6	1170	891
7	184	111
8	2831	2955
9	610	415
10	206	139
11	1189	971
12	2340	2501
13	290	244
14	240	160
15	707	668
16	1076	1109
17	156	151
18	352	238
19	286	273
20	953	1127
21	322	367
22	101	54
23	356	381
24	373	418
25	75*	44
26	336	301
27	92	70
28	215	295
29	176	110
30	104	100
31	54*	63
32	46*	79
33	38*	45
H= 0, K= 4		
0	409	157
1	707	634
2	1876	2259
3	1598	1799
4	3503	4498
5	526	669
6	831	566
7	1389	1213
8	1783	1820
9	199	119
10	933	834
11	2211	2360
12	1016	948
13	828	931
14	919	838
15	414	399
16	722	704
17	429	446
18	756	704
19	840	926
20	154	193
21	74*	30
22	75*	28
23	111	115
24	495	484
25	137	171
26	258	267
27	90	90
28	84	43
29	63*	14
30	58*	93
31	51*	35
32	43*	32
33	32*	28
H= 0, K= 6		
0	2579	3528
1	1906	2249
2	1280	1161
3	650	601
4	799	525
5	2060	2384
6	463	341
7	1843	2029
8	955	1164
9	1874	1904
10	405	308
11	1090	1152
12	842	795
13	228	317
14	217	137
15	862	778
16	840	963
17	480	558
18	325	336
19	373	462
20	201	208
21	249	349
22	429	440
23	332	323
24	169	169
25	134	158
26	157	144
27	321	351
28	159	158
29	59*	58
30	112	142
31	137	155
32	98	137
H= 0, K= 8		
0	1553	1887
1	1970	2229
2	217	68
3	1362	1575
4	854	792
5	1340	1224
6	255	65
7	1989	2096
8	809	898
9	916	1049
10	440	352
11	1412	1534
12	599	595
13	509	577
14	675	650
15	1347	1463
16	258	167
17	141	145
18	101	88
19	453	477
20	381	395
21	365	382
22	245	243
23	593	629
24	164	114
25	127	86
26	68*	3
27	210	227
28	73	87
29	54*	71
30	48*	30
31	65	91
32	15*	75
H= 0, K= 10		
0	1021	1100
1	757	785
2	217	252
3	2677	2631
4	559	459
5	759	772
6	373	329
7	1256	1241
8	374	413
9	748	839
10	129	65
11	1184	1189
12	190	182
13	743	801
14	71*	7
15	832	1020
16	247	206
17	336	401
18	144	177
19	944	1078
20	101	77
21	75*	102
22	74*	4
23	320	366
24	70*	12
25	83	62
26	173	179
27	141	209
28	52*	30
29	45*	69
30	37*	78
H= 0, K= 12		
0	212	235
1	1190	1359
2	129	177
3	1013	962
4	422	409
5	850	881
6	93	107
7	1173	1197
8	438	428
9	237	210
10	218	188
11	1223	1370
12	714	784
13	302	352
14	440	449
15	787	808
16	75*	130
17	201	271
18	345	343
19	490	514
20	370	395
21	72*	80
22	70*	72
23	291	336
24	136	69
25	59*	98
26	65	67
27	175	212
28	41*	28
29	30*	9
H= 0, K= 14		
0	1055	1139
1	714	801
2	241	232
3	661	655
4	739	811
5	729	729
6	208	195
7	896	924
8	849	882
9	536	602
10	249	257
11	477	455
12	203	166
13	176	204
14	246	272
15	498	595
16	613	642
17	74*	0
18	94	119
19	286	351
20	151	182
21	82	104
22	62*	9
23	227	266
24	160	166
25	49*	53
26	50	10
27	32*	145
H= 0, K= 16		
0	684	665
1	249	272
2	102	53
3	787	847
4	726	758
5	75*	102
6	144	137
7	536	609
8	505	567
9	76*	95
10	222	253
11	550	575
12	662	681
13	74*	75
14	94	100
15	366	395
16	333	385
17	68*	1
18	65*	4
19	234	320
20	178	210
21	68	75
22	51*	8
23	45*	117
24	122	223
25	89	164
H= 0, K= 18		
0	647	671
1	196	223
2	75*	79
3	75*	36
4	765	784
5	74*	2
6	96	111
7	95	144
8	689	759
9	72*	27
10	128	180
11	125	204
12	498	586
13	146	130
14	214	231
15	110	157
16	256	319
17	56*	7
18	112	118
19	84	106
20	267	381
21	39*	55
22	29*	66
H= 0, K= 20		
0	693	830
1	68*	7
2	68*	57
3	68*	130
4	594	692
5	66*	49
6	65*	42
7	179	167
8	473	553
9	172	149
10	60*	12
11	160	198
12	330	420
13	113	132
14	62	66
15	115	141
16	215	317
17	170	194
18	51	108
H= 0, K= 22		
0	310	390
1	113	153
2	53*	11
3	53*	30
4	276	365
5	107	135
6	50*	81
7	49*	9
8	250	347
9	75	89
10	42*	85
11	39*	25
12	134	242
13	44	80
H= 0, K= 24		
0	15*	239
H= 1, K= 1		
0	725	750
1	1256	1214
2	1450	1713
3	2135	2269
4	461	409
5	1615	1867
6	2693	3076
7	1474	1712
8	870	936
9	997	899
10	1728	1860
11	734	648
12	674	652
13	1021	898
14	1152	1122
15	862	843
16	783	706
17	392	376
18	506	540
19	349	338
20	556	625
21	258	258
22	807	794
23	499	466
24	443	387
25	305	295
26	339	321
27	142	106
28	237	252
29	144	144
30	65	74
31	48*	66
32	42*	64
33	86	100
H= 1, K= 3		
0	449	542
1	1222	1493
2	1951	3345
3	1060	1259
4	1680	1884
5	1529	1748
6	1751	2126
7	1276	1350
8	958	1026
9	1023	1064
10	1894	1980
11	1279	1233
12	1531	1375
13	642	681
14	1691	1687
15	377	316
16	836	821
17	753	704
18	1120	1180
19	613	591
20	252	178
21	538	561
22	283	239
23	516	508
24	588	597
25	154	153
26	232	236
27	247	231
28	76	92
29	108	81
30	132	162
31	46*	59
32	40*	70
33	74	85
H= 1, K= 5		
0	1340	2007
1	2445	3218
2	1963	2931
3	1292	1438
4	1158	1351
5	1392	1669
6	1481	1593
7	1100	974
8	395	389
9	1563	1690
10	1772	1824
11	1334	1374
12	683	499
13	780	812
14	671	702
15	1249	1195
16	262	285
17	889	849
18	697	699
19	453	384
20	831	830
21	301	292
22	454	447
23	372	308
24	153	216
25	210	222
26	185	144
27	62*	29
28	126	138
29	66	79
30	85	93
31	91	107
32	145	172
33	18*	147
H= 1, K= 7		
0	916	1022
1	848	903
2	774	934
3	1586	1900
4	235	307
5	1564	1841
6	1230	1363
7	1098	1170
8	1491	1637
9	415	368
10	792	815
11	553	559
12	899	901
13	1038	1095
14	711	682
15	673	556
16	705	715
17	680	676
18	489	421
19	238	177
20	416	417
21	812	856
22	238	256
23	424	412
24	149	163
25	248	239
26	207	184
27	59*	69
28	117	119
29	173	203
30	44*	32
31	77	91
32	25*	23
H= 1, K= 9		
0	846	889
1	1204	1364
2	387	815
3	1261	1460
4	1361	1474
5	1448	1530
6	253	276
7	946	1047
8	779	802
9	1526	1688
10	210	119
11	698	643
12	604	562
13	1075	1070
14	423	386
15	480	450
16	655	595
17	687	662
18	385	366
19	302	262
20	257	216
21	155	139
22	124	101
23	146	101
24	325	294
25	336	296
26	145	110
27	148	100
28	170	189
29	159	159
30	43	43
31	25*	70
H= 1, K= 11		
0	827	743
1	1399	1492
2	54*	21
3	976	997
4	1085	1184
5	1062	981
6	646	567
7	1334	1328
8	621	533
9	971	1023
10	532	523
11	600	662
12	657	655
13	744	716
14	201	199
15	373	815
16	416	326
17	589	596
18	181	190
19	356	326
20	303	303
21	408	400
22	350	308
23	111	106
24	74	98
25	286	261
26	179	155
27	48*	66
28	112	102
29	121	133
30	15*	31
H= 1, K= 13		
0	665	662
1	905	913
2	759	761
3	984	976
4	173	170
5	1248	1276
6	537	523
7	548	568
8	674	623
9	1248	1214
10	401	349
11	619	585
12	416	371
13	787	791
14	704	652
15	68*	101
16	237	194
17	468	454
18	173	246
19	65*	76
20	141	176
21	499	497
22	209	168
23	55*	69
24	112	90
25	225	253
26	103	114
27	75	66
28	25*	39
H= 1, K= 15		
0	468	499
1	781	737
2	817	735
3	818	771
4	557	597
5	621	599
6	726	694
7	464	453
8	498	496
9	489	415
10	551	532
11	221	242
12	335	327
13	652	627
14	350	315
15	412	349
16	168	150
17	481	471
18	526	448
19	129	107
20	143	138
21	148	190
22	230	210
23	55	102
24	42*	39
25	139	165
26	86	122
H= 1, K= 17		
0	168	161
1	440	409
2	824	820
3	238	240
4	269	259
5	558	505
6	711	657
7	330	257
8	262	232
9	569	554
10	646	604
11	207	214
12	82	88
13	370	333
14	450	433
15	60*	63
16	163	161
17	310	283
18	328	278
19	149	128
20	55	64
21	168	162
22	165	166
23	79	102
H= 1, K= 19		
0	64*	16
1	286	262
2	546	499
3	329	279
4	81	56
5	242	238
6	523	472
7	324	276
8	77	94
9	169	133
10	449	397
11	216	189
12	69	19
13	116	103
14	402	392
15	190	188
16	55	102
17	91	54
18	238	234
19	139	179
20	25*	24
H= 1, K= 21		
0	54*	21
1	165	134
2	538	507
3	200	175
4	53*	89
5	92	97
6	407	413
7	271	268
8	121	101
9	83	81
10	330	352
11	118	117
12	186	202
13	138	115
14	201	214
15	135	149
16	19*	129
H= 1, K= 23		
0	90	108
1	100	125
2	241	249
3	129	132
4	111	93
5	127	132
6	260	298
7	131	130
8	91	121
9	18*	86
H= 2, K= 0		
0	3921	6694
1	822	525
2	1888	1877
3	864	683
4	1515	1220
5	3202	3169
6	608	845
7	1071	775
8	1443	1407
9	1580	1444
10	507	397
11	1637	1563
12	1009	1059
13	1380	1439
14	351	320
15	839	754
16	936	980
17	585	599
18	69*	90
19	592	572
20	287	183
21	754	827
22	501	566
23	204	143
24	149	121
25	204	195
26	74*	29
27	71*	120
28	66*	0
29	211	214
30	58*	126
31	52*	100
32	44*	65
33	147	149
H= 2, K= 2		
0	655	532
1	2430	3216
2	1716	1660
3	2623	3016
4	2548	2543
5	1542	1501
6	790	768
7	2042	2064
8	1462	1564
9	1548	1540
10	1445	1298
11	705	700
12	1390	1472
13	1187	1174
14	270	199
15	718	751
16	943	918
17	946	1006
18	609	665
19	332	283
20	661	661
21	459	482
22	143	131
23	174	133
24	238	205
25	366	353
26	219	229
27	71*	64
28	199	167
29	149	122
30	58*	59
31	51*	25
32	42*	61
33	29*	72
H= 2, K= 4		
0	1824	2140
1	1277	1581
2	1174	1461
3	1044	989
4	1906	2274
5	1117	1236
6	778	766
7	1102	1179
8	1384	1526
9	956	1020
10	488	541
11	1534	1529
12	942	945
13	606	582
14	867	938
15	635	646
16	470	477
17	569	562
18	561	534
19	349	336
20	141	161
21	145	146
22	341	306
23	173	161
24	265	221
25	367	363
26	297	248
27	167	119
28	105	73
29	210	163
30	190	139
31	48*	22
32	39*	37
H= 2, K= 6		
0	357	194
1	1005	1158
2	1205	1358
3	888	1029
4	331	433
5	1466	1583
6	1549	1715
7	916	921
8	940	1080
9	1216	1385
10	1090	1238
11	981	946
12	653	681
13	713	657
14	1184	1183
15	473	428
16	538	538
17	341	309
18	564	503
19	201	219
20	320	371
21	474	436
22	489	489
23	239	235
24	75*	132
25	128	97
26	272	252
27	227	171
28	180	139
29	94	51
30	116	133
31	145	115
32	29*	35
H= 2, K= 8		
0	1141	1199
1	1206	1395
2	1244	1451
3	1067	1193
4	688	767
5	491	440
6	1463	1621
7	1372	1456
8	423	341
9	895	816
10	1289	1439
11	1004	1035
12	547	601
13	500	417
14	846	824
15	860	893
16	72*	96
17	376	327
18	777	779
19	536	509
20	174	185
21	222	195
22	476	417
23	326	335
24	127	134
25	320	302
26	197	177
27	165	101
28	133	140
29	117	115
30	120	127
31	60	59
H= 2, K= 10		
0	272	254
1	712	604
2	1550	1870
3	1268	1494
4	247	201
5	921	951
6	989	1042
7	757	804
8	304	222
9	625	572
10	1051	1073
11	660	606
12	276	222
13	559	518
14	748	715
15	578	572
16	248	245
17	268	213
18	561	516
19	661	643
20	138	156
21	95	40
22	226	201
23	265	228
24	167	163
25	64*	10
26	201	155
27	222	239
28	49*	34
29	65	19
30	108	132
H= 2, K= 12		
0	104	74
1	1015	1001
2	992	1019
3	761	767
4	392	292
5	532	479
6	1164	1165
7	916	865
8	366	327
9	170	194
10	833	835
11	914	973
12	247	253
13	378	385
14	822	828
15	670	669
16	348	314
17	242	229
18	476	430
19	300	300
20	205	175
21	71*	98
22	290	307
23	293	252
24	61*	90
25	163	133
26	168	162
27	125	139
28	132	135
H= 2, K= 14		
0	442	406
1	573	474
2	616	597
3	479	467
4	375	259
5	483	440
6	691	675
7	571	511
8	729	691
9	536	456
10	563	538
11	535	429
12	438	325
13	282	249
14	591	533
15	539	466
16	455	376
17	159	109
18	321	262
19	332	281
20	270	251
21	133	114
22	123	128
23	217	196
24	155	144
25	44*	44
26	82	85
H= 2, K= 16		
0	516	515
1	552	525
2	452	388
3	747	725
4	560	497
5	568	544
6	200	226
7	631	606
8	465	451
9	471	460
10	413	320
11	498	472
12	558	511
13	333	298
14	220	144
15	276	232
16	222	179
17	279	232
18	170	166
19	278	253
20	231	208
21	183	186
22	110	117
23	114	119
24	126	153
H= 2, K= 18		
0	404	370
1	561	511
2	189	154
3	533	460
4	562	499
5	349	353
6	291	290
7	515	442
8	448	387
9	422	383
10	227	212
11	436	361
12	423	355
13	304	277
14	75	111
15	269	260
16	294	274
17	200	195
18	184	164
19	128	144
20	217	214
21	104	126
H= 2, K= 20		
0	406	363
1	301	305
2	66*	56
3	276	261
4	432	369
5	395	339
6	64*	38
7	211	192
8	385	302
9	291	282
10	58*	59
11	207	171
12	216	234
13	287	285
14	48*	31
15	156	156
16	199	199
17	205	249
H= 2, K= 22		
0	261	286
1	204	224
2	51*	64
3	199	189
4	226	213
5	246	242
6	118	129
7	190	175
8	278	278
9	229	238
10	122	131
11	77	90
12	20*	178
H= 3, K= 1		
0	681	663
1	1894	2222
2	584	499
3	1078	1520
4	456	439
5	983	1151
6	715	907
7	1621	1859
8	298	283
9	961	1116
10	837	962
11	1102	1484
12	526	539
13	499	601
14	350	312
15	1067	1231
16	536	581
17	563	568
18	163	135
19	527	555
20	319	362
21	571	595
22	209	212
23	372	400
24	248	285
25	162	172
26	82*	98
27	216	239
28	160	156
29	69*	26
30	61*	42
31	148	133
32	90	122
H= 3, K= 3		
0	1088	1220
1	506	522
2	819	1047
3	1522	1906
4	1232	1758
5	1162	1506
6	704	623
7	1192	1459
8	855	985
9	837	818
10	600	540
11	1205	1408
12	864	1058
13	595	620
14	278	177
15	583	619
16	501	508
17	145	163
18	433	380
19	829	881
20	145	159
21	354	315
22	293	256
23	509	454
24	282	285
25	110	110
26	168	170
27	222	221
28	101	125
29	66*	28
30	60*	57
31	97	113
32	96	146
H= 3, K= 5		
0	1556	2033
1	1100	1541
2	733	803
3	1165	1500
4	1363	1977
5	725	834
6	525	546
7	1071	1397
8	1044	1251
9	428	488
10	532	561
11	1010	1169
12	915	1057
13	320	281
14	341	326
15	1036	1201
16	695	695
17	355	364
18	252	205
19	544	533
20	678	741
21	334	338
22	98	146
23	457	485
24	366	340
25	87	54
26	81	80
27	198	187
28	179	182
29	63*	42
30	72	72
31	81	117
H= 3, K= 7		
0	1939	2443
1	791	1044
2	557	520
3	598	839
4	1408	1781
5	737	690
6	569	622
7	664	754
8	1639	2040
9	395	367
10	650	690
11	703	708
12	1128	1197
13	498	420
14	350	314
15	756	719
16	872	917
17	325	319
18	86*	129
19	322	347
20	283	244
21	98	114
22	134	140
23	398	321
24	174	191
25	80*	36
26	185	171
27	181	169
28	106	79
29	56*	91
30	86	61
31	28*	107
H= 3, K= 9		
0	1161	1502
1	274	219
2	378	335
3	777	818
4	1272	1632
5	387	322
6	314	297
7	359	365
8	884	1031
9	481	403
10	173	155
11	349	295
12	810	868
13	457	415
14	178	145
15	206	238
16	697	717
17	250	241
18	320	310
19	280	264
20	547	573
21	86*	83
22	156	110
23	85	116
24	338	301
25	234	197
26	69*	62
27	63*	40
28	179	168
29	45*	34
30	25*	42
H= 3, K= 11		
0	917	1250
1	393	348
2	261	246
3	514	481
4	1356	1513
5	528	568
6	77*	146
7	504	416
8	1123	1218
9	339	342
10	598	601
11	272	261
12	1070	1096
13	309	274
14	324	375
15	249	197
16	414	411
17	98	109
18	193	225
19	133	135
20	403	387
21	321	264
22	243	249
23	75*	82
24	209	202
25	63	94
26	168	151
27	68	37
28	116	132
H= 3, K= 13		
0	879	1411
1	571	557
2	251	213
3	580	485
4	964	1031
5	459	416
6	291	230
7	385	344
8	921	1044
9	879	838
10	87*	157
11	177	180
12	535	590
13	447	429
14	418	421
15	136	159
16	549	566
17	387	326
18	83*	112
19	187	183
20	265	260
21	248	192
22	169	155
23	110	115
24	179	194
25	50	86
26	113	122
27	20*	29
H= 3, K= 15		
0	682	737
1	670	682
2	177	148
3	530	564
4	869	924
5	556	491
6	302	319
7	511	517
8	739	668
9	342	323
10	97	134
11	440	427
12	507	538
13	412	345
14	179	138
15	367	365
16	276	278
17	338	274
18	328	296
19	174	173
20	147	150
21	104	108
22	120	131
23	139	143
24	41*	71
H= 3, K= 17		
0	393	430
1	302	270
2	269	191
3	492	418
4	364	341
5	520	478
6	86*	64
7	342	356
8	312	279
9	319	273
10	149	149
11	376	342
12	164	147
13	393	313
14	185	187
15	268	250
16	136	104
17	190	163
18	117	132
19	198	224
20	81	101
21	139	145
22	25*	115
H= 3, K= 19		
0	111	102
1	495	437
2	163	153
3	516	464
4	80	8
5	333	296
6	205	170
7	401	404
8	74*	47
9	278	259
10	219	228
11	282	290
12	65*	79
13	232	187
14	168	177
15	248	283
16	65	60
17	81	94
18	34*	112
H= 3, K= 21		
0	58	55
1	280	280
2	193	147
3	269	284
4	62*	20
5	238	228
6	138	144
7	271	287
8	104	114
9	236	239
10	103	79
11	266	280
12	74	91
13	32*	113
H= 3, K= 23		
0	29*	157
1	28*	212
2	25*	77
3	20*	209
H= 4, K= 0		
0	997	644
1	2326	1999
2	336	245
3	334	196
4	1151	1097
5	1991	1918
6	998	951
7	1663	1540
8	719	727
9	1391	1390
10	149	170
11	1007	945
12	82	68
13	1100	1063
14	61*	33
15	496	503
16	208	191
17	805	864
18	197	167
19	141	107
20	137	48
21	799	801
22	425	422
23	167	145
24	237	242
25	294	293
26	124	93
27	62*	37
28	58*	75
29	251	248
30	44*	17
31	34*	11
H= 4, K= 2		
0	741	622
1	1565	1991
2	926	851
3	2068	2230
4	502	424
5	1538	1543
6	634	648
7	976	967
8	308	342
9	1393	1372
10	528	548
11	626	602
12	422	381
13	1175	1264
14	409	340
15	331	306
16	184	163
17	725	736
18	318	325
19	97	117
20	176	189
21	473	474
22	230	213
23	145	120
24	71*	86
25	282	281
26	87	110
27	61*	18
28	56*	49
29	117	124
30	70	39
31	32*	62
H= 4, K= 4		
0	488	457
1	714	778
2	829	1112
3	1142	1323
4	260	169
5	1259	1360
6	815	962
7	753	803
8	267	175
9	1012	1124
10	841	847
11	792	859
12	321	317
13	625	708
14	449	447
15	563	598
16	262	236
17	614	742
18	584	590
19	385	373
20	433	424
21	241	225
22	156	115
23	72*	35
24	122	126
25	345	343
26	127	155
27	60*	62
28	54*	57
29	110	141
30	40*	31
31	24*	6
H= 4, K= 6		
0	684	681
1	1187	1457
2	915	1106
3	758	795
4	218	222
5	683	902
6	962	1140
7	746	865
8	486	509
9	577	723
10	894	985
11	232	176
12	382	414
13	583	589
14	651	698
15	95	135
16	167	157
17	496	504
18	402	414
19	238	229
20	371	352
21	397	413
22	416	372
23	70*	25
24	82	124
25	64*	68
26	203	184
27	65	57
28	50*	91
29	84	80
30	50	83
H= 4, K= 8		
0	468	486
1	226	258
2	1371	1533
3	303	340
4	184	200
5	322	231
6	1321	1559
7	173	144
8	89	90
9	537	552
10	898	1018
11	132	127
12	230	258
13	317	333
14	834	928
15	72*	18
16	323	321
17	73*	106
18	473	435
19	189	171
20	160	167
21	72*	92
22	395	424
23	68*	6
24	217	168
25	100	144
26	194	206
27	50*	22
28	146	152
29	81	89
H= 4, K= 10		
0	62*	3
1	217	176
2	1594	1801
3	498	485
4	270	273
5	374	334
6	1282	1332
7	360	288
8	546	595
9	68*	90
10	1139	1263
11	554	562
12	465	444
13	292	345
14	934	935
15	257	205
16	397	389
17	134	188
18	603	619
19	239	195
20	214	728
21	186	169
22	250	219
23	128	112
24	205	230
25	107	118
26	108	133
27	112	116
28	87	69
H= 4, K= 12		
0	69*	8
1	69*	67
2	957	938
3	214	212
4	214	210
5	193	169
6	1002	965
7	291	204
8	351	300
9	276	281
10	798	762
11	97	120
12	137	111
13	236	235
14	414	384
15	73*	81
16	225	211
17	71*	53
18	480	438
19	261	198
20	176	214
21	104	111
22	267	256
23	110	120
24	80	96
25	49	23
26	131	133
H= 4, K= 14		
0	407	400
1	364	328
2	695	716
3	477	413
4	413	421
5	466	417
6	582	566
7	290	301
8	320	321
9	287	241
10	445	466
11	310	294
12	391	379
13	239	220
14	522	474
15	363	320
16	261	280
17	195	205
18	168	222
19	72	58
20	132	203
21	148	145
22	76	101
23	81	83
24	115	142
H= 4, K= 16		
0	132	90
1	429	430
2	396	398
3	361	355
4	93	113
5	478	453
6	317	331
7	504	432
8	236	225
9	373	395
10	322	253
11	348	253
12	217	205
13	318	308
14	276	287
15	179	133
16	208	191
17	252	253
18	159	160
19	155	151
20	146	156
21	134	171
22	22*	95
H= 4, K= 18		
0	188	202
1	460	432
2	185	194
3	409	387
4	167	126
5	311	315
6	325	293
7	355	311
8	132	132
9	418	425
10	176	168
11	301	285
12	199	188
13	281	308
14	51*	20
15	155	141
16	122	128
17	152	180
18	50	55
H= 4, K= 20		
0	145	105
1	319	318
2	91	44
3	300	287
4	126	96
5	369	377
6	52*	13
7	219	193
8	159	132
9	284	281
10	44*	55
11	133	125
12	42	84
13	246	281
14	22*	30
H= 4, K= 22		
0	70	18
1	166	183
2	35	57
3	151	174
4	103	101
5	158	229
H= 5, K= 1		
0	170	118
1	1040	1217
2	1171	1237
3	658	637
4	564	608
5	712	688
6	745	746
7	1030	1028
8	227	268
9	432	400
10	652	619
11	613	616
12	60*	64
13	313	246
14	629	706
15	680	698
16	183	195
17	280	266
18	522	552
19	492	412
20	333	301
21	73*	109
22	259	247
23	241	275
24	263	233
25	64*	61
26	158	149
27	197	164
28	50*	28
29	42*	7
30	85	150
H= 5, K= 3		
0	708	675
1	478	412
2	737	730
3	1276	1425
4	1158	1175
5	842	876
6	631	642
7	1008	1030
8	481	468
9	579	636
10	771	838
11	1137	1252
12	566	543
13	301	294
14	342	304
15	552	588
16	357	338
17	351	287
18	266	269
19	444	423
20	73*	59
21	267	251
22	298	294
23	336	324
24	126	94
25	75	60
26	167	148
27	127	136
28	58	70
29	81	80
30	13*	38
H= 5, K= 5		
0	1161	1131
1	910	960
2	683	612
3	936	939
4	476	412
5	795	797
6	670	620
7	826	868
8	517	566
9	694	696
10	473	360
11	746	764
12	612	600
13	578	557
14	464	438
15	642	603
16	550	539
17	302	262
18	283	274
19	415	381
20	373	282
21	277	235
22	145	99
23	284	223
24	221	199
25	96	97
26	87	83
27	94	116
28	64	68
29	92	87
H= 5, K= 7		
0	1061	1259
1	894	888
2	491	493
3	661	725
4	1018	1115
5	360	378
6	466	478
7	756	817
8	891	1010
9	499	491
10	245	241
11	439	405
12	606	581
13	427	473
14	428	500
15	427	341

Table 2 (*cont.*)

L	FO	FC
H= 5, K= 7		
16	252	282
17	188	170
18	243	197
19	467	467
20	246	236
21	288	230
22	249	258
23	195	190
24	61*	114
25	175	158
26	165	158
27	162	145
28	85	65
H= 5, K= 9		
0	540	596
1	588	555
2	238	188
3	639	624
4	756	756
5	655	683
6	185	194
7	666	589
8	684	681
9	366	356
10	165	119
11	525	512
12	428	494
13	252	220
14	73*	89
15	540	488
16	453	405
17	339	306
18	232	231
19	146	99
20	352	320
21	153	130
22	63*	96
23	132	101
24	189	145
25	75	85
26	89	81
27	32*	38
H= 5, K= 11		
0	729	811
1	464	442
2	378	316
3	608	599
4	808	826
5	522	445
6	234	206
7	332	339
8	614	571
9	135	203
10	512	463
11	391	389
12	764	672
13	246	244
14	204	174
15	322	317
16	377	381
17	221	248
18	350	316
19	108	119
20	144	144
21	95	115
22	106	116
23	51*	81
24	107	85
25	39	63
26	13*	125
H= 5, K= 13		
0	787	802
1	447	378
2	436	443
3	269	231
4	860	747
5	380	336
6	250	258
7	540	469
8	717	643
9	554	460
10	274	288
11	201	148
12	404	364
13	333	324
14	457	400
15	139	99
16	268	244
17	73	94
18	170	183
19	159	137
20	208	170
21	162	152
22	177	174
23	39	53
24	20*	147
H= 5, K= 15		
0	434	364
1	564	479
2	383	331
3	348	278
4	489	454
5	177	197
6	362	318
7	149	187
8	615	451
9	324	255
10	338	316
11	211	226
12	355	321
13	128	145
14	248	261
15	179	170
16	143	144
17	215	230
18	190	183
19	129	120
20	139	156
21	97	131
H= 5, K= 17		
0	461	442
1	79	131
2	283	272
3	322	307
4	310	245
5	295	277
6	384	362
7	180	199
8	228	228
9	139	117
10	234	247
11	252	243
12	139	132
13	204	178
14	165	154
15	159	155
16	136	143
17	95	83
18	63	167
H= 5, K= 19		
0	77	114
1	240	230
2	260	257
3	210	240
4	104	138
5	211	194
6	197	206
7	247	249
8	75	62
9	101	122
10	201	228
11	145	141
12	79	91
13	86	100
14	14*	205
H= 5, K= 21		
0	53	42
1	104	174
2	91	138
3	134	188
4	29*	34
5	25*	134
6	14*	137
H= 6, K= 0		
0	838	862
1	538	571
2	211	164
3	148	145
4	1527	1506
5	765	779
6	314	226
7	709	670
8	903	768
9	589	560
10	231	140
11	199	181
12	751	674
13	383	375
14	318	311
15	194	146
16	590	593
17	469	480
18	84*	45
19	84*	79
20	346	326
21	303	284
22	79*	20
23	125	158
24	84	87
25	134	169
26	60*	39
27	52*	63
28	39*	52
H= 6, K= 2		
0	1097	1244
1	685	735
2	160	96
3	680	666
4	974	950
5	681	611
6	93	103
7	200	100
8	1087	1147
9	688	688
10	196	185
11	935	933
12	699	750
13	725	620
14	80*	54
15	167	87
16	445	406
17	320	294
18	84*	92
19	229	190
20	230	231
21	184	221
22	134	124
23	205	217
24	232	248
25	107	106
26	134	128
27	50*	67
28	37*	127
H= 6, K= 4		
0	937	1062
1	307	359
2	271	335
3	678	679
4	816	827
5	454	387
6	344	289
7	408	282
8	714	706
9	406	331
10	406	378
11	169	168
12	546	467
13	499	487
14	117	149
15	401	328
16	319	321
17	305	312
18	376	370
19	241	266
20	334	356
21	96	139
22	76*	103
23	157	156
24	129	176
25	71	90
26	55*	51
27	45*	26
H= 6, K= 6		
0	439	402
1	704	750
2	502	581
3	569	547
4	400	378
5	592	641
6	488	564
7	707	779
8	266	257
9	423	380
10	500	418
11	238	218
12	456	428
13	497	528
14	326	303
15	543	507
16	388	388
17	212	245
18	179	131
19	350	278
20	217	222
21	129	156
22	149	175
23	114	125
24	63*	37
25	56*	100
26	48*	37
27	32*	130
H= 6, K= 8		
0	279	304
1	507	579
2	508	533
3	593	638
4	517	505
5	598	575
6	518	578
7	688	690
8	383	348
9	668	671
10	265	292
11	695	708
12	218	171
13	308	236
14	324	328
15	261	274
16	105	157
17	271	267
18	141	146
19	251	289
20	75*	139
21	85	79
22	112	74
23	124	144
24	90	122
25	46*	89
26	30*	96
H= 6, K= 10		
0	80*	28
1	500	500
2	478	448
3	547	576
4	152	181
5	418	345
6	266	277
7	288	274
8	364	305
9	308	281
10	376	368
11	551	520
12	303	286
13	351	335
14	255	233
15	304	303
16	197	179
17	95	122
18	222	212
19	322	307
20	69*	104
21	128	133
22	68	52
23	193	214
24	65	85
H= 6, K= 12		
0	154	129
1	436	352
2	393	381
3	461	448
4	266	219
5	360	370
6	418	411
7	558	591
8	385	413
9	237	252
10	277	268
11	309	344
12	82*	126
13	139	148
14	79*	103
15	369	390
16	153	159
17	71*	73
18	157	148
19	163	180
20	148	170
21	52*	80
22	82	95
H= 6, K= 14		
0	424	435
1	256	239
2	454	395
3	231	196
4	326	298
5	307	254
6	226	224
7	331	268
8	241	212
9	137	113
10	164	157
11	226	248
12	297	276
13	73*	103
14	232	218
15	234	195
16	231	231
17	117	113
18	54*	61
19	74	108
20	56	130
H= 6, K= 16		
0	305	305
1	226	169
2	184	160
3	158	194
4	338	362
5	126	137
6	262	185
7	193	164
8	278	306
9	163	149
10	112	133
11	75	114
12	227	257
13	117	137
14	89	100
15	50*	85
16	181	230
17	50	109
H= 6, K= 18		
0	280	331
1	63*	97
2	144	134
3	160	144
4	314	330
5	69	96
6	149	173
7	56*	79
8	269	275
9	143	151
10	107	100
11	153	160
12	178	237
H= 6, K= 20		
0	135	251
1	70	101
2	46	58
3	27*	92
H= 7, K= 1		
0	111	96
1	319	268
2	692	766
3	108	81
4	360	337
5	334	279
6	669	719
7	79	104
8	196	148
9	427	404
10	689	596
11	284	258
12	159	130
13	370	322
14	552	533
15	136	147
16	224	201
17	104	116
18	314	333
19	124	111
20	200	135
21	98	94
22	184	215
23	90	96
24	63	103
25	46*	93
26	32*	107
H= 7, K= 3		
0	221	213
1	373	370
2	852	918
3	525	560
4	402	395
5	305	341
6	733	706
7	310	257
8	160	154
9	247	220
10	761	693
11	263	273
12	386	289
13	210	245
14	271	303
15	191	198
16	96	93
17	332	327
18	283	285
19	128	131
20	136	145
21	98	95
22	169	144
23	68	36
24	84	91
25	113	123
H= 7, K= 5		
0	79	83
1	292	354
2	632	595
3	484	461
4	203	167
5	611	657
6	668	677
7	490	470
8	274	282
9	408	394
10	505	508
11	321	328
12	97	71
13	426	430
14	479	488
15	238	227
16	214	202
17	160	172
18	239	251
19	72*	99
20	69*	74
21	187	213
22	122	168
23	63	43
24	75	98
25	33*	91
H= 7, K= 7		
0	69*	41
1	481	507
2	349	310
3	314	262
4	225	252
5	246	225
6	460	411
7	447	478
8	255	227
9	412	478
10	277	230
11	340	230
12	138	123
13	336	320
14	191	181
15	134	166
16	184	175
17	154	194
18	121	147
19	114	161
20	75	120
21	138	171
22	87	96
23	92	128
24	53	93
H= 7, K= 9		
0	75*	33
1	561	552
2	75*	79
3	557	533
4	76*	84
5	609	616
6	76*	178
7	293	279
8	169	101
9	448	437
10	77*	57
11	273	297
12	301	246
13	362	360
14	129	117
15	198	244
16	72*	49
17	245	282
18	65*	110
19	124	96
20	58*	55
21	129	168
22	43*	73
23	20*	27
H= 7, K= 11		
0	77*	25
1	415	386
2	77*	95
3	507	530
4	97	106
5	466	485
6	77*	87
7	346	319
8	77*	98
9	266	285
10	227	250
11	272	280
12	74*	113
13	173	268
14	70*	80
15	68*	123
16	75	121
17	245	271
18	64	93
19	51*	95
20	43*	38
21	84	170
H= 7, K= 13		
0	76*	81
1	294	341
2	246	294
3	131	130
4	92	45
5	272	329
6	156	187
7	217	297
8	73*	63
9	308	384
10	118	201
11	81	128
12	66*	65
13	257	270
14	61*	137
15	58*	76
16	53*	70
17	106	170
18	43	130
H= 7, K= 15		
0	69*	3
1	259	256
2	215	257
3	198	229
4	68*	129
5	193	192
6	288	288
7	64*	132
8	104	111
9	158	192
10	214	252
11	56*	83
12	60	76
13	155	177
14	215	246
15	33*	68
H= 7, K= 17		
0	105	146
1	63	114
2	232	284
3	106	167
4	60	69
5	129	179
6	250	304
7	92	98
8	70	85
9	62	113
10	112	204
H= 8, K= 0		
0	615	630
1	449	423
2	116*	203
3	149	181
4	869	887
5	115*	19
6	256	225
7	207	158
8	579	676
9	113*	155
10	243	225
11	196	161
12	427	403
13	106*	86
14	382	399
15	123	160
16	332	331
17	111	75
18	180	163
19	83*	33
20	126	137
21	70*	69
22	60*	92
23	44*	25
H= 8, K= 2		
0	549	590
1	116*	76
2	151	139
3	116*	110
4	448	449
5	148	128
6	116*	122
7	253	203
8	435	490
9	114*	96
10	113*	105
11	196	154
12	331	406
13	107*	73
14	104*	47
15	101*	32
16	234	281
17	93*	84
18	89*	108
19	136	192
20	76*	156
21	69*	16
22	59*	97
23	40*	105
H= 8, K= 4		
0	567	545
1	145	136
2	411	355
3	500	415
4	538	442
5	286	296
6	142	106
7	313	309
8	392	315
9	136	117
10	189	190
11	260	244
12	283	267
13	93*	67
14	237	258
15	253	231
16	84*	98
17	80*	128
18	267	218
19	87	96
20	191	178
21	95	55
22	45*	119
H= 8, K= 6		
0	277	271
H= 8, K= 8		
0	187	162
H= 8, K= 10		
0	86	76
H= 8, K= 12		
0	76	5
H= 8, K= 14		
0	89	149
H= 8, K= 16		
0	69	132
H= 9, K= 1		
0	108	70
1	207	243
2	238	263
3	205	218
4	117	144
5	232	233
6	257	305
7	195	154
8	92*	36
9	216	215
10	105	145
11	85*	127
12	169	90
13	93	148
14	125	136
15	72*	92
16	66*	66
17	61*	105
18	53*	80
19	43*	85
H= 9, K= 3		
0	128	156
1	216	189
2	403	341
3	261	222
4	80*	59
5	105	71
6	273	190
7	203	170
8	298	279
9	74*	142
10	295	275
11	221	165
12	245	211
13	165	152
14	232	164
15	250	181
16	175	144
17	177	177
18	112	113
19	30*	121
H= 9, K= 5		
0	121	159
H= 9, K= 7		
0	138	201
H= 9, K= 9		
0	191	295
H= 9, K= 11		
0	149	206
H= 9, K= 13		
0	86	135
H= 10, K= 0		
0	110	145
1	143	156
2	86*	29
3	199	190
4	84*	79
5	137	144
6	81*	89
7	92	99
8	76*	81
9	146	120
10	70*	74
11	129	128
12	60*	3
13	53*	94
14	41*	122
H= 10, K= 2		
0	73	66
1	174	173
2	142	134
3	172	167
4	97	85
5	166	217
6	81*	107
7	181	186
8	87	77
9	187	216
10	69*	114
11	64*	114
12	115	68
13	51*	164
14	35*	74
H= 10, K= 4		
0	98	98
1	128	154
2	127	154
3	155	160
4	153	155
5	86	83
6	84	61
7	141	151
8	134	105
9	146	145
10	117	87
11	89	90
12	45*	87
13	34*	119

Table 3. *Magnitudes B and direction cosines relative to* **a**, **b**, *and* **c**, *of the principal axes of the thermal ellipsoids*

	B_1	B_2	B_3	D_{1a}	D_{1b}	D_{1c}	D_{2a}	D_{2b}	D_{2c}	D_{3a}	D_{3b}	D_{3c}
I	5·05	8·40	3·61	−0·867	−0·012	−0·498	−0·465	−0·342	0·816	−0·180	0·940	0·291
N	4·20	5·76	5·08	0·975	0·016	−0·223	0·224	−0·034	0·974	0·008	−0·999	−0·037
O(1)	5·85	4·09	3·62	0·896	0·341	0·285	0·312	−0·939	0·141	−0·316	0·037	0·948
O(2)	6·67	6·99	4·23	−0·642	−0·523	−0·561	−0·752	0·572	0·327	0·151	0·632	−0·760
O(3)	5·38	9·29	3·14	−0·956	−0·137	−0·258	−0·143	0·990	0·003	−0·255	−0·040	0·966
O(4)	5·52	9·29	3·35	−0·925	0·026	−0·379	0·159	0·933	−0·323	−0·345	0·359	0·867
O(5)	7·15	5·44	3·82	0·940	0·082	0·331	−0·001	−0·970	0·243	−0·341	0·229	0·912
O(6)	9·03	6·02	3·52	0·848	−0·438	0·299	−0·391	−0·897	−0·205	−0·358	−0·057	0·932
C(1)	4·23	9·12	5·28	0·857	0·459	0·235	0·186	−0·700	0·690	0·481	−0·547	−0·685
C(2)	4·11	11·30	3·37	0·431	−0·426	−0·795	0·189	0·904	−0·382	0·882	0·015	0·471
C(3)	3·92	5·20	3·88	0·314	−0·073	−0·947	0·424	0·903	0·071	0·849	−0·423	0·315
C(4)	4·33	6·04	3·19	−0·885	0·135	0·446	0·090	0·989	−0·121	0·457	0·067	0·887
C(5)	4·27	5·33	2·44	−0·105	−0·959	−0·265	−0·606	−0·150	0·781	0·789	−0·242	0·565
C(6)	3·96	4·81	3·85	−0·009	−0·765	0·644	−0·505	0·560	0·657	0·863	0·317	0·393
C(7)	5·83	4·33	3·11	0·828	−0·178	−0·531	−0·500	−0·664	−0·556	0·254	−0·726	0·639
C(8)	4·18	5·17	3·83	−0·843	0·523	−0·126	0·531	0·846	−0·040	−0·086	0·101	0·991
C(9)	5·88	3·96	3·20	0·925	0·364	0·111	0·363	−0·931	0·029	−0·114	−0·013	0·993
C(10)	4·71	5·07	2·93	−0·735	−0·677	−0·033	0·505	−0·576	0·643	−0·455	0·455	0·765
C(11)	4·14	5·93	3·06	0·366	0·175	−0·914	0·429	0·840	0·333	0·826	−0·514	0·232
C(12)	8·83	4·91	3·20	0·894	0·447	−0·026	0·417	−0·853	−0·312	0·162	−0·268	0·950
C(13)	5·59	7·02	3·91	−0·727	0·458	−0·511	0·568	0·820	−0·074	−0·386	0·344	0·856
C(14)	7·96	9·00	3·78	−0·992	0·043	−0·122	0·072	0·968	−0·239	−0·108	0·246	0·963
C(15)	4·55	5·35	3·91	−0·803	0·565	0·191	0·564	0·575	0·593	0·223	0·582	−0·782
C(16)	5·27	6·60	2·51	−0·971	−0·223	−0·086	−0·232	0·966	0·112	−0·058	−0·129	0·990
C(17)	5·95	7·03	2·38	−0·884	0·465	0·049	0·464	0·859	0·215	−0·058	−0·213	0·975
C(18)	4·27	6·45	3·56	−0·744	−0·119	0·658	0·225	0·882	0·414	0·629	−0·456	0·629
C(19)	5·37	6·70	4·25	0·142	−0·636	−0·758	0·729	−0·451	0·515	0·669	0·626	−0·400
C(20)	9·08	11·44	3·46	−0·811	0·583	0·053	−0·001	−0·091	0·996	0·585	0·808	0·074
C(21)	3·59	7·42	6·29	0·994	−0·056	−0·096	0·069	0·988	0·135	−0·088	0·141	−0·986

The parameters f and g were re-evaluated several times so as to make $\langle w(K|F_o|-|F_c|)^2\rangle$ essentially independent of $|F_o|$. Atomic scattering factor values were those of Hanson, Herman, Lea & Skillman (1964) for the carbon, nitrogen and oxygen atoms and of Cromer & Waber (1965) for the iodide ion. The real part of the anomalous dispersion correction given by Cromer (1965) was applied to the I^- scattering curve.

Three cycles of least-squares calculations using isotropic temperature factors for all atoms, followed by three cycles in which the iodide atom was refined anisotropically and the other atoms isotropically, resulted in an R index of 0·12. After several further cycles in which all atoms were refined anisotropically, it became clear that agreement between observed and calculated structure factors was generally worse for reflexions with $\sin^2\theta \leq 0{\cdot}200$ than for the rest of the data. It seems probable that inaccuracy in the values of μR assumed for the absorption corrections, and, especially, deviation of the crystals from strictly spherical shape, may be the main factors responsible for the low-angle discrepancies. (Crystal deterioration can be expected to affect all the data adversely.) Because of the apparent unreliability of the low-angle data, reflexions with $\sin^2\theta \leq 0{\cdot}200$ were excluded from further refinement. After a few more least-squares cycles, refinement was terminated; the average parameter shifts were then less than one tenth of their respective estimated standard deviations, and the largest shift was $0{\cdot}8\sigma$. The final R index for the 1944 reflexions used in the last cycles of refinement was 0·092, while for all 2137 observed reflexions it was 0·113.

The estimated standard deviations of the atomic parameters were calculated from the diagonal elements of the inverse to the normal equations matrix. The e.s.d.'s of the bond lengths and angles which were derived from these have been increased by 50% to allow for omission of unobserved reflexions and interactions between atoms.

A difference map computed with the final structure factors showed a number of peaks which could be interpreted as hydrogen atom sites, but only nine of these, less than half the total number of hydrogen atoms, were significantly higher than the background level. Consequently no attempt was made to pursue the refinement including hydrogen atoms.

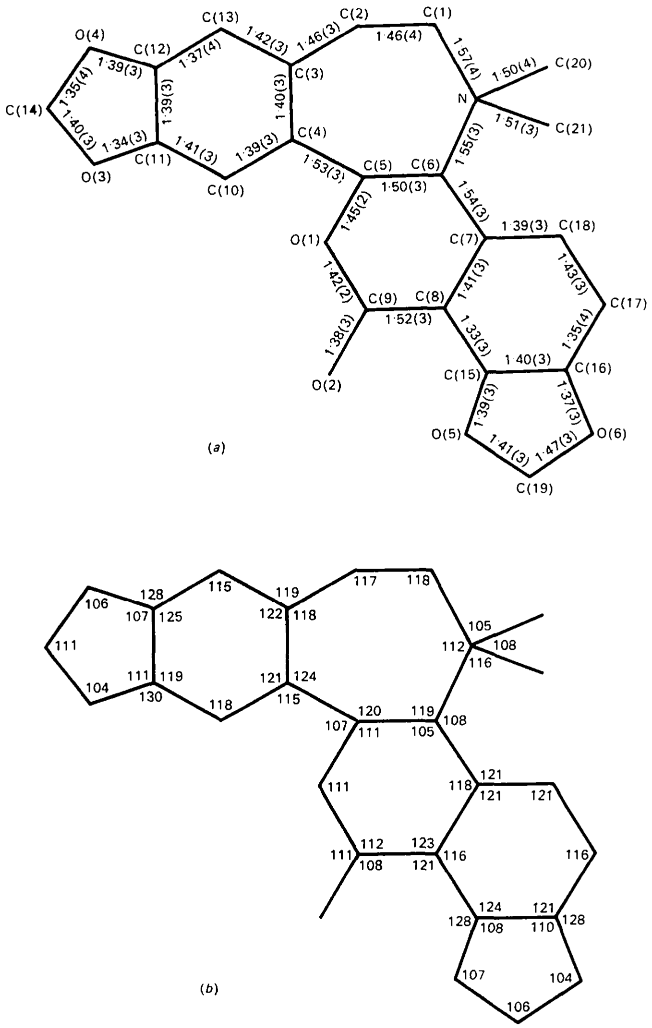

Fig.3. Bond lengths (Å) and their e.s.d.'s ($\times 10^2$), and bond angles (°). E.s.d.'s for the angles range from 1·5 to 2·5°.

Results and discussion

The molecular structure and configuration may be seen in Fig.2, which is a stereoscopic view of the organic cation, prepared with Johnson's (1965) *ORTEP* program.

Final coordinates and anisotropic thermal parameters with corresponding e.s.d.'s are given in Table 1. Observed and calculated structure amplitudes based on these parameters are listed in Table 2. Magnitudes and direction cosines of the principal axes of the individual ellipsoids are given in Table 3.

An analysis of the thermal parameters by Cruickshank's (1956) method, assuming the 28 non-hydrogen atoms of the organic cation to act as a rigid body, indicated that the main rotational vibration was about an axis roughly parallel to the longest dimension of the cation, and that the translational vibration of the ion was nearly isotropic. However, the discrepancies between the observed U_{ij}'s and the U_{ij}'s calculated from the T_{ij} and ω_{ij} tensors were much larger than the e.s.d.'s of the observed U_{ij} values. Since the rigid-body approximation does not appear to be appropriate in this structure, no corrections to the bond lengths were calculated from the ω_{ij} tensor values.

Corrections were, however, made to the C(9)–O(2), N–C(20) and N–C(21) bond lengths, using the formulae for 'riding' motion given by Busing & Levy (1964). The corrections for these three bonds amounted to 0·019, 0·033 and 0·010 Å respectively.

Bond lengths and angles

The numbering scheme and bond lengths with their e.s.d.'s are shown in Fig. 3(*a*), and bond angles are given in Fig. 3(*b*). The two angles not shown in the Figure for simplicity are C(1)–N–C(21), 105°; C(6)–N–C(20), 110°. The values given in Fig. 3(*a*) for the C(9)–O(2), N–C(20) and N–C(21) bonds are the corrected bond lengths.

The four N^+–C sp^3 bonds have an average length of 1·53 Å, and although the two bonds in the seven-membered ring appear longer than the other two, the difference is not significant. This average may be compared with the value 1·52 ± 0·03 Å quoted by Hamilton, Hamor, Robertson & Sim (1962) as characteristic for the N^+–C sp^3 bond length in a number of alkaloids.

As would be expected, the average of the seven C sp^3–O bonds, 1·41 Å, is longer than the average C sp^2–O bond length, 1·37 Å, and each is in satisfactory agreement with respective standard values 1·426 ± 0·005 and 1·37 ± 0·02 Å (Sutton, 1965) or 1·425 and 1·381 Å (Hall & Ahmed, 1968). The two C sp^3–C sp^3 bonds appear shorter than the usual value of 1·537 Å (Sutton, 1965), but their deviations are not significant. The average C sp^2–C sp^3 bond length, 1·51 Å, is also in agreement with the characteristic value 1·510 ± 0·005 Å (Sutton, 1965).

For the twelve aromatic C sp^2–C sp^2 bonds, the average length is 1·39 Å. The deviation of one bond, C(8)–C(15), from the average is in the range of possible significance ($1\% < P < 5\%$) using the *t* test, but since there is no obvious reason for its shortness, this may indicate that the e.s.d.'s are slightly underestimated.

The coordination of the positively charged nitrogen atom is approximately tetrahedral, but the angle C(6)–N–C(21) is significantly enlarged from 109·5° because of repulsion between C(21) and O(1). Even with this angular distortion, C(21) is only 3·04 Å from O(1), whereas the normal $CH_3 \cdots O$ van der Waals separation is 3·4 Å (Pauling, 1960).

The angles in the azacycloheptene ring are all larger than 109·5°; those at C(3) and C(4) are close to 120° as would be expected because of the fused aromatic ring. The average of the other five angles in the ring, 117°, is similar to the values found for cycloheptane ring angles in various compounds; for example: isoclovene hydrochloride (Clunie & Robertson, 1961), 116·5°; bromo-

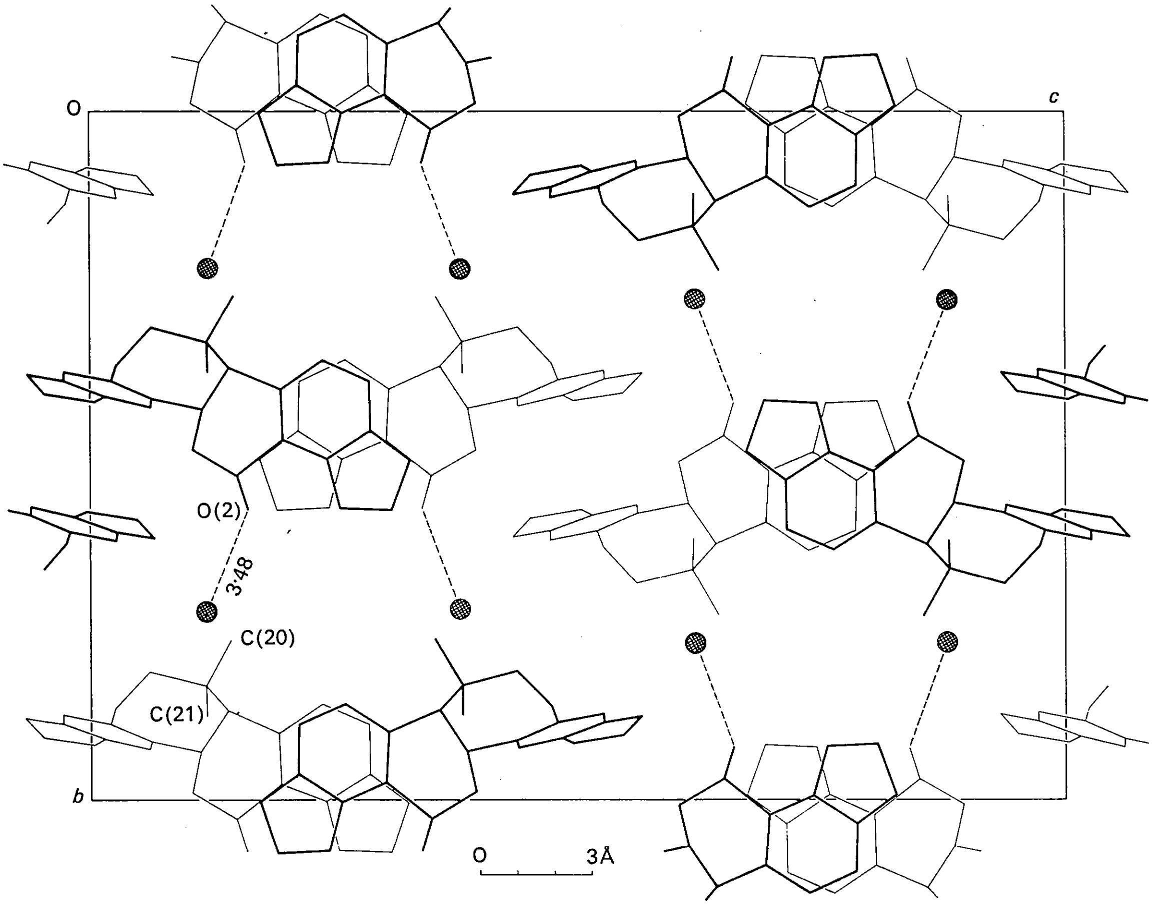

Fig. 4. Projection of the structure on the (100) plane. The hatched circles represent iodide ions, and the proposed hydrogen bonding between the iodide ion and hydroxyl oxygen atom is indicated by dashed lines.

geigerin acetate (Hamilton, McPhail & Sim, 1962), 116°; and 2-bromodihydroisophoto-α-santonic lactone acetate (Asher & Sim, 1965), 115°.

Angles in the benzodioxole groups are similar, within the limits of accuracy of this analysis, to those found by Hall & Ahmed (1968) in the corresponding parts of protopine.

Planarity and conformation of the rings

Both aromatic rings are planar within experimental error, since $\chi^2=4\cdot9$ and $3\cdot7$ for the planes including C(3) and C(7) respectively, and for $\nu=3$, $P>5\%$. Equations of these two planes are respectively

$$-0\cdot1615X+0\cdot9432Y-0\cdot2904Z-5\cdot3912=0$$

and $$-0\cdot9670X-0\cdot1962Y-0\cdot1632Z+8\cdot8923=0$$

where the coefficients of X, Y, and Z are direction cosines with respect to the cell axes a, b and c. The dioxole ring formed by O(3), O(4), C(11), C(12) and C(14) is slightly envelope shaped, with O(3), O(4), C(11) and C(12) coplanar within 0·012 Å and C(14) deviating from this plane by 0·16 Å. The other dioxole ring is slightly more puckered, with O(5), O(6), C(15) and C(16) deviating from planarity by amounts up to 0·044 Å, and C(19) lying 0·30 Å from this approximate plane. The two 1,3-benzodioxole systems are nearly mutually perpendicular; the dihedral angle between the two aromatic rings is 88·9°.

The dihydropyran ring is 'sofa'-shaped (Philbin & Wheeler, 1958). As required by the adjacent aromatic ring C(6), C(7), C(8) and C(9) are coplanar, and O(1) is nearly in this plane although its deviation of 0·12 Å is highly significant ($P<0\cdot1\%$). C(5), however, deviates by 0·66 Å from the plane. The deviation of the hydroxyl oxygen atom, O(2) is 1·16 Å, on the same side of the plane as C(5). This orientation of the hydroxyl group agrees with the recent stereochemical assignment, from nuclear magnetic resonance evidence, by Shamma, Weiss, Pfeifer & Döhnert (1968) for this group in rhoeagenine. The dihydropyran and azacycloheptene rings are *cis*-fused, and the ring junction is characterized by dihedral angles of 63·0° for O(1)–C(5)–C(6)–C(7) and 66·4° for C(4)–C(5)–C(6)–N.

The azacycloheptene ring is in a slightly distorted chair form. Despite the fused aromatic ring, C(2), C(3), C(4) and C(5) deviate significantly from planarity (by amounts up to 0·027 Å). The dihedral angle between the mean plane through these four atoms and the plane defined by C(1), N and C(6) is 5·0°. C(1), C(2), C(5) and C(6) are very significantly non-planar, with deviations up to 0·077 Å from the mean plane through these four atoms. These distortions from normal chair conformation help to increase slightly the distance between C(21) and O(1) and thereby reduce their mutual repulsion.

Packing arrangement

Each iodide ion is equidistant, 4·24 Å, from the two methyl groups of one adjacent cation, and is 3·48 Å from the hydroxyl oxygen atom of another cation. The $I^-\cdots C(20)$ and $I^-\cdots C(21)$ distances are slightly larger than the normal $I^-\cdots CH_3$ van der Waals separation, 4·15 Å (Pauling, 1960). However, the equality of the distances suggests that the packing arrangement may be partially governed by Coulomb attraction between the iodide ion and the positively charged but inaccessible nitrogen atom.

The $I^-\cdots O$ contact mentioned above is slightly shorter than the usual separation, 3·55 Å (Pauling, 1960) for this type of van der Waals interaction. Since the standard deviation of the $I^-\ldots O$ distance is only 0·02 Å, the shortening is considered significant, and this suggests that a weak hydrogen bond may exist between O(2) and I^-. The value of the $C(9)-O(2)\cdots I^-$ angle, 94·7°, is also compatible with the existence of such a hydrogen bond.

Contact distances less than 3·5 Å are listed in Table 4. With the exception of the $I^-\cdots O(2)$ and $C(11)\cdots C(11)$ distances, none is shorter than the corresponding van der Waals contact distance; the $C(11)\cdots C(11)$ distance with an e.s.d. of 0·03 Å, is not significantly shorter than the usual van der Waals distance.

Table 4. *Intermolecular distances less than* 3·5 Å

$O(2)^{i}$	I^{ii}	3·48 Å
$C(2)^{i}$	$O(3)^{iii}$	3·30
$C(21)^{i}$	$O(3)^{iii}$	3·38
$C(14)^{i}$	$O(3)^{iv}$	3·40
$O(3)^{i}$	$O(3)^{iv}$	2·98
$C(11)^{i}$	$O(3)^{iv}$	3·41
$C(19)^{i}$	$O(4)^{v}$	3·40
$O(5)^{i}$	$O(5)^{vi}$	3·35
$C(21)^{i}$	$O(6)^{vi}$	3·31
$C(11)^{i}$	$C(11)^{iv}$	3·35

i	x	y	z
ii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iii	$x-1$	y	z
iv	x	$1-y$	$-z$
v	$2-x$	$1-y$	$\frac{1}{2}+z$
vi	$1-x$	y	$\frac{1}{2}-z$

The packing arrangement is illustrated in Fig. 4. The structure can be thought of as consisting of infinite chains, parallel to [110], of alternating organic cations and iodide ions. The protruding parts of adjacent chains along the c axis are closely interleaved, as is clearly shown in the Figure.

The author wishes to thank Dr J. W. ApSimon for suggesting the problem and for subsequent valuable discussions, Dr D. Rozwadowska for supplying the crystals used in this analysis, and Dr M. Przybylska for her continued interest in the investigation. Dr C. Johnson kindly supplied his computer program *ORTEP* with which Fig. 2 was prepared. Other programs used were those of Ahmed, Hall, Huber & Pippy (1966) for the IBM/360 system. Grateful acknowledgment is made to Mrs H. Sheppard for technical assistance and to the staff of the NRC Computation Centre for their cooperation.

References

AHMED, F. R., HALL, S. R., HUBER, C. P. & PIPPY, M. E. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd Edition, Appendix p. 52.

ASHER, J. D. M. & SIM, G. A. (1965). *J. Chem. Soc.* p. 1584.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

CLUNIE, J. S. & ROBERTSON, J. M. (1961). *J. Chem. Soc.* p. 4382.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.

HALL, S. R. & AHMED, F. R. (1968). *Acta Cryst.* B**24**, 337.

HAMILTON, J. A., HAMOR, T. A., ROBERTSON, J. M. & SIM, G. A. (1962). *J. Chem. Soc.* p. 5061.

HAMILTON, J. A., MCPHAIL, A. T. & SIM, G. A. (1962). *J. Chem. Soc.* p. 708.

HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations.* Oak Ridge National Laboratory Report ORNL-3794, Revised.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

PHILBIN, E. M. & WHEELER, T. S. (1958). *Proc. Chem. Soc.* p. 167.

SANTAVY, F., KAUL, J. L., HRUBAN, L., DOLEJS, L., HANUS, V., BLAHA, K. & CROSS, A. D. (1965). *Coll. Czech. Chem. Comm.* **30**, 3479.

SHAMMA, M., WEISS, J. A., PFEIFER, S. & DÖHNERT, H. (1968). *Chem. Comm.* p. 212.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959. London: The Chemical Society.

Acta Cryst. (1970). B**26**, 380

Structure Cristalline et Moléculaire du (Dinitro-2,'4'-phenyl)-1-chloro-4-pyrazole

PAR J. L. GALIGNÉ ET J. FALGUEIRETTES

Laboratoire de Minéralogie Cristallographie, Faculté des Sciences de Montpellier, France

(*Reçu le* 25 *mars* 1969)

The crystal structure of 1-(2',4'-dinitrophenyl)-4-chloropyrazole has been determined from three-dimensional data collected on a single-crystal diffractometer with Cu $K\alpha$ radiation. The crystals are orthorhombic, space group $Pna2_1$ with $a=15\cdot21\pm0\cdot02$; $b=13\cdot59\pm0\cdot02$; $c=5\cdot20\pm0\cdot01$ Å; $Z=4$. The structure was refined by least-squares methods and the final R is 0·051 for 822 reflexions. The only significant difference from the structure of 1-(2',4'-dinitrophenyl)-4-bromopyrazole is in the three bonds lengths C(3)–N(4), C(7)–N(5) and C(10)–N(14). The small displacements from the plane of the phenyl ring are similar in the two compounds.

Dans une précédente communication nous avons donné la structure cristalline du (dinitro-2',4'-phényl)-1-bromo-4-pyrazole (Galigné & Falgueirettes, 1969). La détermination de la structure du (dinitro-2',4'-phényl)-1-chloro-4-pyrazole a été entreprise en vue de préciser certains détails concernant la déformation du cycle benzénique et la géométrie du noyau pyrazole.

La synthèse et l'étude chimique de ces produits ont été réalisées dans le laboratoire de M. le Professeur Jacquier (Elguero, Jacquier & Tien Duc, 1966).

Partie experimentale

La préparation des cristaux, les mesures des intensités des réflexions à l'aide d'un diffractomètre à compteur ont été effectuées dans les mêmes conditions que pour le (dinitro-2',4'-phényl)-1-bromo-4-pyrazole. Nous avons utilisé les intensités des réflexions pour lesquelles σ/N était inférieur à 3% [σ=écart type, $N=N(\text{pic})-N$ (fond continu)]. Sur un total de 1081 réflexions possibles, 822 avaient une intensité répondant à cette condition.

Données cristallographiques

$a=15{,}21\pm0{,}02$ Å
$b=13{,}59\pm0{,}02$
$c=\ \ 5{,}20\pm0{,}01$
Groupe spatial $Pna2_1$
$Z=4$
$V=1082$ Å^3
Densité mesurée $D_m=1{,}63\pm0{,}04$ g.cm^{-3}
Densité calculée $D_c\ =1{,}65$ g.cm^{-3}
Coefficient linéaire d'absorption $\mu_l=24{,}68$ cm^{-1}

Détermination de la structure

Les deux structures étant isotypes, les coordonnées et paramètres d'agitation thermique obtenus en fin d'affinement avec agitation thermique isotrope du (dinitro-2',4'-phényl)-1-bromo-4-pyrazole ont été utilisés com-