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The Crystal Structure of the Monohydrated Potassium Salt of 4-Hydroxy-5,7-Dinitrobenzfurazan

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The crystal and molecular structure of the hydrated potassium salt of 4-hydroxy-5,7-dinitrobenzfurazan, $K^+[OC_6H(NO_2)_2N_2O]^-.H_2O$, has been determined by X-ray diffraction techniques. The complex crystallizes as bright yellow, monoclinic needles with $a = 10{\cdot}944 \pm 0{\cdot}010$, $b = 4{\cdot}694 \pm 0{\cdot}004$, $c = 21{\cdot}310 \pm 0{\cdot}010$ Å and $\beta = 117{\cdot}42 \pm 0{\cdot}08°$, measured at room temperature. The space group is $P2_1/c$ and with four molecules of the monohydrate (M.W. 282·2) per unit cell, $D = 1{\cdot}921$ g.cm^{-3} compared with $D_m = 1{\cdot}91$ g.cm^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to a final R of 0·081 for the 1321 observed reflections, measured by the stationary-crystal stationary-counter technique with molybdenum radiation. The C–O bond length of $1{\cdot}234 \pm 0{\cdot}008$ Å is close to the C–O double-bond distance. The resulting distortions in the ring are similar to those found in potassium picrate, modified by the furazan system. A C–H (ring)$\cdots$O (nitro) hydrogen bond appears to exist in the crystal.

Introduction

The crystal structure of potassium and ammonium picrate (Maartmann-Moe, 1969) revealed a very strong interaction of the deprotonated phenol oxygen with the aromatic ring. In fact, the term 'benzene ring' may not be appropriate since the distortions in the ring are so extreme. Subsequently, a comparison of the Meisenheimer complex of trinitrophenetole (Destro, Gramaccioli & Simonetta, 1968) with a similar dinitrobenzfurazan complex led Messmer & Palenik (1971) to conclude that the furazan ring had a greater electron withdrawing power than a nitro group. Therefore, the potassium salt of 4-hydroxy-5,7-dinitrobenzfurazan should exhibit distortions similar to potassium picrate but perturbed by the furazan system. We undertook an investigation of the structure of the potassium salt of 4-hydroxy-5,7-dinitrobenzfurazan, henceforth K$^+$ HDNBF, to examine the interaction in salts of nitrophenols and also the electron withdrawing power of the furazan ring.

Experimental

Bright yellow needles of $K^+[C_6HN_4O_6]^-.H_2O$ were obtained by recrystallization from water. Preliminary Weissenberg photographs indicated that the crystals are monoclinic with the systematic absences of $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$, suggesting that the space group is $P2_1/c$ (C_{2h}^5).

A crystal of dimensions $0{\cdot}10 \times 0{\cdot}18 \times 0{\cdot}08$ mm (parallel to **a**, **b** and **c** respectively) which was dipped in liquid nitrogen to minimize extinction effects was used for the intensity measurements. The resulting mosaic spread of the crystal was sufficiently smaller (peak width at half-height was less than 0·1° at a 1° take-off angle) than the effective source width at the 4° take-off angle used for the intensity measurements. The unit-cell dimensions determined from diffractometer measurements are given in Table 1. Diffraction data for reflections in a hemisphere with $2\theta < 60°$ (Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70926$ Å) were measured using the stationary crystal-stationary counter method. A 20 sec count was taken for each reflection with a zirconium filter in front of the counter window. A General Electric XRD-5 diffractometer controlled by a prepunched paper tape was used for measuring the intensity data. Four standard reflections which were measured after every 100 reflections were used to correct the data for a slight decrease (maximum 9%) in the intensity with time. A background curve as a function of 2θ was derived from the systematically absent reflections which were not affected by a radiation streak. A total of 2862 unique reflections was obtained after averaging symmetry equivalent reflections, and the 1321 reflections which were greater than or equal to 1·2 times the appropriate background count were considered to be observed; the remaining reflections were considered to be unobserved and entered as 0·1 times the local background count and flagged with a minus sign. Since the linear absorption coefficient for Mo $K\alpha$ is only 5·7 cm^{-1}, no absorption corrections were applied (the maximum error in an intensity is 9%). The α_1–α_2 doublet could be contained within the counter window under the experimental conditions employed (take-off angle was 3·7°) and no correction for the splitting was applied. The intensity data were reduced to a set of observed amplitudes on an arbitrary scale in the usual manner.

Table 1. *Crystal data*

$a = 10{\cdot}944 \pm 0{\cdot}010$ Å	$K[C_6HN_4O_6].H_2O$
$b = 4{\cdot}694 \pm 0{\cdot}004$	M.W. 282·2
$c = 21{\cdot}310 \pm 0{\cdot}010$	$Z = 4$
$\beta = 117{\cdot}42 \pm 0{\cdot}08°$	$D_m = 1{\cdot}91$ g.cm^{-3}
Space group $P2_1/c$ (C_{2h}^5)	$D_x = 1{\cdot}921$ g.cm^{-3}

Determination and refinement of the structure

The position of the potassium ion was determined from a sharpened three-dimensional Patterson function. A Fourier synthesis based on phases determined by the potassium ion alone yielded the positions of the atoms in the anion. A computed difference Fourier synthesis, using the anion and cation for phasing, was utilized to locate the water molecule. At this point the conventional R value ($R=\Sigma|\Delta F|/\Sigma F_o$) was 0·18.

Four full-matrix least-squares cycles using individual isotropic thermal parameters reduced R to 0·12. The thermal parameters were converted to their anisotropic equivalent form and four full-matrix least-squares cycles reduced R to 0·081. The shifts in the parameters in the last cycles were all less than 0·1σ and thus the refinement was considered completed. The final parameters are given in Table 2. The structure factors calculated with these parameters are presented in Table 3 together with the corresponding observed values. A final difference Fourier synthesis was computed using the heavier atom parameters given in Table 2. The three hydrogen atoms were easily located and their coordinates are given in Table 2. The contribution of the hydrogen atoms were not included in any of the calculations.

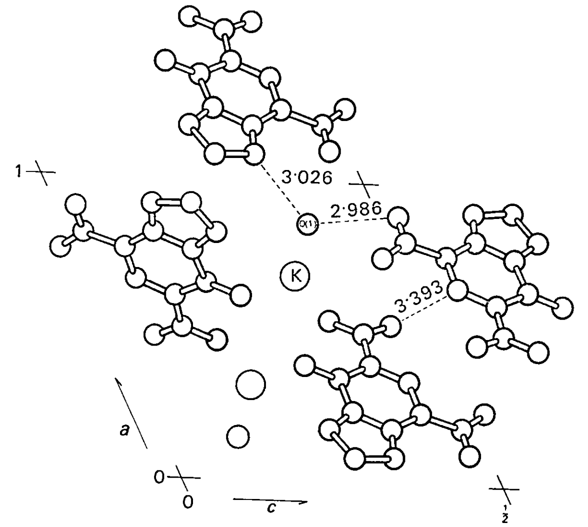

Fig. 1. A projection of the structure on the (010) plane illustrating the molecular packing. The hydrogen bonds are shown as dotted lines.

The quantity minimized by the least-squares calculations was $\Sigma w(|F_o|-|F_c|)^2$ where the weights were as follows:

$$\sqrt{w}=|F_o|/2\ F_{\min} \text{ if } F_o<2\ F_{\min}$$

$$\sqrt{w}=1 \text{ if } 2\ F_{\min}\le F_o\le 6\ F_{\min}$$

$$\sqrt{w}=6\ F_{\min}/|F_o| \text{ if } F_o>6\ F_{\min}$$

and where $F_{\min}$ is the nominal minimum observable F, in this case 4·2 (or 42 on the scale of Table 3). Atomic scattering factors for all atoms were taken from the *International Tables for X-ray crystallography* (1962)

Discussion

The crystal consists of K$^+$, $[OC_6H(NO_2)_2N_2O]^-$ ions and a water molecule packed together (as illustrated in Fig. 1) with no unusually short intermolecular contacts. The K$^+$ ion is surrounded by 8 oxygen atoms and a nitrogen atom at distances from 2·858 to 3·112 Å. The atoms of the coordination polyhedra about the K$^+$ ion and their distances are tabulated in Table 4. The

Table 2. *Final parameters with estimated standard deviations in parentheses*

All values are multiplied by 10^4. The temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	6849 (2)	6662 (5)	3249 (1)	121 (2)	607 (11)	26 (1)	28 (9)	58 (2)	31 (4)
O(1)	8606 (6)	1715 (16)	3831 (3)	129 (7)	939 (48)	25 (1)	177 (33)	51 (5)	19 (15)
C(1)	6525 (6)	1195 (16)	1804 (3)	81 (6)	419 (39)	14 (1)	40 (26)	17 (5)	25 (12)
C(2)	6080 (6)	−705 (16)	1216 (3)	82 (6)	401 (36)	16 (1)	−22 (26)	28 (5)	6 (12)
C(3)	6586 (6)	−689 (16)	718 (3)	82 (6)	401 (37)	14 (1)	20 (27)	19 (5)	12 (11)
C(4)	7610 (7)	1145 (16)	768 (3)	94 (7)	433 (38)	13 (1)	1 (28)	27 (5)	11 (11)
C(5)	8173 (6)	3076 (17)	1348 (3)	70 (6)	434 (39)	16 (1)	22 (27)	20 (5)	7 (13)
C(6)	7641 (6)	3080 (16)	1837 (3)	85 (6)	333 (34)	15 (1)	35 (27)	18 (5)	14 (12)
N(1)	5060 (6)	−2832 (14)	1110 (3)	87 (6)	442 (35)	21 (1)	45 (24)	28 (5)	4 (11)
N(2)	8070 (6)	1049 (15)	243 (3)	104 (6)	586 (40)	17 (1)	−27 (28)	40 (5)	−18 (12)
N(3)	9123 (6)	5046 (14)	1532 (3)	88 (6)	464 (35)	19 (1)	−20 (25)	28 (5)	−1 (12)
N(4)	8241 (6)	5029 (14)	2315 (3)	85 (5)	439 (32)	17 (1)	26 (24)	23 (4)	−9 (12)
O(2)	6113 (5)	1445 (13)	2252 (2)	109 (5)	641 (35)	18 (1)	−86 (25)	46 (4)	−37 (11)
O(3)	4603 (6)	−2993 (14)	1539 (3)	152 (7)	572 (35)	32 (2)	−122 (28)	85 (6)	−55 (13)
O(4)	4722 (6)	−4484 (13)	616 (3)	127 (7)	549 (34)	28 (2)	−151 (25)	54 (5)	−69 (12)
O(5)	7551 (6)	−646 (15)	−244 (3)	178 (8)	725 (41)	25 (1)	−104 (31)	81 (6)	−69 (13)
O(6)	8976 (6)	2722 (16)	304 (3)	146 (7)	959 (50)	30 (2)	−270 (33)	83 (6)	−84 (15)
O(7)	9168 (5)	6288 (12)	2136 (2)	83 (5)	504 (31)	22 (1)	−40 (21)	25 (4)	−26 (10)
H(1)	8860	1670	4310						
H(2)	9430	1560	3900						
H(3)	6250	−1940	300						

K^+ ion is approximately in the center of a distorted trigonal prism, with the three remaining atoms roughly in the center of each rectangular face. The result is approximately a 3–3–3 type of nine coordination. The O···O distances in the triangular faces [3·214 Å for O(1) to O(2), 3·032 Å for O(2) to O(3′) and 2·904 Å for O(3′) to O(1)] are close to the value for van der Waals contacts.

Table 3. *Observed and calculated structure amplitudes*

The three columns in each group contain the values, reading from left to right, of l, $10F_o$ and $10F_c$. A negative F_o indicates an unobserved reflection which was not included in the least-squares refinement.

L	FO	FC
H= -15, K= 0		
8	-26	-15
10	79	64
12	49	-49
14	-26	4
16	46	38
18	-26	23
H= -14, K= 0		
2	39	21
4	-26	8
6	41	-37
8	45	38
10	-25	21
12	79	25
14	-25	17
16	-25	-14
18	57	46
20	101	81
22	70	-50
H= -13, K= 0		
2	123	-110
4	-25	-14
6	77	63
8	-25	-5
10	105	-98
12	109	84
14	-25	7
16	-25	-32
18	98	90
20	41	-21
22	-25	30
24	103	80
26	-26	0
H= -12, K= 0		
2	129	-113
4	-25	28
6	56	-30
8	180	-164
10	90	80
12	46	-28
14	50	-45
16	61	42
18	88	-87
20	46	-35
22	68	41
24	60	-36
26	38	41
H= -11, K= 0		
2	52	50
4	47	45
6	-25	32
8	74	68
10	384	-352
12	171	-169
14	155	166
16	139	-142
18	60	-70
20	121	114
22	-25	-11
24	-25	-19
26	-25	21
28	-26	-36
H= -10, K= 0		
2	80	73
4	194	-174
6	53	62
8	107	89
10	197	161
12	-27	-46
14	-26	-9
16	215	-223
18	149	137
20	72	-62
22	41	-51
24	97	92
26	60	-54
28	56	-30
H= -9, K= 0		
2	96	99
4	127	115
6	228	215
8	289	-263
10	411	397
12	-29	45
14	-28	-65
16	161	180
18	270	-274
20	46	47
22	41	46
24	103	-107
26	-25	-34
28	68	63
H= -8, K= 0		
2	322	285
4	-27	-23
6	243	-225
8	185	174
10	117	118
12	-28	-13
14	-28	2
16	104	109
18	58	-51
20	-25	2
22	170	-179
24	97	-88
26	72	73
28	-25	-7
H= -7, K= 0		
2	383	360
4	448	-406
6	204	198
8	290	265
10	425	-409
12	52	-52
14	85	-62
16	129	-141
18	62	85
20	105	118
22	80	-74
24	150	130
26	44	-36
28	-25	22
30	48	44
H= -6, K= 0		
2	806	-722
4	50	-45
6	72	-53
8	172	-157
10	96	99
12	382	358
14	316	-302
16	515	506
18	78	-76
20	144	-136
22	184	164
24	77	-73
26	-25	-22
28	-25	22
H= -5, K= 0		
2	-24	34
4	693	643
6	164	-167
8	805	783
10	304	278
12	506	-492
14	424	418
16	158	162
18	171	-153
20	88	-78
22	180	175
24	101	-96
26	-25	13
28	185	-159
H= -4, K= 0		
2	572	571
4	499	-485
6	89	83
8	306	-258
10	-24	-67
12	646	590
14	96	95
16	233	-225
18	212	199
20	49	-51
22	184	-176
24	87	86
26	-25	-30
28	36	-48
H= -3, K= 0		
2	806	-835
4	522	488
6	92	-51
8	1042	-994
10	431	-378
12	375	352
14	413	-383
16	202	202
18	172	157
20	225	-218
22	267	249
24	65	56
26	-25	-35
28	96	93
H= -2, K= 0		
2	360	-419
4	161	130
6	1166	-1166
8	547	-536
10	40	-45
12	297	-295
14	-25	19
16	158	-136
18	331	312
20	373	364
22	112	-104
24	42	-29
26	66	61
28	56	45
H= -1, K= 0		
2	349	-372
4	379	426
6	373	-318
8	862	865
10	301	-310
12	118	124
14	-26	9
16	432	-426
18	228	-234
20	192	180
22	-25	-23
24	76	81
26	50	46
H= 0, K= 0		
2	305	-361
4	414	-395
6	544	592
8	209	-204
10	142	-136
12	39	10
14	179	-181
16	-29	-13
18	90	98
20	364	-387
22	53	-19
24	86	-81
26	44	19
H= 1, K= 0		
0	507	-524
2	473	562
4	590	675
6	440	460
8	61	-72
10	340	364
12	468	-510
14	118	119
16	-27	9
18	65	-72
20	-25	-29
22	-25	-20
24	-25	-25
H= 2, K= 0		
0	578	-595
2	327	374
4	682	-734
6	46	68
8	728	750
10	168	-182
12	244	-231
14	348	369
16	47	-59
18	-25	45
20	147	162
22	60	-63
24	55	47
H= 3, K= 0		
0	443	-447
2	339	-334
4	254	-257
6	563	614
8	410	-451
10	348	358
12	262	273
14	-27	3
16	-25	18
18	-25	-6
20	-25	-18
22	-26	9
H= 4, K= 0		
0	288	-253
2	291	327
4	233	249
6	-24	9
8	198	-208
10	-28	0
12	-27	-31
14	82	-88
16	126	132
18	176	-182
20	115	117
22	-26	8
H= 5, K= 0		
0	421	-420
2	44	52
4	40	42
6	331	-335
8	173	176
10	101	-95
12	-25	20
14	-25	37
16	-25	-2
18	78	-109
20	-26	-29
H= 6, K= 0		
0	165	162
2	462	437
4	352	-352
6	51	64
8	-28	-5
10	54	-50
12	56	62
14	83	-94
16	38	46
18	118	130
H= 7, K= 0		
0	350	-316
2	319	-294
4	193	173
6	63	-70
8	-25	31
10	117	116
12	-25	-12
14	44	-24
16	51	44
H= 8, K= 0		
0	95	-73
2	58	52
4	-26	-12
6	194	-190
8	41	33
10	126	133
12	97	-80
14	-26	-21
H= 9, K= 0		
0	66	48
2	-25	16
4	87	-71
6	126	115
8	192	-172
10	166	-147
12	162	149
H= 10, K= 0		
0	98	91
2	155	-137
4	125	112
6	42	46
8	78	76
10	83	-89
H= 11, K= 0		
0	-25	-2
2	45	-45
4	87	75
6	50	-50
8	51	46
H= 12, K= 0		
0	135	101
2	-25	23
4	-26	-36
H= 13, K= 0		
0	62	-42
2	-26	-1
H= -15, K= 1		
9	-26	27
10	-26	-23
11	-26	7
12	-26	-35
13	45	-29
14	66	50
15	40	25
16	48	-20
17	47	-11
18	-26	-9
H= -14, K= 1		
3	-26	14
4	-26	-12
5	-26	-1
6	-26	35
7	-25	27
8	-25	0
9	-25	-19
10	-25	13
11	-25	-30
12	-25	22
13	-25	37
14	-25	-6
15	45	17
16	45	-28
17	-25	-6
18	58	52
19	-26	25
20	43	-27
21	56	48
22	-26	-36
23	-26	-17
H= -13, K= 1		
1	-26	22
2	-25	-27
3	44	-40
4	-25	0
5	41	-38
6	-25	-1
7	-25	30
8	-25	14
9	43	51
10	99	96
11	41	4
12	-25	-16
13	37	20
14	66	-57
15	-25	-18
16	80	82
17	-25	14
18	-25	-1
19	-25	-28
20	-25	-12
21	-25	-17
22	-25	6
23	68	60
24	-26	-14
25	-26	2
H= -12, K= 1		
1	-25	18
2	-25	-16
3	60	61
4	38	44
5	-25	-4
6	84	-77
7	111	-109
8	48	-57
9	-25	-19
10	65	65
11	65	62
12	-25	-20
13	114	-118
14	99	102
15	54	52
16	-25	-6
17	-25	-10
18	-25	-10
19	-25	-35
20	98	96
21	-25	0
22	-25	-16
23	-25	-16
24	-25	-16
25	-26	-24
26	80	45
27	82	62
H= -11, K= 1		
1	67	-66
2	-25	0
3	119	109
4	196	-186
5	48	-60
6	124	132
7	-25	26
8	-25	-1
9	42	-45
10	139	-139
11	-25	-26
12	-25	23
13	46	-52
14	-25	6
15	-25	-5
16	47	48
17	-25	8
18	-25	41
19	-25	-20
20	-25	18
21	-25	-4
22	-25	-1
23	50	-42
24	97	96
25	-25	15
26	-26	-6
27	-26	-12
28	-26	23
H= -10, K= 1		
1	-25	-32
2	-25	-50
3	-25	19
4	-25	-1
5	-25	-9
6	62	58
7	165	145
8	163	-157
9	-26	32
10	139	-115
11	-26	0
12	126	129
13	-25	5
14	94	-102
15	108	-127
16	-25	18
17	84	91
18	-25	13
19	65	56
20	62	-46
21	-25	-23
22	87	94
23	43	54
24	-25	-18
25	-25	16
26	39	-38
27	64	-63
28	52	58
H= -9, K= 1		
1	160	-146
2	63	68
3	-28	-27
4	104	103
5	69	76
6	135	-128
7	71	-89
8	120	121
9	52	46
10	-28	43
11	247	271
12	359	-366
13	101	118
14	75	91
15	-27	21
16	-26	32
17	82	90
18	209	-221
19	130	-145
20	61	66
21	-25	6
22	-25	15
23	-25	-12
24	-25	-39
25	-25	-28
26	-25	29
27	-25	6
28	-26	-33
29	-26	0
H= -8, K= 1		
1	-28	-45
2	272	246
3	69	74
4	84	-87
5	125	128
6	-28	-31
7	-28	-27
8	-28	25
9	74	80
10	149	-164
11	341	-369
12	218	240
13	118	143
14	132	-154
15	-28	6
16	178	-180
17	-27	22
18	-26	23
19	-25	4
20	52	56
21	-25	4
22	54	-65
23	-25	-6
24	39	35
25	-25	19
26	-25	34
27	-25	-15
28	55	-62
29	-26	-42
H= -7, K= 1		
1	60	61
2	94	-93
3	313	-295
4	96	98
5	42	-58
6	-25	35
7	242	-212
8	140	-141
9	111	-125
10	153	154
11	46	-72
12	183	210
13	-28	55
14	243	-254
15	127	-141
16	54	69
17	47	-67
18	127	152
19	197	212
20	244	-259
21	127	-125
22	103	104
23	52	63
24	-25	-2
25	37	42
26	-25	1
27	-25	44
28	86	95
29	-26	18
H= -6, K= 1		
1	130	-121
2	223	198
3	220	-197
4	329	304
5	285	278
6	140	-139
7	51	-54
8	55	57
9	269	-290
10	53	86
11	130	155
12	116	-133
13	144	-143
14	101	107
15	-28	-16
16	-28	-4
17	-29	-42
18	69	-65
19	-27	-9
20	158	162
21	108	103
22	89	-79
23	74	76
24	129	-126
25	47	-50
26	39	39
27	45	44
28	-26	28
29	-26	16
H= -5, K= 1		
1	336	312
2	81	-65
3	116	111
4	-24	13
5	107	-102
6	-24	-40
7	79	69
8	760	788
9	253	264
10	206	-214
11	-25	31
12	83	-91
13	96	99
14	-27	15
15	99	99
16	175	-182
17	117	-110
18	61	67
19	100	102
20	85	-71
21	106	-101
22	118	-101
23	132	-122
24	-25	22
25	-25	-14
26	-25	5
27	-25	-14
28	65	-69
29	54	-49
H= -4, K= 1		
1	332	323
2	408	-353
3	383	368
4	541	-298
5	102	-96
6	439	474
7	536	572
8	101	-96
9	150	147
10	-24	8
11	-24	-12
12	71	86
13	63	64
14	137	133
15	57	-68
16	127	-118
17	318	-307
18	-28	-4
19	49	55
20	158	-148
21	-25	0
22	84	74
23	89	-89
24	-25	31
25	49	54
26	113	-105
27	52	-50
28	-26	24
29	-26	13
H= -3, K= 1		
1	375	376
2	751	-746
3	773	-750
4	520	502
5	48	-48
6	120	-137
7	324	-312
8	97	-97
9	300	-270
10	594	549
11	155	-138
12	190	-182
13	-25	13
14	105	110
15	184	174
16	534	508
17	268	268
18	160	-142
19	212	-198
20	63	-65
21	49	51
22	-25	27
23	-25	-15
24	-25	-15
25	-25	-21
26	-25	27
27	43	43
28	-26	-14
H= -2, K= 1		
1	143	-140
2	552	536
3	258	-259
4	-28	-4
5	-27	15
6	247	-249
7	121	-133
8	233	232
9	503	478
10	191	-201
11	259	-264
12	196	170
13	330	-305
14	415	410
15	201	185
16	213	-212
17	-28	29
18	198	183
19	92	93
20	155	150
21	134	130
22	-25	-1
23	49	59
24	-25	-2
25	-25	-21
26	-25	-24
27	-26	25
H= -1, K= 1		
1	62	105
2	488	-514
3	164	149
4	560	-577
5	496	-491
6	497	497
7	339	325
8	690	-669
9	69	-74
10	102	-81
11	94	92
12	219	221
13	92	93
14	-27	-63
15	76	79
16	83	-82
17	136	-139
18	194	185
19	-25	11
20	-25	0
21	-25	15
22	80	-79
23	-25	34
24	140	136
25	41	19
26	62	-51
27	-26	-50
H= 0, K= 1		
1	329	334
2	147	-192
3	369	354
4	502	464
5	218	220
6	805	-821
7	112	45
8	537	-538
9	156	-124
10	282	262
11	360	347
12	268	-273
13	151	-144
14	211	-219
15	88	-77
16	-28	48
17	-27	37
18	196	-214
19	210	-212
20	198	189
21	125	-128
22	78	86
23	40	50
24	117	-115
25	-26	-18
26	71	61
H= 1, K= 1		
0	409	397
1	420	-409
2	-29	-17
3	1154	1153
4	593	-572
5	42	-67
6	-24	70
7	292	-290
8	96	-66
9	348	-330
10	117	-109
11	45	59
12	178	-176
13	165	-170
14	67	78
15	-28	58
16	-27	-60
17	-25	40
18	66	-71
19	60	74
20	-25	-8
21	-25	36
22	-25	-12
23	94	-98
24	-26	15
25	-26	-29
H= 2, K= 1		
0	603	544
1	1434	-1415
2	1400	1377
3	-24	24
4	707	-710
5	282	-297
6	266	293
7	189	189
8	239	232
9	209	205
10	155	-155
11	-27	-9
12	142	149
13	123	127
14	158	-160
15	82	-90
16	-25	50
17	47	51
18	-25	52
19	-25	-30
20	69	-77
21	88	105
22	62	-52
23	-26	11
24	38	47
H= 3, K= 1		
0	310	272
1	450	614
2	431	-435
3	437	-452
4	497	505
5	74	83
6	187	204
7	134	-147
8	49	54
9	-27	-39
10	43	55
11	45	59
12	61	-77
13	91	97
14	76	-98
15	141	-192
16	143	149
17	188	197
18	-25	17
19	-25	2
20	-25	-48
21	43	-53
22	-26	12
23	-26	42
H= 4, K= 1		
0	793	-791
1	261	-255
2	283	304
3	-24	34
4	103	119
5	197	201
6	187	-185
7	90	-88
8	160	179
9	-28	45
10	88	99
11	-28	-50
12	62	-83
13	-25	9
14	-25	28
15	55	-54
16	57	-69
17	50	-62
18	42	-55
19	-25	-3
20	56	62
21	-26	-29
H= 5, K= 1		
0	100	81
1	192	186
2	125	-122
3	-24	34
4	140	-142
5	-27	-7
6	115	116
7	-28	-21
8	-28	0
9	62	70
10	218	-246
11	199	-192
12	185	196
13	-25	-7
14	-25	20
15	-25	19
16	-25	-34
17	53	-66
18	-25	8
19	-26	27
20	-26	-23
H= 6, K= 1		
0	102	106
1	62	77
2	212	-197
3	195	-193
4	297	304
5	110	118
6	48	60
7	57	69
8	162	-167
9	137	-145
10	57	67
11	134	128
12	42	57
13	36	46
14	-25	-28
15	-25	3
16	-25	10
17	-25	-11
18	-26	-3
H= 7, K= 1		
0	146	-145
1	157	-140
2	100	92
3	-28	30
4	-28	-18
5	84	89
6	-26	-22
7	135	129
8	183	179
9	-25	3
10	-25	-42
11	-25	-27
12	56	-58
13	-25	5
14	-25	58
15	-25	29
16	-26	0
17	-26	-12
H= 8, K= 1		
0	-29	-20
1	-28	30
2	82	83
3	51	-65
4	-25	-32
5	125	-116
6	173	-168
7	60	-61
8	97	99
9	118	118
10	-25	32
11	-25	-11
12	-25	13
13	37	37
14	-26	21
15	-26	15
H= 9, K= 1		
0	165	148
1	223	206
2	210	-189
3	-25	-11
4	-25	-8
5	-25	-25
6	-25	40
7	-25	-33
8	115	-106
9	55	-66
10	62	62
11	38	-36
12	-26	-38
13	-26	10
H= 10, K= 1		
0	50	-41
1	-25	0
2	-25	-7
3	-25	-20
4	-25	10
5	-25	23
6	37	-53
7	-25	-15
8	38	-37
9	-26	34
10	-26	24
H= 11, K= 1		
0	-25	-2
1	-25	-7
2	-25	29
3	-25	37
4	-25	-18
5	-25	-7
6	52	42
7	-26	-4
8	-26	13
H= 12, K= 1		
0	42	54
1	-25	0
2	-25	-17
3	-26	18
4	-26	-14
5	-26	-30
H= 13, K= 1		
0	-26	-13
1	-26	-40
2	-26	-1
H= -14, K= 2		
5	-26	39
6	53	54
7	67	66
8	-26	-37
9	-26	-43
10	-26	-10
11	-26	-10
12	-26	41
13	-26	-8
14	-26	-10
15	-26	-15
16	-26	0
17	-26	13
18	-26	-5
19	-26	1
20	-26	-16
H= -13, K= 2		
1	-26	-18
2	-26	21
3	-26	-18
4	-25	-5
5	-25	-8
6	-25	-19
7	-23	17
8	48	55
9	-25	-19
10	-25	21
11	75	65
12	-25	-20
13	-25	4
14	-25	-16
15	-25	-43
16	-25	19
17	-25	47
18	-25	-16
19	84	-66
20	-26	22
21	-26	26
22	-26	-22
23	-26	19
H= -12, K= 2		
1	-25	-50
2	-25	3
3	75	68
4	-25	-8
5	-25	-48
6	-25	-29
7	47	-49
8	-25	46
9	69	78
10	-25	-35
11	108	-116
12	60	66
13	56	58
14	-25	27
15	42	55
16	48	-47
17	77	-73
18	-25	1
19	-25	17
20	-25	-4
21	44	47
22	89	-74
23	-26	0
24	-26	4
25	-26	16
H= -11, K= 2		
1	-25	34
2	-25	-42
3	-25	-7
4	-25	33
5	-25	-57
6	62	37
7	-25	1
8	-25	-55
9	43	-57
10	-25	16
11	-25	-11
12	-25	-3
13	-25	38
14	59	-36
15	-25	-43
16	-25	23
17	-25	36
18	78	77
19	47	64
20	-25	-20
21	50	-57
22	-25	25
23	-25	35
24	-25	-33
25	50	44
26	-26	-10
H= -10, K= 2		
1	-25	2
2	60	-62
3	-25	0
4	58	-69
5	86	105
6	-25	42
7	84	-90
8	-25	26
9	-25	39
10	-25	23
11	60	62
12	-25	-15
13	66	-71
14	106	117
15	101	-117
16	-25	20
17	87	95
18	42	-39
19	65	-70
20	-25	35
21	-25	-24
22	39	44
23	-23	9
24	-25	-38
25	52	-62
26	-26	38
27	47	53
H= -9, K= 2		
1	-25	-3
2	106	100
3	66	69
4	84	-97
5	92	115
6	-26	1
7	90	-101
8	44	61
9	147	130
10	-26	-41
11	75	-92
12	-26	14
13	-25	-60
14	92	116
15	70	89
16	-25	-39
17	152	-160
18	49	48
19	45	60
20	48	58
21	-25	-16
22	-25	-18
23	99	-90
24	-25	9
25	44	-50
26	-25	-25
27	-26	2
28	-26	3
H= -8, K= 2		
1	82	71
2	-28	15
3	99	-109
4	102	-122
5	91	-100
6	-29	52
7	241	262
8	-29	-27
9	-28	64
10	140	-158
11	-26	-2
12	-28	-38
13	-27	51
14	66	93
15	40	-67
16	81	87
17	-25	-31
18	84	-95
19	-25	39
20	-25	-18
21	60	-71
22	-25	30
23	-25	39
24	50	46
25	67	76
26	62	-68
27	61	-61
28	-26	30
H= -7, K= 2		
1	121	119
2	-28	-31
3	293	-291
4	148	160
5	141	152
6	282	-284
7	114	-109
8	-28	-45
9	119	-148
10	92	109
11	81	107
12	147	-164
13	169	199
14	259	-278
15	77	95
16	63	93
17	75	94
18	-25	-45
19	-25	15
20	60	71
21	-25	-10
22	81	82
23	103	106
24	-25	-2
25	-25	-27
26	38	48
27	-26	17
28	-26	20
H= -6, K= 2		
1	283	-264
2	103	100
3	64	77
4	-26	44
5	112	115
6	337	-308
7	126	-143
8	-27	-18
9	134	150
10	81	-102
11	-28	-35
12	-28	-5
13	285	-304
14	120	120
15	445	472
16	-28	-12
17	-27	-54
18	58	-62
19	-25	-37
20	-25	-18
21	104	104
22	-25	37
23	64	-65
24	-25	4
25	-25	31
26	-25	26
27	-26	8
28	-26	10
H= -5, K= 2		
1	244	232
2	110	112
3	117	117
4	111	116
5	207	-186
6	231	247
7	192	182
8	-25	5
9	221	-231
10	76	98
11	73	-96
12	72	88
13	-28	3
14	282	-290
15	308	-308
16	109	-126
17	53	-64
18	236	219
19	79	84
20	105	-103
21	51	55
22	56	-61
23	50	-55
24	-25	19
25	-25	22
26	-25	-25
27	50	-52
28	-26	-17
H= -4, K= 2		
1	192	190
2	-24	38
3	420	-380
4	434	380
5	-24	35
6	-24	0
7	-24	-30
8	148	-151
9	333	-326
10	257	271
11	312	325
12	100	-112
13	-27	-11
14	-28	43
15	284	-266
16	-28	-38
17	-27	-34
18	121	-118
19	105	-109
20	90	-89
21	152	-137
22	-25	22
23	138	117
24	63	-57
25	-25	-14
26	47	-22
27	-26	-3
28	-26	17
H= -3, K= 2		
1	128	-141
2	38	-48
3	765	689
4	179	-179
5	210	-210
6	251	255
7	182	-178
8	113	98
9	74	76
10	72	44
11	100	112
12	151	-148
13	188	-180
14	-28	29
15	258	235
16	-28	-35
17	-27	0
18	-26	-48
19	-25	-27
20	-25	53
21	153	138
22	99	-90
23	205	-172
24	46	42
25	-25	26
26	-26	31
27	41	44
H= -2, K= 2		
1	206	-193
2	-24	1
3	150	164
4	173	-150
5	103	-119
6	183	173
7	343	320
8	52	-59
9	262	261
10	178	-161
11	84	-79
12	252	238
13	327	281
14	-28	-34
15	-29	-13
16	186	181
17	67	86
18	90	85
19	40	52
20	-25	-29
21	-25	12
22	-25	-18
23	55	-50
24	43	48
25	-25	-6
26	39	-48
H= -1, K= 2		
1	541	486
2	670	-626
3	398	-367
4	41	47
5	135	-131
6	390	345
7	602	544
8	229	197
9	250	-236
10	124	110
11	-26	-34
12	280	260
13	-28	-39
14	126	-115
15	71	-83
16	-27	-17
17	106	110
18	-25	9
19	-25	-19
20	-25	-5
21	48	-51
22	-25	21
23	122	102
24	-25	6
25	-26	-23
26	-26	1
H= 0, K= 2		
0	197	-183
1	888	-869
2	187	208
3	69	75
4	338	339
5	76	-74
6	388	-363
7	414	-390
8	-23	-9
9	82	83
10	139	-147
11	-27	-37
12	-28	34
13	185	-196
14	216	197
15	-27	-31
16	-26	-15
17	94	103
18	-25	-32
19	159	-152
20	-25	-1
21	56	59
22	46	-56
23	-25	-8
24	-26	-25
25	-26	0
H= 1, K= 2		
0	117	126
1	79	-65
2	160	-160
3	263	275
4	327	-333
5	93	-94
6	75	86
7	73	-69
8	-24	41
9	175	177
10	150	-148
11	297	-290
12	-28	9
13	226	231
14	44	70
15	46	-63
16	188	-197
17	159	-135
18	93	96
19	42	51
20	83	88
21	-25	-25
22	-25	-11
23	45	52
24	-26	-57
H= 2, K= 2		
0	-24	-58
1	171	170
2	293	-263
3	-24	-15
4	149	-147
5	102	97
6	133	113
7	121	122
8	359	-366
9	147	-164
10	-28	57
11	92	101
12	-28	-29
13	218	216
14	62	60
15	-25	17
16	40	68
17	-25	45
18	-25	-37
19	58	59
20	-25	9
21	108	-122
22	94	101
23	-26	-30
H= 3, K= 2		
0	-24	17
1	298	-279
2	350	332
3	140	138
4	440	-408
5	645	604
6	214	-205
7	332	-329
8	245	251
9	178	168
10	62	70
11	53	65
12	85	-100
13	111	-113
14	-25	11
15	-25	21
16	-25	50
17	-25	26
18	-25	-35
19	-25	4
20	-25	10
21	95	114
22	-26	-14
H= 4, K= 2		
0	-24	-37
1	91	94
2	426	379
3	389	-368
4	112	109
5	199	-183
6	46	-75
7	-28	5
8	-28	38
9	-28	56
10	186	-177
11	88	-86
12	41	-48
13	-25	-21
14	-25	-6
15	-25	29
16	-25	-14
17	64	-75
18	-25	-4
19	-25	40
20	-26	14
H= 5, K= 2		
0	212	197
1	357	329
2	115	-112
3	-27	-57
4	-28	-51
5	395	-369
6	107	-107
7	-28	19
8	94	99
9	-26	-35
10	67	82
11	-25	-9
12	38	-56
13	-25	28
14	98	-110
15	39	-47
16	37	43
17	-25	-22
18	-26	-27
19	-26	20
H= 6, K= 2		
0	54	-57
1	55	75
2	41	-61
3	73	-76
4	353	344
5	330	299
6	-27	-56
7	154	-148
8	132	-126
9	-25	-39
10	38	41
11	-25	6
12	-25	1
13	108	-104
14	-25	11
15	79	76
16	-25	12
17	-26	25
H= 7, K= 2		
0	49	-66
1	-28	-30
2	-28	17
3	128	122
4	50	-62
5	-25	30
6	135	123
7	107	108
8	40	50
9	49	63
10	-25	18
11	-25	43
12	-25	-7
13	69	-74
14	-25	27
15	-26	11
16	-26	-21
H= 8, K= 2		
0	-27	3
1	42	57
2	-25	8
3	-25	-1
4	-25	-6
5	-25	-39
6	86	93
7	97	94
8	48	-55
9	63	-62
10	-25	7
11	-25	13
12	-25	42
13	59	73
14	-26	-7
H= 9, K= 2		
0	44	-49
1	57	-56
2	-25	-9
3	91	-97
4	-25	4
5	-25	54
6	59	-58
7	-25	-7
8	-25	-17
9	-25	-48
10	-25	29
11	-26	48
12	-26	-8
H= 10, K= 2		
0	-25	-38
1	-25	-44
2	-25	6
3	86	77
4	-25	23
5	95	-100
6	-25	1
7	-25	7
8	-26	9
9	-26	7
H= 11, K= 2		
0	69	65
1	-25	7
2	41	-49
3	37	60
4	-25	-27
5	-26	-31
6	-26	-3
7	-26	-15
H= 12, K= 2		
0	-25	15
1	-25	6
2	-26	-15
3	-26	-27
H= 13, K= 2		
0	-26	0
H= -13, K= 3		
4	-26	-11
5	-26	32
6	-26	15
7	-26	-27
8	-26	3
9	-26	32
10	-26	21
11	-26	-16
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14	44	-29
15	69	57
16	-26	-35
17	39	-34
18	-26	-7
19	-26	-8
H= -12, K= 3		
1	-26	29
2	-26	16
3	-26	-6
4	-25	-23
5	-25	-28
6	-25	-12
7	59	45
8	-25	-10
9	-25	-2
10	-25	-9
11	-25	-32
12	-25	-14
13	37	40
14	43	52
15	-25	-32
16	-25	2
17	-25	-4
18	-25	-10
19	-26	41
20	-26	8
21	39	-33
22	-26	-12
H= -11, K= 3		
1	-25	-3
2	-25	12
3	46	-53
4	-25	-7
5	-25	35
6	-25	18
7	-25	-15
8	-25	0
9	59	-57
10	-25	23
11	-25	41
12	-25	-16
13	-25	-8
14	-25	-37
15	-25	34
16	-25	30
17	-25	-9
18	-25	-8
19	-25	-20
20	-25	10
21	-25	-17
22	-26	6
23	96	82
24	49	32
H= -10, K= 3		
1	80	-78
2	-25	42
3	77	84
4	-25	-19
5	-25	-19
6	-25	-15
7	105	-102
8	-25	16
9	-25	55
10	-25	13
11	-25	37
12	-25	13
13	126	-136
14	-25	-22
15	60	72
16	-25	32
17	-25	11
18	-25	0
19	-25	-33
20	-25	-21
21	59	58
22	-25	-40
23	-26	-30
24	38	-38
25	42	14
H= -9, K= 3		
1	-25	45
2	-25	6
3	-25	49
4	-25	61
5	-25	-43
6	65	88
7	-25	-28
8	-25	6
9	-25	9
10	-25	-15
11	51	-67
12	-25	25
13	96	98
14	-25	-8
15	45	-62
16	-25	-45
17	-25	-52
18	-25	-47
19	47	52
20	-25	4
21	-25	-43
22	-25	-20
23	52	-59
24	-26	-36
25	57	55
26	-26	-29
H= -8, K= 3		
1	97	98
2	-25	-25
3	121	-135
4	46	-58
5	169	192
6	-25	-17
7	-25	18
8	87	75
9	110	-123
10	-25	-2
11	168	180
12	-25	23
13	99	-112
14	-25	-48
15	155	-171
16	68	70
17	98	106
18	-25	23
19	-25	14
20	-25	-25
21	63	-67
22	-25	28
23	-25	23
24	-25	9
25	-26	-25
26	-26	-8
H= -7, K= 3		
1	-26	-44
2	-26	-51
3	-27	-15
4	-27	-36
5	-27	34
6	48	-83
7	-27	-23
8	-27	-17
9	-27	31
10	-27	-11
11	-26	50
12	157	176
13	-25	-11
14	122	145
15	-25	44
16	-25	-38
17	-25	-25
18	-25	12
19	71	-72
20	-25	32
21	57	49
22	51	51
23	-25	-31
24	-25	5
25	-26	-14
26	-26	34
H= -6, K= 3		
1	-28	48
2	-28	-7
3	-28	7
4	-29	54
5	127	-146
6	61	-46
7	176	207
8	-28	-10
9	-28	28
10	45	-74
11	118	-146
12	155	-162
13	145	161
14	63	62
15	50	75
16	171	180
17	129	-131
18	55	76
19	165	166
20	-25	13
21	56	-57
22	-25	-6
23	-25	-28
24	-23	0
25	63	65
26	-26	-2
H= -5, K= 3		
1	-28	32
2	44	-66
3	68	-76
4	-28	21
5	67	-81
6	-28	-50
7	261	272
8	-28	-4
9	225	-261
10	-29	15
11	-28	58
12	-28	29
13	-27	14
14	191	-204
15	93	95
16	138	-149
17	89	77
18	-25	12
19	74	-73
20	-25	0
21	-25	13
22	-25	42
23	-25	7
24	-25	-18
25	-26	-5
26	-26	-7
H= -4, K= 3		
1	253	-239
2	-27	-8
3	-27	-16
4	-27	-11
5	115	133
6	-27	-66
7	49	-75
8	74	-95
9	-28	42
10	94	-109
11	-28	38
12	78	-82
13	134	-127
14	-27	-16
15	91	-102
16	110	-107
17	98	103
18	-25	-16
19	140	-124
20	82	-76
21	145	122
22	-25	7
23	-25	6
24	62	55
25	60	-45
26	-26	3
H= -3, K= 3		
1	-26	13
2	58	46
3	401	339
4	-26	30
5	389	-373
6	121	-125
7	85	-94
8	-27	31
9	154	137
10	-28	54
11	299	-269
12	-28	-4
13	196	188
14	115	114
15	-26	25
16	-25	1
17	157	-145
18	-25	-21
19	-25	37
20	36	41
21	-25	8
22	79	-67
23	-25	-15
24	-25	-21
25	46	35
H= -2, K= 3		
1	165	161
2	110	-108
3	57	-69
4	334	279
5	-26	-28
6	331	277
7	43	59
8	-27	15
9	-28	-24
10	-28	37
11	-28	-15
12	-28	-1
13	181	171
14	-27	7
15	244	-209
16	-25	12
17	42	54
18	74	70
19	65	65
20	-25	17
21	-25	-41
22	-25	29
23	-25	-4
24	-26	-15
25	-26	0
H= -1, K= 3		
1	-25	-49
2	73	80
3	-25	-22
4	247	-218
5	450	376
6	-26	43
7	445	-413
8	-27	41
9	194	170
10	114	91
11	73	72
12	-28	-43
13	152	-132
14	-26	67
15	164	148
16	-25	-6
17	-25	12
18	61	-67
19	87	-73
20	-25	-30
21	-25	11
22	-25	-1
23	-26	45
24	-26	13
H= 0, K= 3		
1	-24	-18
2	-25	22
3	133	126
4	-25	37
5	264	-238
6	-27	27
7	130	131
8	-28	-60
9	217	205
10	-28	-27
11	113	-101
12	135	-136
13	155	-169
14	130	-128
15	150	129
16	-25	1
17	124	-108
18	-25	-2
19	-25	47
20	-25	25
21	-25	0
22	-25	-26
23	-26	-19
H= 1, K= 3		
0	128	-118
1	146	133
2	-25	40
3	-26	-46
4	155	-153
5	77	-88
6	-27	-35
7	-28	68
8	-28	-53
9	119	-113
10	-28	63
11	-27	6
12	93	104
13	-25	8
14	-25	34
15	46	-72
16	-25	-51
17	92	89
18	-25	-32
19	-25	-17
20	-25	-16
21	37	-55
22	-26	9
H= 2, K= 3		
0	71	-67
1	-26	-43
2	100	95
3	281	-234
4	-27	36
5	219	202
6	187	169
7	-28	-42
8	73	72
9	-28	0
10	-27	28
11	170	163
12	-25	30
13	70	-72
14	-25	51
15	-25	-27
16	71	82
17	62	48
18	-25	-10
19	-25	-31
20	-25	-10
21	-26	-40
H= 3, K= 3		
0	106	-108
1	345	-321
2	-27	54
3	433	376
4	161	153
5	104	116
6	-28	-35
7	224	-208
8	-27	-49
9	60	72
10	-25	37
11	-25	-31
12	43	47
13	-25	47
14	-25	-13
15	67	79
16	-25	58
17	-25	-32
18	-25	4
19	-26	8
20	51	59
H= 4, K= 3		
0	111	-107
1	217	197
2	221	-209
3	273	-257
4	274	-230
5	127	140
6	121	127
7	96	97
8	75	74
9	74	-75
10	68	-87
11	-25	3
12	-25	7
13	60	65
14	-25	-34
15	64	-59
16	-25	-28
17	-25	-15
18	-26	1
19	63	51
H= 5, K= 3		
0	-28	-16
1	-28	59
2	105	120
3	232	-227
4	98	-105
5	66	75
6	315	-296
7	-25	49
8	56	-59
9	212	-213
10	-25	-9
11	151	134
12	-25	42
13	-25	-29
14	-25	-2
15	-25	-21
16	-26	2
17	-26	19
H= 6, K= 3		
0	-28	1
1	74	-75
2	-27	-46
3	104	113
4	156	147
5	264	-237
6	-25	27
7	-25	16
8	-25	-8
9	81	73
10	-25	-45
11	40	-43
12	-25	-51
13	-25	0
14	-25	5
15	-26	30
16	-26	14
H= 7, K= 3		
0	85	86
1	96	92
2	40	56
3	78	93
4	-25	14
5	82	-84
6	-25	24
7	45	59
8	-25	30
9	-25	-29
10	-25	18
11	-25	-57
12	-25	0
13	-26	9
14	-26	-40
H= 8, K= 3		
0	-23	6
1	-25	22
2	-25	-38
3	-25	-27
4	-25	19
5	-25	-5
6	-25	4
7	-25	40
8	-25	26
9	-25	3
10	-25	-5
11	-26	20
12	-26	25
H= 9, K= 3		
0	-25	43
1	81	-79
2	-25	-36
3	-25	34
4	-25	15
5	64	70
6	-25	3
7	39	-57
8	-26	-17
9	-26	35
H= 10, K= 3		
0	-25	-11
1	-25	34
2	-25	-1
3	-25	-15
4	-25	-35
5	-26	-38
6	-26	-6
7	-26	29
H= 11, K= 3		
0	-25	20
1	-25	12
2	-26	21
3	-26	2
4	-26	41
H= 12, K= 3		
0	-26	-4
H= -12, K= 4		
7	-26	-17
8	52	45
9	52	-53
10	-26	-37
11	61	49
12	-26	39
13	-26	7
14	-26	-18
15	-26	-24
H= -11, K= 4		
1	-26	-34
2	-26	-19
3	-26	-37
4	-26	-4
5	-26	17
6	-26	16
7	-25	-2
8	-25	-2
9	-25	9
10	-25	0
11	-25	-19
12	-25	19
13	-25	-24
14	-26	5
15	-26	46
16	-26	-13
17	-26	35
18	-26	-2
19	-26	-30
H= -10, K= 4		
1	-25	17
2	-25	17
3	-25	10
4	-25	-10
5	-25	-39
6	-25	-40
7	-25	26
8	-25	-8
9	-25	5
10	-25	0
11	-25	-17
12	-25	-13
13	74	67
14	-25	10
15	-25	-24
16	-25	21
17	81	-70
18	-26	-14
19	37	48

Table 3 (*cont.*)

L	FO	FC
20	-26	-4
21	-26	-6
H= -9, K=		4
1	-25	30
2	-25	46
3	-25	-4
4	-25	-13
5	-25	1
6	-25	8
7	-25	30
8	53	87
9	52	-54
10	77	-79
11	-25	-51
12	-25	-53
13	-25	2
14	-25	45
15	-25	16
16	52	-53
17	-25	26
18	-25	28
19	-25	-29
20	-26	-11
21	-26	-30
22	-26	-14
H= -8, K=		4
1	-25	-34
2	-25	8
3	-25	-12
4	-25	1
5	-25	42
6	-25	14
7	72	-81
8	-25	12
9	48	63
10	-25	49
11	62	75
12	-25	-7
13	105	-107
14	-25	-51
15	-25	-27
16	-25	4
17	-25	0
18	-25	-24
19	-25	-24
20	-25	-3
21	-26	32
22	-26	1
23	-26	8
H= -7, K=		4
1	-25	-1
2	38	-65
3	55	71
4	82	90
5	64	-81
6	-25	-28
7	-25	-48
8	-25	63
9	-25	-5
10	-25	21
11	-25	8
12	-25	24
13	-25	32
14	-25	13
15	-25	38
16	-25	47
17	-25	-4
18	64	-66
19	-25	28
20	-25	-18
21	-25	12
22	-26	43
23	-26	-29
H= -6, K=		4
1	69	86
2	-25	40
3	-25	-46
4	-25	32
5	-25	-8
6	125	-121
7	125	135
8	-25	57
9	76	-76
10	-25	30
11	-25	-12
12	-25	1
13	119	119
14	101	105
15	78	-86
16	-25	-41
17	-25	30
18	70	61
19	-25	49
20	-25	-7
21	47	-56
22	-26	-39
23	-26	1
H= -5, K=		4
1	46	-62
2	70	-81
3	-25	16
4	-25	33
5	128	119
6	-25	32
7	-25	-48
8	87	-103
9	-25	44
10	-25	28
11	-25	0
12	-25	-24
13	133	-138
14	-25	1
15	-25	-5
16	-25	55
17	-25	12
18	-25	24
19	-25	-21
20	-25	-16
21	-25	14
22	-26	29
23	-26	9
H= -4, K=		4
1	38	-62
2	92	-111
3	-27	6
4	-27	-10
5	100	-116
6	-26	8
7	-26	-9
8	124	-133
9	91	95
10	106	114
11	77	-86
12	82	-85
13	40	52
14	73	-66
15	97	97
16	-25	9
17	157	-146
18	-25	51
19	57	-63
20	-25	-13
21	47	52
22	-26	24
23	-26	-27
H= -3, K=		4
1	146	154
2	103	121
3	-28	-54
4	83	-93
5	-27	23
6	-27	37
7	63	67
8	-26	-36
9	41	-59
10	-25	38
11	-25	-37
12	-25	-49
13	-25	-17
14	-25	30
15	-25	15
16	90	-77
17	158	135
18	-25	-21
19	-25	29
20	60	53
21	71	-67
22	61	-48
23	-26	37
H= -2, K=		4
1	-28	-50
2	-28	25
3	-28	-34
4	79	-79
5	79	73
6	88	79
7	-27	-7
8	40	-57
9	-26	-25
10	-25	-35
11	244	205
12	161	136
13	-25	18
14	70	-59
15	-25	-47
16	61	55
17	-25	27
18	-25	-38
19	-25	0
20	-25	-3
21	-26	20
22	53	-51
H= -1, K=		4
1	233	-180
2	46	-60
3	198	164
4	104	95
5	-28	9
6	123	101
7	86	-76
8	85	-77
9	72	61
10	-25	-47
11	114	-95
12	-25	43
13	-25	-7
14	-25	-41
15	-25	37
16	64	63
17	-25	-44
18	-25	0
19	-25	6
20	-25	-6
21	-26	2
22	-26	11
H= 0, K=		4
0	111	-110
1	131	130
2	-28	53
3	-28	4
4	-28	-62
5	166	-147
6	-27	-41
7	-27	-56
8	118	118
9	54	-60
10	97	-99
11	-25	-35
12	-25	-18
13	-25	31
14	-25	16
15	-25	-36
16	-25	-35
17	44	-59
18	-25	2
19	71	62
20	70	74
21	-26	8
H= 1, K=		4
0	-28	41
1	53	-75
2	-28	-46
3	228	-207
4	-28	-55
5	193	190
6	-26	20
7	54	68
8	-25	20
9	99	-120
10	38	-56
11	-25	58
12	-25	45
13	36	-57
14	-25	-30
15	-25	-49
16	-25	-51
17	-25	38
18	-25	3
19	-26	-57
20	-26	-23
H= 2, K=		4
0	136	132
1	109	122
2	123	118
3	66	71
4	74	-91
5	126	-133
6	-25	16
7	-25	-50
8	-25	-29
9	155	145
10	-25	39
11	-25	1
12	-25	-8
13	-25	-1
14	41	10
15	43	71
16	-25	-9
17	-25	15
18	-26	-1
19	-26	-46
H= 3, K=		4
0	163	-164
1	47	66
2	112	122
3	138	124
4	107	120
5	-25	2
6	-25	-47
7	150	146
8	107	103
9	-25	-2
10	-25	-32
11	53	-68
12	-25	-25
13	-25	21
14	40	48
15	-25	-33
16	-26	-2
17	-26	0
H= 4, K=		4
0	48	59
1	-26	-59
2	-25	-19
3	63	-75
4	-25	-2
5	-25	7
6	-25	-19
7	-25	-33
8	81	84
9	-25	0
10	-25	-10
11	-25	33
12	-25	-4
13	-25	4
14	-25	-8
15	-26	-22
16	-26	38
H= 5, K=		4
0	-25	-34
1	109	-117
2	102	-109
3	-25	-30
4	-25	18
5	43	58
6	-25	1
7	67	-85
8	-25	4
9	-25	9
10	-25	10
11	38	34
12	-25	32
13	-26	-20
14	-26	-14
H= 6, K=		4
0	-25	-5
1	-25	29
2	-25	-56
3	49	67
4	-25	53
5	-25	-18
6	173	-141
7	-25	24
8	-25	28
9	40	-58
10	-25	29
11	-26	-27
12	49	-45
13	-26	45
H= 7, K=		4
0	-25	24
1	38	52
2	-25	5
3	111	-92
4	-25	15
5	-25	-3
6	-25	21
7	103	94
8	44	-82
9	-26	20
10	-26	28
11	-26	-24
H= 8, K=		4
0	-25	8
1	-25	-11
2	-25	22
3	55	69
4	-25	-11
5	-25	-24
6	-25	58
7	93	-101
8	57	-47
H= 9, K=		4
0	-25	-36
1	-25	-31
2	-25	-25
3	-25	-4
4	-26	10
5	-26	3
6	-26	5
H= 10, K=		4
0	-26	22
1	-26	46
2	-26	9
3	-26	-25
H= -10, K=		5
7	-26	9
8	-26	-7
9	83	-69
10	-26	18
11	-26	19
H= -9, K=		5
1	-26	-6
2	-26	-6
3	-26	-11
4	-26	-11
5	-26	9
6	-26	36
7	-26	2
8	-26	-2
9	-26	-19
10	-26	-38
11	-26	-18
12	-26	23
13	-26	-16
14	-26	-20
15	-26	-27
16	-26	0
H= -8, K=		5
1	-26	-35
2	-25	-17
3	-25	6
4	-25	34
5	-25	4
6	-25	-15
7	-25	-7
8	-25	-23
9	-25	40
10	-25	29
11	-25	-30
12	56	-56
13	-25	7
14	-26	-7
15	-26	18
16	-26	8
17	59	-51
H= -7, K=		5
1	47	59
2	-25	-4
3	-25	-45
4	-25	-13
5	-25	16
6	-25	-14
7	-25	3
8	-25	32
9	-25	-11
10	-25	22
11	-25	41
12	-25	-20
13	-25	3
14	39	36
15	-25	-12
16	-26	-18
17	-26	13
18	-26	-36
H= -6, K=		5
1	-25	27
2	-25	28
3	-25	0
4	-25	-21
5	-25	0
6	53	61
7	-25	12
8	-25	-17
9	-25	-44
10	-25	-38
11	-25	50
12	-25	32
13	-25	-5
14	-25	-2
15	-25	2
16	-25	9
17	-26	17
18	-26	30
19	-26	4
H= -5, K=		5
1	39	-53
2	-25	-20
3	-25	39
4	-25	7
5	-25	-41
6	-25	35
7	-25	5
8	-25	-35
9	-25	-42
10	92	90
11	-25	12
12	-25	-4
13	-25	-1
14	-25	-44
15	-25	-8
16	-25	14
17	-26	-15
18	-26	-28
19	-26	25
H= -4, K=		5
1	-25	-13
2	-25	45
3	-25	11
4	-25	29
5	-25	-63
6	-25	-52
7	78	74
8	-25	-9
9	-25	-26
10	-25	-41
11	107	-98
12	-25	3
13	-25	41
14	-25	26
15	-25	-6
16	-25	10
17	-25	-12
18	-26	-38
19	-26	7
H= -3, K=		5
1	-25	15
2	-25	16
3	-25	-34
4	111	-99
5	-25	8
6	-25	33
7	-25	16
8	-25	41
9	42	59
10	-25	-53
11	-25	-11
12	42	41
13	-25	5
14	-25	-8
15	-25	-40
16	-25	-9
17	-26	-11
18	82	68
19	-26	-14
H= -2, K=		5
1	-25	12
2	-25	-26
3	-25	26
4	-25	44
5	-25	39
6	-25	28
7	61	-64
8	-25	-26
9	96	75
10	45	42
11	-25	-8
12	-25	9
13	-25	-9
14	42	-47
15	73	74
16	-25	8
17	-26	4
18	-26	-18
H= -1, K=		5
1	153	132
2	-25	-44
3	-25	4
4	-25	3
5	41	-50
6	104	-84
7	-25	30
8	79	59
9	-25	16
10	-25	1
11	-25	-25
12	-25	-17
13	-25	19
14	40	52
15	-25	-8
16	-26	21
17	40	46
18	61	-49
H= 0, K=		5
1	139	-129
2	149	125
3	42	63
4	-25	-31
5	-25	23
6	-25	7
7	-25	-27
8	-25	-2
9	-25	-14
10	77	-74
11	-25	7
12	-25	-2
13	-25	-15
14	-25	-10
15	-25	-7
16	-26	-24
17	-26	-13
H= 1, K=		5
0	-25	-24
1	130	-113
2	134	-124
3	-25	-42
4	-25	6
5	-25	-5
6	-25	19
7	62	-68
8	-25	-8
9	-25	30
10	-25	-6
11	-25	47
12	-25	18
13	-25	-43
14	-25	-7
15	-26	25
16	-26	7
H= 2, K=		5
0	-25	15
1	-25	28
2	-25	-22
3	-25	32
4	90	82
5	-25	36
6	80	-74
7	-25	-39
8	-25	10
9	-25	-43
10	39	63
11	-25	3
12	-25	-46
13	-26	9
14	-26	12
15	-26	-15
H= 3, K=		5
0	-25	4
1	91	95
2	73	75
3	49	-57
4	-25	-26
5	-25	15
6	-25	13
7	-25	48
8	-25	-11
9	-25	-17
10	-25	-39
11	-25	-21
12	-26	14
13	-26	14
H= 4, K=		5
0	50	61
1	-25	-10
2	42	-54
3	-25	-9
4	-25	15
5	-25	53
6	-25	42
7	-25	-22
8	-25	-8
9	-25	21
10	-26	9
11	-26	14
12	-26	-4
H= 5, K=		5
0	-25	19
1	-25	14
2	-25	-8
3	-25	3
4	-25	0
5	-25	-38
6	-25	-26
7	-25	5
8	-26	-24
9	-26	16
10	37	41
H= 6, K=		5
0	49	-63
1	-25	-39
2	-25	48
3	-25	-18
4	-25	-9
5	-25	15
6	-26	28
7	-26	28
8	-26	27
H= 7, K=		5
0	-25	41
1	-25	34
2	-25	-26
3	-26	-15
4	-26	-25
5	-26	-14
6	-26	15
H= 8, K=		5
0	-26	-13
1	-26	-13
2	-26	0
3	-26	34
H= -6, K=		6
2	-26	-15
3	-26	-13
4	-26	27
5	-26	-5
6	-26	0
7	-26	11
8	-26	6
9	-26	26
H= -5, K=		6
1	-26	29
2	-26	-22
3	-26	25
4	-26	29
5	-26	-6
6	50	-47
7	-26	-22
8	-26	-4
9	-26	7
10	-26	29
11	-26	3
H= -4, K=		6
1	-26	-32
2	-26	27
3	-25	-8
4	-25	-34
5	-26	9
6	-26	31
7	-26	-14
8	-26	-11
9	-26	-6
10	-26	-19
11	-26	-3
12	-26	-4
H= -3, K=		6
1	-25	17
2	-25	0
3	-25	3
4	-25	8
5	-25	6
6	-25	24
7	-25	-5
8	-26	-31
9	-26	-3
10	-26	25
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H= -2, K=		6
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2	-25	-22
3	-25	-25
4	42	40
5	-25	16
6	-25	-7
7	-25	-6
8	-26	-3
9	-26	34
10	-26	15
11	-26	6
12	-26	9
H= -1, K=		6
1	72	63
2	-25	27
3	-25	-11
4	-25	-10
5	-25	12
6	-25	-17
7	-25	-14
8	-26	29
9	-26	-5
10	46	-45
11	-26	14
12	-26	5
H= 0, K=		6
0	-25	35
1	-25	41
2	92	-74
3	-25	-14
4	-25	-2
5	-25	2
6	44	47
7	-25	20
8	-26	-15
9	-26	-27
10	-26	-6
11	-26	9
H= 1, K=		6
0	-25	25
1	-25	-34
2	-25	-17
3	-25	43
4	-25	-31
5	-25	-9
6	-26	-10
7	-26	4
8	-26	5
9	-26	17
10	-26	24
H= 2, K=		6
0	-25	-28
1	-25	-31
2	95	81
3	38	-45
4	-25	-22
5	-26	4
6	-26	-21
7	-26	-9
8	-26	14
H= 3, K=		6
0	-25	-7
1	-25	31
2	-25	3
3	-26	14
4	-26	-1
5	-26	0
6	-26	36
7	-26	1
H= 4, K=		6
0	-26	0
1	-26	-6
2	-26	-22
3	-26	-10
4	-26	7
5	-26	-11
H= 5, K=		6
0	-26	-23
1	-26	11
2	-26	

Table 4. *Coordination about the K^+ ion*

	Position	Distance
O(1)	*A*(000)	2·904 (8) Å
O(1)	*A*(010)	2·943 (8)
O(2)	*A*(000)	3·097 (6)
O(2)	*A*(010)	2·938 (6)
O(3)	*B*(100)	2·858 (7)
O(3)	*B*(010)	3·112 (7)
O(2)	*B*(100)	2·910 (6)
O(5)	*C*(000)	2·976 (6)
N(4)	*A*(000)	3·108 (6)

* The positions are given followed by the translations in x, y, z respectively. A is x, y, z; B is $-x, \frac{1}{2}+y, \frac{1}{2}-z$; C is $x, \frac{1}{2}-y, \frac{1}{2}+z$ where x, y, z refer to the coordinates given in Table 2.

The bond distances and angles in the anion are shown in Figs. 2 and 3. The C(1)–O(2) bond distance of 1·234(8) Å is close to the value for C=O found in ketones, aldehydes and carboxylic acids tabulated by Sutton (1965) which indicates that a strong interaction with the ring occurs on removal of the proton from O(2). A similar effect was found in potassium picrate by Maartmann-Moe (1969) where the corresponding C–O distance of 1·243 (7) Å is not significantly different from that observed in the present study. The question of whether a similar interaction is present in all phenol salts or only in polynitrophenol salts is unanswerable at present but further studies in this area are in progress.

The presence of C=O on the ring greatly perturbs the C–C bonds in the ring. The distortions are sufficiently large that the term 'benzene ring' seems inappropriate. As expected, the furazan ring introduces an asymmetry in the ring in comparison with the dimensions found in potassium picrate. The C–C bonds in the ring in K^+ HDNBF are longer on the average than those observed in potassium picrate. This observations must reflect the greater electron withdrawing power of the furazan ring relative to a nitro group. A similar observation was made by Messmer & Palenik (1971). In fact, the dimensions of the furazan ring in the two studies are almost identical; the largest difference is 0·010 Å, suggesting that the electronic requirements of the furazan ring are satisfied at the expense of the rest of the molecule.

The two C–N (nitro) distances of 1·422 (9) and 1·436 (10) Å are intermediate compared to the C–N (nitro) distances (1·389 to 1·497 Å) found in other aromatic nitro compounds. A comparison of the values in other aromatic compounds suggests that the C–N bond depends on the strength of the interaction of the NO_2 group and the ring. The longer C–N bonds were found in *m*-dinitrobenzene (1·493 Å) by Trotter & Williston (1966) and in *m*-nitroperchlorylbenzene (1·497 Å) by Palenik, Donohue & Trueblood (1969), where the interaction is expected to be weak. Conversely, the shorter C–N distances of 1·389 and 1·436 Å in a Meisenheimer complex (Messmer & Palenik, 1971), 1·436 and 1·457 Å in potassium picrate (Maartmann-Moe, 1969), 1·42 and 1·43 Å in 1,3-diamino-2,4,6-trinitrobenzene (form I) (Holden, 1967), and 1·460 Å in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), were all found in compounds where a strong interaction with the ring was anticipated. The two nitro groups are very close to being coplanar with the ring [3° 48′ for N(1)–O(3)–O(4) and 0° for N(2)–O(5)–(6)] in spite of the presence of *ortho* substituent in both cases. The O(2)···O(3) distance of 2·658(8) Å is shorter than the van der Waals contact, nevertheless the NO_2 group lies essentially in the plane of the ring.

The C–C–C angles in the ring also illustrate an interesting feature of the molecule. In all the other aromatic nitro compounds reported to date, the C–C(nitro)–C angle is always greater than 120°. Bailey & Prout (1965) and Carter, McPhail & Sim (1966) have suggested that an increased *s*-character in the C–C bonds causes the angle to open. The C(1)–C(2)–C(3) angle of 124·5(6)° found in K$^+$HDNBF is consistent with these previous observations. However, the C(3)–C(4)–C(5) angle of 118·4(6)° is smaller, although perhaps not significantly so, than 120·0°. This angle is also very close to the value of 118·5 (4)° observed for the corresponding angle in the other benzfurazan structure by Messmer & Palenik (1971). Apparently, the five-membered furazan ring fused to the six-membered ring may constrain the angle so that the generalizations regarding the value of the C–C(nitro)–C angles may not be valid.

The 'benzene ring' and furazan ring are both planar (Table 5) within the accuracy of the present analysis. The two rings are folded slightly so that the angle between the normals is 1°, similar to the value of 1·2° reported by Messmer & Palenik (1971) for a benzfurazan system. The two nitrogens of the nitro groups and the phenol oxygen are bent slightly out of plane of the 'benzene ring', presumably to minimize steric interactions with the corresponding *ortho* groups.

Table 5. *Least-squares planes*

Deviations (Å × 10^3) in boldface type indicate atoms which were used to define the plane.

	(I)	(II)	(III)	(IV)
C(1)	**−015**			
C(2)	**016**		069	
C(3)	**−003**			
C(4)	**−010**			−012
C(5)	**009**	**−003**		
C(6)	**003**	**002**		
N(1)	085		**000**	
N(2)	−032	**000**		**000**
N(3)	−003	**002**		
N(4)	−022			
O(2)				
O(3)			**000**	
O(4)			**000**	
O(5)				**000**
O(6)				**000**
O(7)	−059	**−002**		

Parameters of the plane.*

	(I)	(II)	(III)	(IV)
$A \times 10^4$	4876	4890	5528	5039
$B \times 10^4$	−6749	−6626	−6068	−6773
$C \times 10^4$	5539	5673	5711	5361
D(Å)	4·144	4·219	4·465	4·242

* Equation of the plane in the form deviation (Å) $= AX + BY + CZ + D$ with X, Y, Z the coordinates of the atom in Å relative to a, b, $c \sin \beta$.

There are three hydrogen atoms in the asymmetric unit (two from the water molecule and one on C(3) of the ring) and all apparently have contacts which suggest hydrogen bonding. The dimensions for the possible hydrogen bonds are tabulated in Table 6 and are shown as dotted lines in Fig. 1. The water molecule forms two hydrogen bonds to two different molecules. The hydrogen bond involving H(1) appears to be a weak but normal O–H···O hydrogen bond. The bond involving

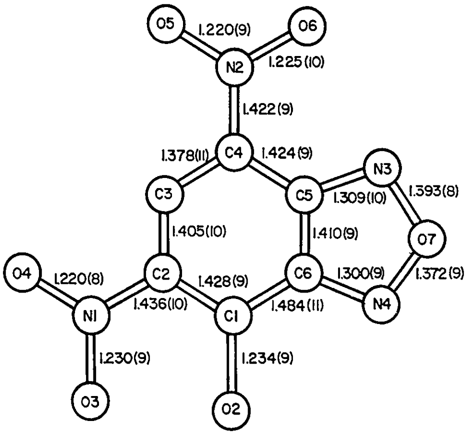

Fig. 2. The atomic numbering and bond distances in the $OC_6H(NO_2)_2N_2O$ anion. The estimated standard deviations are given in parentheses.

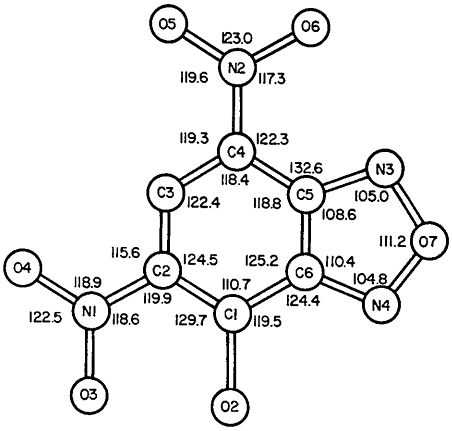

Fig. 3. The bond angles in the $OC_6H(NO_2)_2N_2O$ anion. The estimated standard deviations are 0·6° except for N(3)–O(7)–N(4) which is 0·5° and C(2)–C(1)–O(2) and C(4)–C(5)–N(3) which are 0·7°.

Table 6. *Intermolecular contacts involving the hydrogen atoms*

D–H···A	Position of A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(1)–H(1)···O(6)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0·93	2·08	2·986	165
O(1)–H(2)···N(3)	$2-x, y-\frac{1}{2}, \frac{1}{2}-z$	0·85	2·28	3·026	146
O(1)–H(2)···O(6)	$2-x, y-\frac{1}{2}, \frac{1}{2}-z$	0·85	2·54	3·069	122
C(3)–H(3)···O(4)	$1-x, -1-y, -z$	0·99	2·42	3·393	170

H(2), O(1)–H(2)···N(3) has a relatively small O–H··· *N* angle but otherwise appears normal. The alternative for H(2), O(1)–H(2)···O(6) has a poor O–H···O angle and also the H···O distance is very close to the value for a van der Waals contact. The third hydrogen H(3) bonded to C(3) of the ring has a relatively short C–H···O contact, very suggestive of a hydrogen bond. The angles involving H(3) are all very reasonable for a hydrogen bond and the H(3)···O(4) distance of 2·42 Å is less than that expected for a van der Waals contact. A similar C–H···O hydrogen contact was found in potassium picrate.* Although the existence of C–H···O hydrogen bonds has been questioned by Donohue (1968), the present study (together with the potassium picrate example) suggests that C–H···O hydrogen bonds may indeed exist in special cases.

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* H. Cady first pointed out to one of us (GJP) that a possible C–H···O hydrogen bond existed in our unpublished refinement of potassium picrate.

References

Bailey, A. S. & Prout, C. K. (1965). *J. Chem. Soc.* p. 4867.

Carter, O. L., McPhail, A. T. & Sim, G. A. (1966). *J. Chem. Soc.* (*A*), p. 822.

Destro, R., Gramaccioli, C. M. & Simonetta, M. (1968). *Acta Cryst.* **B24**, 1369.

Donohue, J. (1968) in *Structural Chemistry and Molecular Biology*, p. 443. Ed. A Rich & N. Davidson. San Francisco: W. H. Freeman and Company.

Holden, J. R. (1967). *Acta Cryst.* **22**, 545.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202, Birmingham: Kynoch Press.

Maartmann-Moe, K. (1969). *Acta Cryst.* **B25**, 1452.

Messmer, G. G. & Palenik, G. J. (1971). *Acta Cryst.* **B27**, 314.

Palenik, G. J., Donohue, J. & Trueblood, K. N. (1969). *Acta Cryst.* **B24**, 1139.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement. Special Publication No. 18. London: The Chemical Society.

Trotter, J. & Williston, C. S. (1966). *Acta Cryst.* **21**, 285.

Trueblood, K. N., Goldish, E. & Donohue, J. (1961). *Acta Cryst.* **14**, 1009.

Acta Cryst. (1971). B**27**, 1393

Die Struktur des Ammoniumparawolframates $(NH_4)_{10}[H_2W_{12}O_{42}]\,.\,10H_2O$

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(*Eingegangen am* 17. *Juli* 1970)

Ammonium paratungstate, $(NH_4)_{10}[H_2W_{12}O_{42}].10H_2O$ crystallizes in space group *Pbca*: $a=19{\cdot}07$, $b=24{\cdot}42$, $c=10{\cdot}915$ Å, $Z=4$, $D_m=4{\cdot}13$, $D_x=4{\cdot}23$ g.cm^{-3}. The W atoms were located by a Patterson map, and the lighter atoms by a ΔF-map. Using 3002 visually estimated reflexions, including 609 unobserved ones, the structure was refined to $R=8{\cdot}5\%$ ($8{\cdot}1\%$ for observed reflexions only; isotropic temperature factors). The positional uncertainties are: $\sigma(W)=0{\cdot}002$, $\sigma(O)=0{\cdot}03$, $\sigma(H_2O, NH_4^+)=0{\cdot}05$ Å. The paratungstate ion $[H_2W_{12}O_{42}]^{10-}$ (not $[H_{10}W_{12}O_{46}]^{10-}$ as earlier formulated) consists of 4 corner-sharing groups, each containing 3 edge-sharing WO_6 octahedra. The oxygen atoms of the anion are hexagonal close packed (average O–O 2·78 Å, 2·49–2·97 Å). Six octahedra have one unshared oxygen and the other six have two unshared oxygen atoms. The W atoms are shifted into the direction of these unshared oxygen atoms away from the centres of the octahedra by 0·33–0·37 Å. W–W (edge-sharing) = 3·34, W–W (corner-sharing) = $3{\cdot}75_5$ Å, W–O = 1·70–2·32 Å, average 1·96 Å. By estimation of the W–O bond strengths, the non-acid protons were located in the inside of the isopolyanion in accordance with the results of some recent H nuclear magnetic resonance broad-line spectra. The anion has pseudo-symmetry 2/*m*, which is also obeyed in part by the NH_4^- environment. *Via* ammonium ions each complex $[H_2W_{12}O_{42}]^{10-}$ is connected to 10 other complexes. All N–N distances are greater than 3·6 Å. A probable network of hydrogen bonds is suggested. The shortest possible H-bonds are: OH ··· O = 2·64 Å and NH ··· O = 2·69 Å.

Einleitung

Die erste röntgenographische Strukturuntersuchung eines Parawolframates erfolgte 1952 (Lindqvist) am $5Na_2O.12WO_3.28H_2O$ mit Hilfe einer Pattersonsynthese. Aus dieser konnten die Lagen der Wolframatome des Isopolyanions eindeutig ermittelt werden. Die Lage der Sauerstoffatome wurde aber nur aus der