Acta Cryst. (1965). **19**, 260

A Centered Hydrogen Bond in Potassium Hydrogen Chloromaleate: A Neutron Diffraction Structure Determination*

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(*Received* 24 *November* 1964)

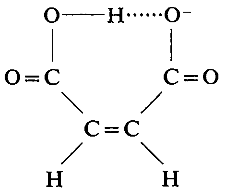
The crystal structure of potassium hydrogen chloromaleate has been directly determined from three-dimensional neutron diffraction data by means of the Patterson synthesis. The nearly plane anion has a ring structure with a 2·40 Å $O \cdots H \cdots O$ bridge in which the hydrogen atom is effectively centered.

Introduction

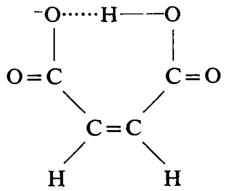
Hydrogen bonds between oxygen atoms are known to occur with $O \cdots O$ distances ranging upward from about 2·4 Å. In the great majority of cases the hydrogen atom is situated unsymmetrically in the bridge at about 1 Å from one of the two oxygen atoms. The actual O–H distances and the fundamental O–H stretching frequencies show a pronounced correlation with the length of the hydrogen bond, such that the longest O–H distances and the lowest frequencies tend to occur in the shortest $O \cdots O$ bridges. The available data have been summarized by Bacon (1963), Pimentel & McClellan (1960), Rundle & Parasol (1952), and Lord & Merrifield (1953).

The trend of the variation in O–H distance with $O \cdots O$ distance suggests that the hydrogen atom may take a symmetric location in some of the shortest of the hydrogen bonds, those with $O \cdots O$ distances less than about 2·5 Å. A similar indication is derived from the behavior of the O–H stretching frequency, which becomes rapidly lower as the $O \cdots O$ distance approaches the neighborhood of 2·5 Å.

The most firmly established example of a centered hydrogen bond is the bifluoride ion $F-H-F^-$, for which definitive evidence from thermodynamics (Westrum & Pitzer, 1949), spectroscopy (Mathieu & Couture-Mathieu, 1950), nuclear magnetic resonance (Waugh, Humphrey & Yost, 1953), and neutron diffraction (Peterson & Levy, 1952; McGaw & Ibers, 1963; Ibers, 1964) is available. Among $O \cdots H \cdots O$ bonds, one, that in chromous acid, appears to be firmly established as centered (Hamilton & Ibers, 1963), and centering has been suggested in several other cases, among them potassium hydrogen maleate (Cardwell, Dunitz & Orgel, 1953). This crystal contains one of the shortest $O \cdots H \cdots O$ bonds known. Its structure has been studied by both neutron (Peterson & Levy, 1958) and X-ray (Darlow & Cochran, 1961) diffraction. Both studies fixed the apparent position of the hydrogen atom at the center of a 2·44 Å intraionic $O \cdots H \cdots O$ bridge. The apparent centering of the hydrogen atom as given by the diffraction studies can be given two interpretations; namely, the hydrogen atom is truly localized at the center of the bond, or it is randomly distributed in one or the other of two equivalent sites displaced perhaps as much as 0·1 Å from the center, as indicated by the structural formulas:



and



The equivalence of the two carboxyl groups, as required by the presence of a mirror plane in the crystal, makes the two alternatives indistinguishable. If this equivalence is removed, as by substitution for one of the ethylenic hydrogen atoms, the two non-centered configurations become non-equivalent; and there is a chance of directly establishing the existence of the non-centered situation, should it occur. Accordingly, the crystal structure of the potassium salt of the chlorine-substituted acid has been studied. To our knowledge, this is the first study of a very short $O \cdots H \cdots O$ bond in which the oxygen atoms are crystallographically and chemically non-equivalent.

Experimental

The space group and cell parameters of potassium hydrogen chloromaleate, already reported by Ellison, Levy & Peterson (1961), are as follows: *Pbcn*, $a = 15{\cdot}815$ (standard deviation 0·015), $b = 10{\cdot}928$ (0·006), $c = 7{\cdot}707$ (0·005) Å, eight molecules in the unit cell. A crystal specimen with volume about 5 mm^3, grown from aqueous solution, was used for this study.

A three-dimensional set of 1959 symmetrically non-equivalent intensitites, complete to $\sin\theta/\lambda = 0{\cdot}71$ Å^{-1}, was measured with the Oak Ridge automatic neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) using a neutron wave length of 1·078 Å. Net counts were obtained in a manner already described (Brown

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* Research sponsored by the U.S. Atomic Energy Comission under contract with the Union Carbide Corporation.

& Levy, 1964). Absorption corrections were computed with a FORTRAN program written by Wehe, Busing & Levy (1962). The range of transmission factors was 0·844 to 0·899. Squared structure factor amplitudes were derived in the usual manner after averaging replicate and crystallographically equivalent intensities. Standard errors for use in least-squares weighting were estimated according to the expression (Brown & Levy, 1964)

$$\sigma^2(F^2)=K^2[G+(t_P/t_B)^2B+(0\cdot03N)^2]$$

in which G is the gross peak count (including background), B the background count, N the net count, (t_P/t_B) the ratio of counting times of peak to background, and K the appropriate scaling constant. The third term within the brackets is an empirical one justified by previous experience with the instrument employed (Brown & Levy, 1964).

Solution of the structure

In preliminary trials it became apparent that the high symmetry of the space group, which results in a Patterson function containing the superposed interactions of eight molecules, makes direct interpretation excessively difficult, particularly in the absence of a pronounced 'heavy' atom (The largest neutron scattering factor, that for chlorine, is 1·7 times the mean. The total number of atoms in the unit cell is 96; of these, 72 are of approximately equal scattering power).

The procedure that proved successful was derived independently in this work. Although closely similar methods have been described by others (Hamilton, 1963; Mighell & Jacobson, 1963), a description in mathematical terms seems worthwhile here. The procedure consists of a systematic examination of the Patterson function through the use of the Buerger minimum function. This was accomplished by computation of the function

$$Q(\mathbf{r})=\mathrm{Min}_i[w_iP(\mathbf{r}-\mathbf{S}_i\mathbf{r})] \qquad (1)$$

for values of the position vector $\mathbf{r}$ ranging over the asymmetric unit of *Pbcn*. In the foregoing equation, $\mathbf{S}_i$ is a symmetry operator of the space group, w_i is a weighting factor equal to the reciprocal of the number of operations $\mathbf{S}_i$ which generate a given vector $\mathbf{r}-\mathbf{S}_i\mathbf{r}$, P is the Patterson function, and the symbol Min_i designates the minimum value of the quantity in brackets over the set of symmetry operations of the space group.

Of the several Patterson values compared in the minimum function of Q, one is $P(0, 0, 0)$, corresponding to the identity symmetry element; one is evaluated at a general point in Patterson space, corresponding to the inversion center (for centrosymmetric space groups); and the remainder are evaluated at points in the several Harker sections and lines. The latter components of $Q(\mathbf{r})$, considered separately, contain the same vector sets as the corresponding Buerger implication diagrams (Buerger, 1959), to which they are closely related. They are, however, expressed in terms of continuous, rather than discrete variables. It seems appropriate to name $Q(\mathbf{r})$ the continuous multiple implication function.

The quantity $Q(\mathbf{r})$ will tend to assume positive maxima at those positions $\mathbf{r}$ for which the corresponding Patterson–Harker values are all large and which are thus suitable candidates for atomic positions. These positions $\mathbf{r}$ will occur in the function with respect to each of the eight centers of symmetry which are possible origins of *Pbcn*; this additional symmetry (over that of the unit cell) is reflected in the fact that for this space group $Q(\mathbf{r})$ is periodic in each dimension with a period of one-half that of the crystal lattice. This 'false symmetry' arises from the same considerations as do the ambiguities in implication diagram theory (Buerger, 1959).

In addition, positive regions may appear because of accidental coincidence of interaction vectors. For a neutron Patterson function, accidental cancellation of Patterson interaction vectors may also occur, since scattering amplitudes of both signs may be present.

In applying this method, we used a gradient-sharpened* Patterson function (Jacobson, Wunderlich & Lipscomb, 1961) with coefficients $F_S^2=(\frac{1}{6}+\lambda^{-2}\sin^2\theta)F_{\text{obs}}^2$. In the corresponding function $Q(\mathbf{r})$ there appeared one well-resolved sizeable maximum, the third largest on the diagram, with height intermediate between those expected for Cl–Cl and C–C. The second largest peak although less well resolved, was successfully used in subsequent analysis. The largest peak was obviously perturbed by overlap.

The resolved peak was made the basis for a multiple superposition diagram, in which the Buerger minimum function and the symmetry of the unit cell were again used. This function can be expressed in a fashion similar to that used for $Q(\mathbf{r})$:

$$S(\mathbf{r})=\mathrm{Min}_i[P(\mathbf{r}-\mathbf{S}_i\mathbf{r}_o)] \qquad (2)$$

where $\mathbf{r}_o$ is the tentatively assigned atomic position found from $Q(\mathbf{r})$. In $S(\mathbf{r})$, the eightfold ambiguity of origin is, of course, no longer present.

Comparison of the first S map with the Q map, taking suitable account of symmetry, suggested two other atomic positions, one of which corresponded to the second largest peak, and the other to a shoulder on the fourth largest peak of $Q(\mathbf{r})$. Calculations of $S(\mathbf{r})$ based on these vectors confirmed their self-consistency as atomic positions, and detailed comparison of the three superposition diagrams disclosed common features suggesting the expected shape of the chloromaleate ion. At this stage, the minimum of all three functions

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* Because of a programming error, the Patterson function was at first sharpened only in the x direction. Nevertheless, the structure was successfully solved from this Patterson function and the subsequent Q and S maps. Fig. 1 is prepared from the correctly sharpened Patterson function. In retrospect, it appears that the structure could probably have been seen in the first S map, and certainly in the second, had the error not been made.

$S(\mathbf{r})$ was prepared; the resulting diagram displayed maxima assignable to all atoms except one potassium and the two hydrogen atoms. These peaks are absent because of the relatively small scattering amplitudes of K for neutrons, and because of the negative sign of interaction of H with the peaks chosen for superposition. This 24-fold minimum function contains no extra peaks large enough to be troublesome. A composite contour diagram is presented in Fig. 1.

Refinement of the structure

A preliminary Fourier synthesis of the scattering density with phases based on the atomic positions deduced from the Patterson function analysis revealed peaks corresponding to all atoms. The carbon and oxygen atoms are in general positions of the space group; the potassium atoms appear in special positions on diad axes parallel to **b** and are of two crystallographically distinct kinds. The two hydrogen atoms in the asymmetric unit were indicated to be in general positions by the only two sizeable regions of negative density. A second Fourier synthesis followed, with phases based on atomic parameters derived from the first.

Following the Fourier syntheses, a sequence of least-squares refinements was carried out in which were varied successively (1) the overall scale factor and individual isotropic atomic thermal parameters, (2) the foregoing plus atomic position coordinates, (3) the scale factor, anisotropic temperature coefficients, and atomic position coordinates, and (4) the scattering amplitudes of chlorine, hydrogen, oxygen, and potassium along with those parameters listed under (3). In refinement (4), the four strongest reflections, which

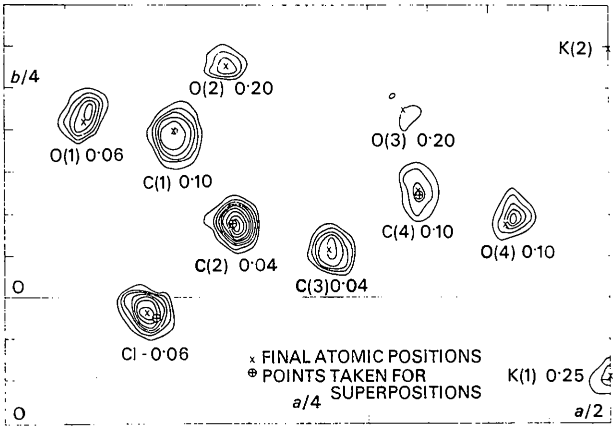

Fig. 1. Composite contour map of the multiple superposition diagram. The decimal fractions indicate the z coordinates of the levels from which the contoured portions were taken.

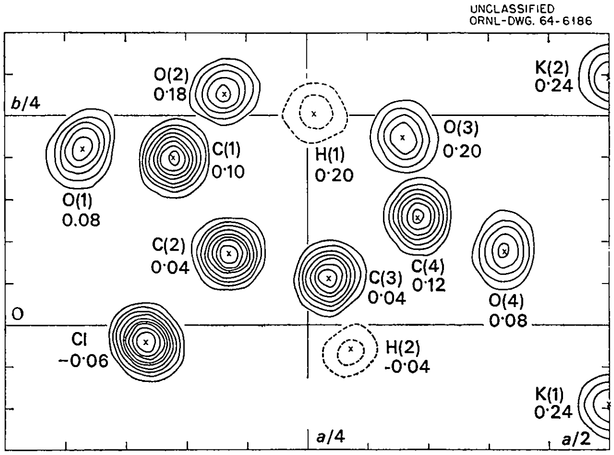

Fig. 2. Composite contour map of the final three-dimensional Fourier synthesis of the structure. The contour interval is $0{\cdot}48\,\mathrm{cm} \times 10^{-12}\,\text{Å}^{-3}$; zero contours are omitted, and negative contours are dotted. The decimal fractions indicate the z coordinates of the levels from which the contoured portions were taken. The crosses indicate final x and y coordinates.

Table 1. *Parameters of the structure of potassium hydrogen chloromaleate*

Least-squares standard errors are given in parentheses

	Fractional position parameter $\times 10^4$			Thermal parameter* $\times 10^5$					
Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	1161(1)	−197(1)	−534(2)	265(4)	642(10)	1407(21)	−74(5)	−7(8)	−268(13)
C(1)	1394(1)	1988(1)	1041(2)	200(4)	524(11)	871(21)	64(6)	−15(9)	−59(14)
C(2)	1850(1)	860(1)	381(2)	181(4)	459(10)	868(22)	21(6)	25(8)	−22(14)
C(3)	2677(1)	575(1)	387(2)	189(4)	530(12)	1315(26)	57(6)	29(9)	−3(16)
C(4)	3414(1)	1281(2)	1108(2)	167(4)	701(13)	1323(29)	26(6)	−20(10)	188(17)
O(1)	638(1)	2100(2)	727(3)	226(6)	902(19)	1412(40)	173(9)	−82(12)	−302(23)
O(2)	1817(1)	2767(2)	1918(3)	293(7)	571(16)	1832(43)	54(9)	−76(15)	−360(21)
O(3)	3290(1)	2234(2)	2039(4)	245(7)	975(24)	2139(55)	−41(11)	−131(16)	−392(28)
O(4)	4131(1)	880(2)	787(3)	173(6)	963(21)	1984(49)	81(9)	21(13)	297(27)
H(1)	2558(3)	2522(4)	2032(6)	384(14)	868(31)	1932(68)	−66(16)	−97(29)	−332(41)
H(2)	2863(2)	−289(3)	−203(6)	346(13)	785(33)	2755(107)	132(16)	131(31)	−368(47)
K(1)	5000	−946(4)	2500	258(13)	473(31)	1099(69)	0	−73(24)	0
K(2)	5000	2973(4)	2500	191(12)	749(39)	1162(73)	0	80(23)	0
				C	Cl	O	H	K	
Scattering amplitudes, cm × 10^{-15}				661	937(5)	586(3)	−367(3)	363(4)	

(Amplitudes of atoms of the same chemical element were constrained to be equal. That of carbon was not varied).

* Coefficients in the expression $B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl$.

were clearly subject to extinction error, were omitted. The value of $\Sigma w(F_o^2 - F_c^2)^2$ was minimized.

The final value of the standard deviation of fit

$$\sigma_1 = [\Sigma w(F_o^2 - F_c^2)^2/(N-P)]^{\frac{1}{2}}$$

(N is the number of observations and P the number of adjusted parameters) is 1·015 (1·19 before adjusting scattering factors). The conventional discrepancy indices $R_x = \Sigma||F_o|^x - |F_c|^x|/\Sigma|F_o|^x$ are summarized in the following table.

	A	*B*	*C*
$x=1$	0·122	0·123	0·079
$x=2$	0·095	0·092	0·081
Number of data:	1959	1955	1447

A – all data are included.
B – data which are affected by extinction are omitted.
C – data which are affected by extinction or have $F^2 < \sigma$ are omitted.

Although the values of the discrepancy factors are not especially low by modern standards, the close approach of the standard deviation of fit to unity indicates that the parameters have been refined as fully as the data warrant. This conclusion is confirmed by an $F_o - F_c$ Fourier synthesis, which shows no interpretable features, the extreme density values being +0·166 and –0·162 cm × 10^{-12} per Å^3. For comparison, a hydrogen peak has density –1·30 and a potassium peak +1·95.

The precision of the parameters is also quite satisfactory: the mean positional parameter standard errors range from 0·0013 Å for Cl to 0·0043 Å for H and K.

The final parameters and the least-squares standard errors are listed in Table 1. The observed and calculated values of F^2 are shown in Table 2. A composite Fourier synthesis of the structure is illustrated in Fig. 2.

Results

Structure of the ion

As expected, the hydrogen chloromaleate ion has a closed-ring structure, analogous to that of the unsubstituted hydrogen maleate ion. This structure is illustrated in Figs. 3 and 4 by means of stereoscopic drawings prepared on a computer-controlled plotter, which was programmed by our colleague C. K. Johnson (Johnson, 1965). Bond distances and angles are shown in Fig. 5.

The internal hydrogen bond distance O(2) · · · O(3) has the unusually small value 2·403 Å, slightly shorter

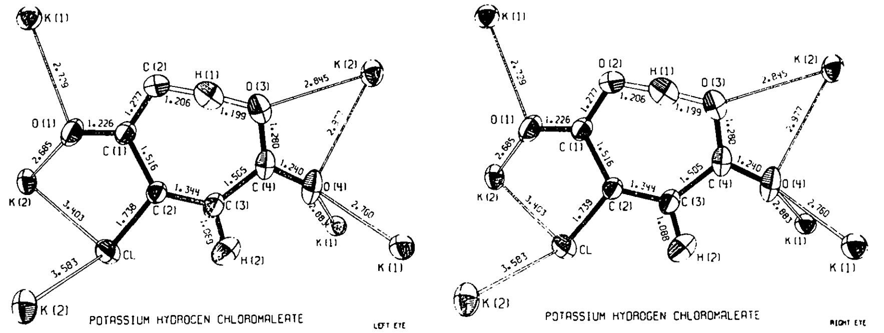

Fig. 3. A stereoscopic pair of drawings of the chloromaleate ion viewed in its own plane. The atoms are represented by ellipsoids of thermal displacement including 50% probability. Figs. 3 and 4 are best viewed by means of an inexpensive stereoscope. (The addresses of manufacturers of suitable stereoscopes may be obtained from the authors on request).

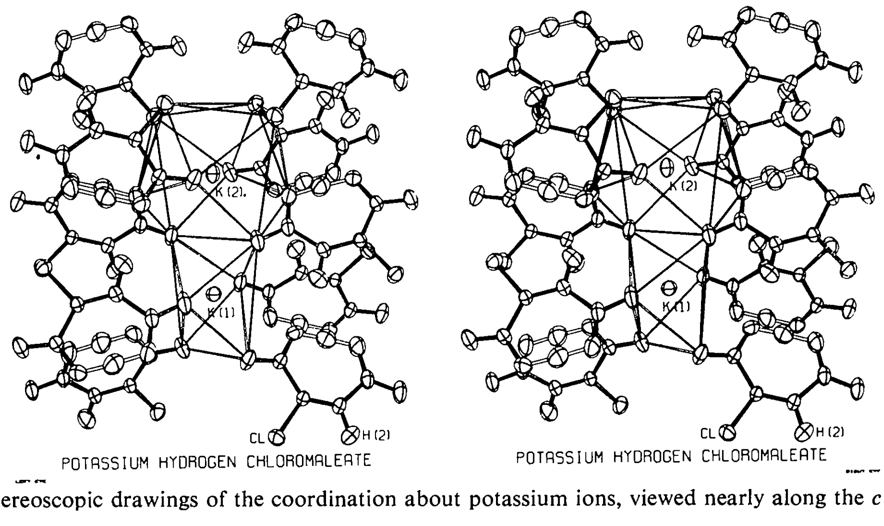

Fig. 4. Stereoscopic drawings of the coordination about potassium ions, viewed nearly along the *c* axis.

Table 2. *Calculated and observed squared structure factors for neutrons*

The columns headed H, CALC, OBS and SIG contain, respectively, the Miller index *h*, the calculated and observed values of F^2, and the standard error of F_o^2 in units of 10^{-26} cm^2 for reflections whose indices *k* and *l* are recorded in subheadings. The signs are those of the calculated structure factors. The symbol *E* denotes a reflection judged to be perturbed by extinction.

	H	CALC	OBS	SIG	
	••• H 0 0 •••				
	2	786	901	40	-
E	4	31015	27615	815	-
	6	11870	12225	355	+
	8	1354	1441	110	-
	10	0	4	78	+
	12	8955	9260	293	+
	14	547	660	87	-
	16	3164	2853	188	+
	18	1317	1305	147	+
	20	1338	1230	85	-
	22	1810	1803	98	+
	••• H 1 0 •••				
	1	737	752	35	+
	3	2535	2642	49	-
	5	651	673	72	-
	7	387	391	74	+
	9	1421	1489	114	+
	11	72	8	85	-
	13	21902	21531	660	-
	15	6561	6748	214	+
	17	1414	1530	151	+
	19	4	65	65	+
	21	568	602	74	-
	••• H 2 0 •••				
	0	253	149	45	-
	2	245	458	52	-
	4	500	486	65	+
	6	19805	19285	576	-
	8	17844	17747	540	+
	10	2016	1990	134	+
	12	306	364	100	-
	14	6223	6370	222	-
	16	1	52	103	-
	18	1	27	107	-
	20	6	53	65	-
	22	60	64	92	-
	••• H 3 0 •••				
	1	1011	1023	72	+
	3	9958	9876	303	-
	5	3	17	58	+
	7	554	718	85	+
	9	109	302	83	+
	11	3698	3846	195	+
	13	3071	3259	187	-
	15	3230	3348	198	-
	17	106	206	103	+
	19	1665	1711	96	+
	21	3693	3402	169	-
	••• H 4 0 •••				
	0	243	279	61	+
	2	1482	1467	95	+
	4	5681	5789	188	-
	6	0	0	70	-
	8	232	274	82	+
	10	327	294	98	+
	12	2707	2785	174	-
	14	1330	1431	141	-
	16	3691	3177	203	+
	18	1186	1109	71	+
	20	1435	1318	89	-
	••• H 5 0 •••				
	1	17430	15766	479	+
	3	309	193	68	+
	5	15197	14815	455	-
	7	1049	999	103	+
	9	7957	7826	311	+
	11	7515	7860	262	-
	13	7468	7467	254	+
	15	1789	1800	162	+
	17	587	620	65	-
	19	2164	2128	107	+
	21	46	88	91	-
	••• H 6 0 •••				
	0	5373	5485	182	-
	2	1755	1842	121	+
	4	1614	1419	112	-
	6	1902	1957	133	-
	8	14584	14517	438	+
	10	3315	3479	191	-
	12	5185	4896	242	-
	14	47	0	107	+
	16	22	0	114	+
	18	356	298	73	+
	20	856	808	110	+
	••• H 7 0 •••				
	1	12	29	74	-
	3	251	385	88	-
	5	18	0	85	-
	7	2272	2444	158	-
	9	7028	7092	241	+
	11	860	945	126	+
	13	678	655	124	-
	15	4920	4866	253	-
	17	968	1122	84	+
	19	219	312	95	-
	••• H 8 0 •••				
	0	2777	2704	97	-
	2	1172	1244	118	+
	4	4933	5076	179	-
	6	2496	2564	162	+
	8	763	586	115	-
	10	527	493	117	+
	12	97	202	111	+
	14	778	911	136	-
	16	1008	978	85	-
	18	1181	1263	120	+
	••• H 9 0 •••				
	1	12	0	96	+
	3	991	1044	123	+
	5	1696	1524	139	-
	7	1501	1397	141	-
	9	4654	4853	240	+
	11	3737	3686	214	-
	13	144	43	59	+
	15	114	3	98	+
	••• H 10 0 •••				
	0	9079	8938	296	+
	2	630	687	118	+
	4	1490	1443	146	-
	6	550	508	116	+
	8	24	0	106	-
	10	274	287	115	+
	12	8	0	67	+
	14	228	199	70	+
	16	1410	1534	125	+
	••• H 11 0 •••				
	1	739	742	126	+
	3	9966	10312	329	-
	5	3184	3173	196	+
	7	405	411	121	+
	9	1434	1449	157	-
	11	105	67	69	+
	13	611	669	77	-
	15	842	960	115	-
	••• H 12 0 •••				
	0	1207	1201	143	-
	2	133	292	111	+
	4	88	263	116	+
	6	100	65	116	-
	8	720	705	78	-
	10	4634	4786	179	+
	12	101	34	96	-
	14	676	674	107	-
	••• H 13 0 •••				
	1	451	585	77	-
	3	157	198	70	+
	5	18	0	67	+
	7	182	205	69	-
	9	95	162	67	-
	11	387	328	103	+
	••• H 14 0 •••				
	0	2399	2478	120	+
	2	747	800	84	-
	4	27	63	68	+
	6	27	0	96	+
	8	390	351	106	-
	••• H 15 0 •••				
	1	203	255	98	+
	3	86	177	97	+
	5	42	210	94	-
	••• H 1 1 •••				
	1	113	57	28	-
	2	789	862	59	-
	3	51	56	49	+
	4	53	63	55	-
	5	26	2	57	+
	6	384	453	71	-
	7	545	713	82	+
	8	693	703	89	-
	9	128	143	81	-
	10	331	414	92	+
	11	1165	1175	73	+
	12	64	13	94	+
	13	1291	1369	139	+
	14	6696	6633	290	+
	15	2802	2575	180	-
	16	1004	1200	139	-
	17	77	113	106	-
	18	1549	1632	157	-
	19	1471	1334	121	+
	20	490	435	103	+
	21	753	550	76	-
	22	620	523	98	-
	••• H 2 1 •••				
	0	6822	6349	195	-
E	1	21041	17745	525	-
	2	1230	1219	75	+
	3	7	0	54	-
	4	4954	5319	170	+
	5	60	0	59	+
	6	2	24	63	+
	7	1186	1291	99	-
	8	419	441	86	+
	9	418	500	88	+
	10	2630	2768	157	+
	11	4371	4480	143	+
	12	339	421	103	-
	13	321	392	105	-
	14	5	29	103	-
	15	1105	1261	141	-
	16	1014	1171	138	+
	17	6	97	106	-
	18	56	38	107	+
	19	131	107	96	+
	20	39	78	96	+
	21	381	314	98	+
	22	66	102	91	+
	••• H 3 1 •••				
	1	343	300	59	+
	2	10274	9888	287	+
	3	1831	1879	101	-
	4	2251	2230	115	+
	5	974	995	85	-
	6	420	434	75	-
	7	1483	1648	113	-
	8	3229	3409	167	-
	9	429	498	93	-
	10	2591	2633	157	+
	11	1062	1114	121	-
	12	9858	10149	328	-
	13	807	880	124	+
	14	3924	4146	220	+
	15	124	82	106	-
	16	21	21	107	+
	17	717	673	123	-
	18	13	51	66	-
	19	461	467	73	-
	20	24	33	65	+
	21	146	150	95	+
	••• H 4 1 •••				
	0	1	141	57	+
	1	2858	2688	105	-
	2	166	120	61	+
	3	12579	11947	361	+
	4	717	751	80	-
	5	3718	3690	130	-
	6	470	734	87	+
	7	110	65	75	-
	8	85	55	79	+
	9	5495	5851	199	+
	10	3308	3468	184	-
	11	86	0	99	-
	12	94	42	99	-
	13	5591	5842	207	-
	14	1017	947	134	+
	15	68	194	105	-
	16	25	0	108	-
	17	115	132	110	+
	18	19	0	95	+
	19	105	0	96	+
	20	36	0	65	+
	21	2069	1860	133	+
	••• H 5 1 •••				
	1	439	410	73	-
	2	308	405	73	+
	3	916	831	87	+
	4	187	188	72	+
	5	111	75	70	-
	6	48	52	71	-
	7	135	151	79	-
	8	6799	6685	223	-
	9	174	216	90	+
	10	8895	9112	289	+
	11	25	0	98	-
	12	284	313	109	-
	13	7	30	105	+
	14	132	233	105	+
	15	23	0	107	-
	16	949	1052	136	-
	17	17	96	98	-
	18	294	171	70	+
	19	28	0	97	-
	20	118	230	95	-
	21	17	44	93	+
	••• H 6 1 •••				
	0	395	346	79	-
	1	771	776	89	-
	2	48	52	71	-
	3	1603	1698	118	+
	4	403	514	86	+
	5	6351	6169	206	-
	6	977	1137	111	+
	7	233	40	86	+
	8	775	739	104	-
	9	413	462	106	-
	10	796	834	117	+
	11	1182	1076	132	+
	12	636	534	120	+
	13	2620	2702	181	+
	14	117	0	111	-
	15	689	624	128	-
	16	213	210	113	-
	17	282	382	100	-
	18	3	0	94	+
	19	6	0	64	+
	20	142	8	96	+
	••• H 7 1 •••				
	1	387	363	93	-
	2	259	335	87	+
	3	1307	1144	112	+
	4	1372	1342	118	-
	5	2092	2094	140	+
	6	730	833	78	+
	7	227	220	99	-
	8	3555	3708	197	-
	9	560	582	110	+
	10	2215	2492	167	+
	11	471	575	123	+
	12	1093	944	134	+
	13	2	0	106	+
	14	579	483	125	-
	15	1	121	110	+
	16	1558	1777	130	-
	17	422	413	103	+
	18	1651	1527	93	+
	19	38	24	93	-
	••• H 8 1 •••				
	0	13	32	85	+
	1	3374	3196	175	+
	2	63	45	91	-
	3	7635	7597	251	+
	4	558	458	106	-
	5	1108	1218	122	-
	6	485	434	109	-
	7	57	60	94	-
	8	772	879	125	-
	9	579	348	114	-
	10	861	914	132	-
	11	3	67	103	+
	12	72	160	110	+
	13	23	11	103	+
	14	81	0	114	+
	15	822	704	113	-
	16	381	319	104	-
	17	1064	920	83	+
	18	216	368	98	-
	••• H 9 1 •••				
	1	190	279	101	+
	2	10780	10388	335	+
	3	597	673	113	-
	4	3749	3170	189	-
	5	277	323	104	+
	6	289	105	104	-
	7	775	817	125	+
	8	1179	1037	134	+
	9	1339	1663	148	-
	10	221	257	111	+
	11	168	91	109	-
	12	12	0	114	+
	13	72	93	98	+
	14	2500	2957	160	-
	15	261	412	103	+
	16	118	58	70	-
	17	56	66	97	-
	18	437	598	102	+
	••• H 10 1 •••				
	0	86	5	101	-
	1	1272	1073	129	+
	2	111	211	106	-
	3	231	0	105	+
	4	417	554	117	+
	5	123	25	105	-
	6	62	0	107	-
	7	962	885	127	-
	8	340	498	120	-
	9	167	0	112	-
	10	602	532	128	+
	11	2530	2297	182	+
	12	132	242	97	-
	13	323	367	75	+
	14	60	0	97	-
	15	2355	2180	112	-
	16	153	163	101	+
	••• H 11 1 •••				
	1	260	101	106	-
	2	176	178	107	+
	3	203	307	114	+
	4	150	233	108	-
	5	341	282	116	+
	6	440	555	122	-
	7	3	21	107	+
	8	22	108	111	-
	9	123	0	75	-
	10	0	111	97	+
	11	441	531	110	+
	12	2297	2229	150	+
	13	102	161	69	+
	14	212	103	99	-
	15	244	60	98	-
	••• H 12 1 •••				
	0	141	27	108	-
	1	365	446	116	+
	2	13	0	111	+
	3	6	11	113	+
	4	855	770	132	+
	5	165	342	113	+
	6	0	26	99	-
	7	1766	1709	135	-
	8	29	0	98	+
	9	314	295	73	+
	10	10	5	96	-
	11	11	0	69	+
	12	362	326	72	+
	13	160	147	102	+
	••• H 13 1 •••				
	1	124	36	101	-
	2	532	657	118	+
	3	11	46	98	+
	4	1461	1639	132	+
	5	192	191	72	-
	6	1091	1223	126	-
	7	245	251	102	-
	8	54	5	67	-
	9	261	308	72	-
	10	35	229	97	+
	11	1	37	96	-
	••• H 14 1 •••				
	0	329	269	72	+
	1	637	651	120	+
	2	70	78	98	-
	3	188	193	70	+
	4	1	0	67	-
	5	90	76	66	-
	6	293	262	72	+
	7	1254	1208	130	-
	8	9	0	101	+
	9	2577	2778	159	+
	••• H 15 1 •••				
	1	107	0	96	-
	2	8	18	95	-
	4	842	672	118	+
	••• H 0 2 •••				
	0	14346	13761	421	+
E	1	26561	25598	755	-
	2	1095	1087	79	-
	3	1015	1145	83	-
	4	2545	2998	107	-
	5	3575	3769	130	-
	6	19024	19392	580	-
	7	11659	12028	372	-
	8	2464	2444	140	+
	9	919	1011	109	+
	10	1475	1598	130	-
	11	13004	13018	394	+
	12	392	331	102	-
	13	92	99	101	-
	14	853	694	133	-
	15	3278	2985	193	-
	16	720	527	127	+
	17	40	0	108	-
	18	763	852	70	-
	19	171	195	67	+
	20	213	204	67	-
	21	544	536	106	+
	22	5	0	89	-
	••• H 1 2 •••				
	1	3291	3247	109	+
	2	6025	6277	197	+
	3	4289	4640	151	-
	4	6	110	60	+
	5	216	240	69	+
	6	1243	1368	102	-
	7	866	962	97	+
	8	1526	1404	114	-
	9	46	0	82	+
	10	380	247	99	+
	11	1374	1573	132	+
	13	8933	9185	293	-
	14	3364	3357	199	+
	15	2143	2197	173	+
	16	1028	1326	143	-
	17	1059	877	138	+
	18	184	244	100	-
	19	191	226	68	+
	20	387	331	102	+
	21	547	443	98	-
	••• H 2 2 •••				
	0	11165	9791	296	+
	1	3217	3253	110	+
	2	1361	1388	86	-
	3	8880	8831	274	+
	4	3697	3908	133	-
	5	8145	8344	262	-
	6	3065	3292	120	+
	7	1054	964	98	+
	8	4	55	78	+
	9	334	296	91	+
	10	2940	2979	168	+
	11	0	0	92	+
	12	717	820	117	+
	13	1277	1138	135	-
	14	7134	7237	248	-
	15	887	893	131	-
	16	523	404	115	+
	17	229	299	111	+
	18	1009	781	108	+
	19	780	843	79	+
	20	1246	1267	86	-
	21	150	225	94	+
	••• H 3 2 •••				
	1	211	215	61	+
	2	2024	1850	104	+
	3	2	0	61	+
	4	2558	2503	128	+
	5	1368	1371	102	-
	6	1330	1227	106	-
	7	490	452	86	+
	8	1653	1638	123	-
	9	5170	5535	190	+
	10	6127	6082	192	+
	11	0	124	92	-
	12	669	661	117	-
	13	1200	1542	144	-
	14	3221	3295	199	-
	15	127	47	111	+
	16	111	64	110	+
	17	59	0	113	-
	18	899	953	110	+
	19	1039	1137	116	+
	20	118	125	66	-
	21	509	390	99	-
	••• H 4 2 •••				
	0	276	213	66	-
	1	1514	1304	93	+
	2	2455	2371	125	+
	3	936	823	84	+
	4	6	0	68	-
	5	644	654	87	-
	6	8003	8163	262	-
	7	1907	1750	125	-
	8	11655	11852	366	+
	9	355	377	99	+
	10	619	481	108	-
	11	9	160	98	+
	12	1042	1094	130	-
	13	816	647	126	+
	14	110	41	112	+
	15	32	0	107	+
	16	445	385	117	+
	17	620	533	84	-
	18	146	315	97	+
	19	46	133	94	-
	20	139	165	67	+
	21	315	278	97	+
	••• H 5 2 •••				
	1	2975	2830	143	+
	2	1355	1335	103	-
	3	4851	4677	160	-
	4	2814	2920	150	-
	5	4256	4224	149	-
	6	526	491	89	+
	7	724	712	101	-
	8	629	511	100	-
	9	16	0	92	-
	10	46	149	101	+
	11	1336	1399	134	-
	12	9855	9696	324	+
	13	22	107	109	+
	14	1425	1298	146	-
	15	577	533	135	-
	16	3081	2811	196	-
	17	0	68	95	+
	18	857	775	110	+
	19	37	0	67	+
	20	110	57	94	+
	••• H 6 2 •••				
	0	1158	1090	103	-
	1	2457	2578	142	+
	2	3170	3064	158	+
	3	964	1057	106	+
	4	2916	2658	151	-
	5	125	30	84	-
	6	1588	1346	122	+
	7	2	63	91	-
	8	1185	1084	124	+
	9	3534	3165	184	-
	10	18	71	101	+
	11	279	235	110	+
	12	664	715	122	-
	13	1897	2019	165	+
	14	26	91	109	-
	15	343	334	118	-
	16	30	13	98	+
	17	0	81	67	+
	18	1296	1485	124	+
	19	236	272	96	+
	20	16	0	91	+
	••• H 7 2 •••				
	1	276	487	90	-
	2	3827	3848	187	+
	3	2230	2042	137	+
	4	8	0	85	+
	5	2868	2632	159	-
	6	1884	1931	144	-
	7	212	270	99	-
	8	1860	1837	147	+
	9	11182	11145	359	+
	10	231	54	105	+
	11	2466	2307	170	-
	12	1204	1103	138	-
	13	504	472	118	+
	14	928	1154	145	-
	15	580	657	108	-
	16	407	228	103	+
	17	141	261	100	-
	18	57	63	65	-
	19	226	117	98	+
	••• H 8 2 •••				
	0	863	714	110	-
	1	1355	1306	125	+
	2	1141	1335	125	+
	3	229	69	96	+
	4	276	319	100	-
	5	709	715	117	+
	6	3	0	93	-
	7	3037	2931	178	-
	8	981	782	127	+
	9	563	658	122	+
	10	79	118	110	+
	11	656	615	122	+
	12	2	59	112	-
	13	789	959	141	-
	14	2	1	68	-
	15	581	688	113	-
	16	0	0	96	-
	17	833	936	81	+
	18	49	141	95	+
	••• H 9 2 •••				
	1	1637	1476	137	+
	2	1198	1089	129	+
	3	2160	2062	151	-
	4	853	873	125	-
	5	744	626	119	+
	6	237	244	108	-
	7	462	363	111	-
	8	397	432	113	+
	9	2	0	105	+
	10	674	855	130	-
	11	78	130	115	+
	12	1469	1376	155	+
	13	10	0	97	-
	14	8	289	95	+
	15	326	349	103	-
	16	261	288	70	-
	17	1565	1608	127	+
	••• H 10 2 •••				
	0	1	97	101	+
	1	743	802	119	-
	2	124	234	110	+
	3	657	581	118	-
	4	3257	3148	192	-
	5	133	116	111	+
	6	149	0	112	+
	7	299	193	111	-
	8	2317	2197	169	-
	9	9	102	108	+
	10	117	191	112	+
	11	256	201	71	+
	12	472	525	116	-
	13	496	492	106	+
	14	56	143	68	-
	15	38	15	68	-
	16	7	118	98	+
	••• H 11 2 •••				
	1	1	123	106	+
	2	1130	1201	142	-
	3	1	0	108	+
	4	4008	4199	230	+
	5	336	269	117	+
	6	114	203	112	-
	7	22	124	107	+
	8	1728	1786	169	-
	9	511	561	105	+
	10	73	221	99	+
	11	56	36	89	-
	12	48	34	97	+
	13	20	57	88	-
	14	7	129	95	-
	15	3	47	94	-
	••• H 12 2 •••				
	0	629	578	129	+
	1	1233	937	139	+
	2	568	515	124	-
	3	76	140	114	+
	4	9	152	115	+
	5	338	222	107	-
	6	185	244	99	+
	7	8	49	96	+
	8	693	744	82	-
	9	1161	1292	129	+
	10	923	1016	117	+
	11	824	1004	85	-
	12	104	0	103	+
	13	156	303	99	-
	••• H 13 2 •••				
	1	84	185	101	+
	2	431	314	103	+
	3	371	309	73	-
	4	7	69	69	+
	5	800	803	118	+
	6	178	128	99	-
	7	6	3	67	+
	8	11	0	68	+
	9	610	612	80	-
	10	92	16	100	+
	11	1282	1244	134	+
	••• H 14 2 •••				
	0	14	124	66	+
	1	588	742	80	-
	2	5	0	67	+
	3	3	60	68	+
	4	62	131	69	+
	5	51	39	68	+
	6	75	91	96	-
	7	153	227	102	-
	8	34	70	99	-
	••• H 15 2 •••				
	1	192	148	98	-
	2	176	119	101	-
	3	174	28	99	+
	••• H 1 3 •••				
	1	2247	2040	110	-
	2	18	100	61	-
	3	95	0	65	+
	4	0	0	68	+
	5	95	206	76	+
	6	5	129	75	-
	7	347	187	88	-
	8	1316	1444	121	-
	9	675	434	102	+
	10	2756	2803	168	+
	11	723	656	113	+
	12	137	0	127	-
	13	433	363	111	+
	14	185	51	110	-
	15	4883	4716	244	-
	16	50	210	112	+
	17	700	664	128	-
	18	128	70	93	+
	19	143	0	97	+
	20	933	898	78	-
	21	36	77	95	-
	••• H 2 3 •••				
E	0	36253	29389	877	-
	1	884	813	80	-
	2	56	122	62	+
	3	2679	2594	132	+
	4	1871	2089	121	+
	5	2091	2104	126	-
	6	474	301	85	-
	7	171	249	88	-
	8	3	143	83	-
	9	2211	2413	154	+
	10	92	255	95	+
	11	378	405	110	-
	12	2317	2265	166	-
	13	149	95	75	-
	14	859	733	139	-
	15	743	871	133	+
	16	19	0	110	-
	17	519	666	123	-
	18	21	13	94	+
	19	6	193	96	-
	20	69	80	65	-
	21	704	557	105	+
	••• H 3 3 •••				
	1	6716	6428	207	+
	2	281	322	74	-
	3	80	192	69	+
	4	2248	2133	128	+
	5	697	770	92	-
	6	61	77	76	-
	7	24	71	80	+
	8	2159	2261	146	-
	9	89	101	91	-
	10	2846	3075	179	+
	11	259	311	106	-
	12	2057	1981	161	-
	13	13973	14100	426	+
	14	865	1059	140	+
	15	39	80	111	-
	16	291	343	114	-
	17	401	307	105	-
	18	7	0	67	-
	19	274	128	99	+
	20	627	771	105	+
	21	59	33	93	+
	••• H 4 3 •••				
	0	957	850	90	-
	1	4721	4754	161	-
	2	2029	2013	122	+
	3	2663	2499	137	+
	4	232	158	80	-
	5	61	127	80	-
	6	729	747	96	+
	7	25	137	85	-
	8	9	66	87	+
	9	153	226	99	-
	10	3797	3944	207	-
	11	561	629	117	+
	12	1162	1187	99	-
	13	22	31	107	-
	14	4439	4011	226	+
	15	252	119	116	-
	16	271	280	116	+
	17	12	3	94	+
	18	41	0	96	-
	19	28	0	66	+
	20	704	684	102	+
	••• H 5 3 •••				
	1	1029	1049	101	-
	2	1371	1296	54	+
	3	1610	1412	113	+
	4	597	605	94	-
	5	181	159	92	+
	6	46	0	85	+
	7	1647	1804	139	-
	8	1404	1447	130	-
	9	1372	1294	131	+
	10	2585	2556	172	+
	11	204	186	108	-
	12	821	827	129	-
	13	306	251	117	+
	14	714	536	128	+
	15	236	295	116	-
	16	568	508	75	-
	17	2	0	68	-
	18	26	89	94	+
	19	624	664	74	-
	20	1	70	94	-
	••• H 6 3 •••				
	0	4813	4771	167	-
	1	1140	993	111	-
	2	325	117	90	-
	3	2515	2385	148	+
	4	121	0	86	+
	5	1451	1537	127	-
	6	2510	2596	161	+
	7	473	539	108	-
	8	2280	2219	157	-
	9	450	505	116	+
	10	81	0	102	+
	11	457	339	111	+
	12	2268	2097	167	+
	13	89	0	114	-
	14	599	725	127	-
	15	284	386	78	-
	16	3182	3245	166	-
	17	132	297	100	+
	18	49	1	65	+
	19	21	0	94	-
	••• H 7 3 •••				
	1	5526	5362	187	-
	2	4098	4002	199	+
	3	800	818	112	+
	4	1177	985	120	-
	5	1402	1508	132	+
	6	4	130	96	-
	7	2168	2143	156	-
	8	104	143	107	-
	9	209	345	107	-
	10	297	132	105	+
	11	108	276	107	+
	12	0	0	107	-
	13	242	278	117	-
	14	12	0	112	-
	15	260	89	101	-
	16	135	171	101	-
	17	11	11	67	+
	18	197	47	98	+
	••• H 8 3 •••				
	0	5608	5499	191	+
	1	751	740	112	+
	2	316	328	103	+
	3	649	633	111	+
	4	305	128	104	+
	5	825	824	120	-
	6	110	195	104	+
	7	544	770	124	+
	8	2314	2253	163	-
	9	1180	906	130	-
	10	204	178	116	+
	11	435	359	119	+
	12	1190	1135	146	+
	13	241	310	79	+
	14	1611	1574	128	+
	15	1807	1947	137	-
	16	197	203	70	+
	17	455	456	106	+
	18	757	718	108	-
	••• H 9 3 •••				
	1	209	250	104	+
	2	265	138	104	+
	3	1826	1772	149	-
	4	172	218	106	-
	5	2272	2493	173	+
	6	329	180	113	+
	7	881	827	127	+
	8	801	744	132	-
	9	4944	4978	252	-
	10	45	92	109	+
	11	197	0	115	-
	13	253	341	103	+
	12	1245	1255	122	+
	14	626	643	108	-
	15	316	451	72	+
	16	278	415	101	-
	17	4	47	95	+
	••• H 10 3 •••				
	0	281	304	106	-
	1	985	780	130	+
	2	199	211	104	-
	3	86	61	102	+
	4	1679	1557	148	+
	5	424	387	117	-
	6	40	29	74	-
	7	109	11	108	-
	8	314	264	122	-
	9	162	109	115	+
	10	393	256	72	+
	11	30	18	96	-
	12	26	0	67	+
	13	416	485	104	+
	14	12	0	67	-
	15	115	331	97	-
	••• H 11 3 •••				
	1	2154	2295	172	-
	2	773	830	136	+
	3	510	518	121	+
	4	137	80	105	-
	5	594	595	130	+
	6	294	206	115	-
	7	17	99	74	-
	8	21	57	95	+
	9	1068	1054	125	-
	10	1	0	69	+
	11	1312	1520	130	+
	12	635	611	77	+
	13	26	84	101	-
	14	910	724	116	-
	••• H 12 3 •••				
	0	604	733	70	-
	1	516	548	83	+
	2	738	787	116	-
	3	79	99	98	+
	4	1557	1648	131	+
	5	11	0	94	+
	6	155	158	97	-
	7	562	431	79	-
	8	650	611	108	-
	9	84	0	67	+
	10	95	17	69	-
	11	54	16	99	+
	12	274	437	102	+
	••• H 13 3 •••				
	1	13	0	93	+
	2	4	163	100	+
	3	1232	1287	130	+
	4	454	359	112	+
	5	23	0	98	-
	6	610	747	78	-
	7	23	1	67	+
	8	24	42	98	+
	9	361	431	104	-
	10	45	187	97	+
	••• H 14 3 •••				
	0	0	78	95	-
	1	82	88	67	-
	2	123	178	69	-
	3	6	135	99	-
	4	68	10	97	+
	5	593	603	114	+
	6	14	187	96	+
	7	1275	1451	126	-
	••• H 0 4 •••				
	0	480	402	73	-
	1	3958	4114	144	-
	2	65	119	75	+
	3	1004	957	97	+
	4	5829	6196	206	+
	5	11454	12242	382	-
	6	44	0	86	+
	7	220	302	97	+
	8	4	71	92	-
	9	6	31	100	+
	10	6180	6493	225	+
	11	6991	7271	248	+
	12	219	247	115	+
	13	690	541	129	+
	14	3448	3217	204	-
	15	3672	3452	216	-
	16	3554	3179	207	+
	17	970	889	67	-
	18	860	743	76	+
	19	1559	1621	94	+
	20	637	491	102	-
	••• H 1 4 •••				
	1	644	520	81	+
	2	3160	3366	123	+
	3	2827	2799	146	-
	4	1562	1851	125	+
	5	39	0	81	+
	6	2637	2725	158	-
	7	22	0	93	-
	8	5570	5840	202	-
	9	657	677	119	-
	10	6076	6325	201	+
	11	1579	1811	152	+
	12	393	372	118	-
	13	386	282	116	-
	14	1837	1764	164	+
	15	62	16	112	-
	16	768	814	134	-
	17	238	85	98	-
	18	19	0	92	-
	19	284	227	69	+
	••• H 2 4 •••				
	0	2544	2390	131	+
	1	801	757	89	-
	2	341	312	80	-
	3	9063	9477	294	+
	4	596	591	95	-
	5	224	212	62	+
	6	229	355	97	-
	7	8848	9453	305	-
	8	1642	1678	137	+
	9	4311	4585	169	+
	10	1845	1933	155	-
	11	383	391	125	+
	12	193	0	111	-
	13	4730	4704	179	-
	14	11	0	117	+
	15	257	108	116	-
	16	335	386	121	+
	17	280	197	107	+
	18	316	420	99	-
	19	35	126	66	+
	20	5	70	95	+
	••• H 3 4 •••				
	1	238	281	77	+
	2	10606	10000	309	+
	3	336	415	85	-
	4	64	228	85	-
	5	550	405	94	-
	6	262	281	96	-
	7	0	71	89	+
	8	493	643	112	-
	9	182	100	107	+
	10	951	1144	134	+
	11	736	814	126	-
	12	4	0	112	-
	13	985	945	143	-
	14	939	1107	144	-
	15	1252	1212	151	+
	16	926	948	116	-
	17	28	91	98	-

Table 2 (*cont.*)

H	CALC	CHS	SIG	
*** H 3 4 ***				
18	1298	1345	121	+
19	198	261	67	-
20	65	0	94	+
*** H 4 4 ***				
0	405	380	88	+
1	4540	4504	158	+
2	11	7	78	+
3	2241	1955	133	+
4	1827	2038	139	-
5	8611	8741	283	-
6	316	263	92	+
7	990	781	115	+
8	24	94	97	-
9	1519	1629	143	-
10	412	362	120	-
11	1266	1301	143	+
12	1068	1305	147	+
13	2532	2446	183	+
14	96	0	115	-
15	1433	1493	157	-
16	945	1033	115	-
17	152	219	70	-
18	458	465	71	+
19	361	507	100	+
*** H 5 4 ***				
1	1233	1370	116	-
2	1135	1115	115	-
3	7429	7242	240	+
4	221	396	93	-
5	298	308	103	+
6	572	659	112	-
7	376	353	102	-
8	941	1083	129	-
9	5133	5138	187	+
10	3013	2985	188	+
11	60	92	108	+
12	4057	4274	229	+
13	21	38	114	-
14	1862	1920	169	-
16	558	387	106	-
17	363	480	101	+
18	52	49	65	+
19	559	673	104	+
*** H 6 4 ***				
0	2941	2731	163	-
1	4002	3960	148	+
2	711	777	111	+
3	347	105	100	+
4	19	0	94	-
5	673	687	109	+
6	1917	2058	152	-
7	3429	3239	190	-
8	213	389	112	+
9	23[illegible]	158	107	-
10	6	0	110	-
11	263	136	110	+
12	15	0	112	+
13	665	678	131	+
14	6	31	76	-
15	268	311	100	-
16	416	649	111	-
17	171	304	70	+
18	2	0	94	-
*** H 7 4 ***				
1	795	657	117	+
2	9476	9267	294	+
3	1946	1736	142	-
4	2203	2203	157	-
5	2	0	100	-
6	15	0	105	-
7	844	1008	128	+
8	2082	2046	162	+
9	226	435	110	-
10	2070	2061	166	-
11	1740	1672	161	-
12	963	967	139	+
13	1541	1667	107	+
14	2541	2377	149	-
15	122	45	98	-
16	137	193	70	-
17	47	50	96	-
18	643	662	103	+
*** H 8 4 ***				
0	722	605	122	-
1	2651	2677	173	+
2	782	812	123	+
3	463	484	116	+
4	742	639	120	-
5	33	5	101	-
6	51	50	103	-
7	228	208	110	-
8	1	47	105	+
9	5	0	110	-
10	21	210	113	+
11	229	225	116	+
12	1473	1599	128	-
13	3	0	100	-
14	204	179	101	+
15	540	645	76	-
16	264	470	104	+
17	0	0	91	-
*** H 9 4 ***				
1	2	182	103	+
2	565	698	120	-
3	41	25	107	-
4	1227	1372	139	+
5	26	0	108	+
6	2024	1937	160	-
7	192	231	114	-
8	15	0	109	-
9	28	0	117	+
10	566	935	139	+
11	37	241	96	-
12	346	410	74	+
13	233	277	100	+
14	140	85	69	-
15	294	242	98	-
16	189	401	99	+
*** H 10 4 ***				
0	262	330	113	-
1	3	57	107	+
2	61	16	106	+
3	1223	1251	145	-
4	905	1087	141	+
5	594	626	130	+
6	680	616	127	+
7	1832	1967	168	-
8	169	38	77	-
9	561	475	109	+
10	722	719	113	+
11	82	118	99	+
12	370	398	72	+
13	359	378	74	+
14	155	147	99	-

H	CALC	OBS	SIG	
*** H 11 4 ***				
1	166	0	114	-
2	263	124	116	+
3	4	0	110	-
4	355	309	115	+
5	141	0	98	+
6	81	203	97	-
7	1070	1364	123	-
8	16	8	68	-
9	29	5	97	-
10	645	637	77	-
11	590	727	78	+
12	229	126	98	+
13	249	107	98	-
*** H 12 4 ***				
0	1136	1134	89	+
1	141	185	98	-
2	199	267	100	-
3	303	289	100	+
4	329	304	72	-
5	42	13	97	+
6	1258	1373	128	+
7	355	366	101	-
8	328	378	73	-
9	948	883	82	+
10	112	147	101	-
11	211	68	99	-
*** H 13 4 ***				
1	7	0	66	+
2	203	174	69	-
3	40	43	67	-
4	1122	1349	92	+
5	40	9	69	-
6	295	509	101	-
7	22	39	97	+
8	166	133	99	-
*** H 14 4 ***				
0	[illegible]	111	95	-
1	1	130	96	+
2	70	199	101	-
3	111	60	99	-
4	198	305	100	+
*** H 1 5 ***				
1	383	346	84	-
2	257	198	88	+
3	107	71	85	+
4	619	665	103	+
5	27	17	90	+
6	507	411	107	-
7	60	72	98	+
8	337	361	118	+
9	1479	1229	146	+
10	1135	1244	145	+
11	28	0	117	-
12	2098	2093	170	-
13	157	208	121	+
14	739	725	141	-
15	235	161	126	-
16	377	220	106	+
17	105	154	97	-
18	101	205	68	+
19	76	111	96	-
*** H 2 5 ***				
0	4451	4625	162	-
1	1406	1281	115	+
2	1811	2072	137	+
3	3787	3584	183	+
4	101	4	86	+
5	1512	1576	131	-
6	1229	1294	132	+
7	14	90	105	+
8	1774	2104	162	+
9	321	420	122	+
10	267	428	123	-
11	1542	1429	156	-
12	18	47	112	+
13	121	177	116	-
14	1233	991	152	+
15	1338	1378	103	+
16	507	499	121	-
17	26	94	98	-
18	221	215	69	+
19	271	150	97	-
*** H 3 5 ***				
1	406	352	90	-
2	5240	5083	177	-
3	1583	1523	125	+
4	8	0	94	-
5	2499	2891	172	-
6	1015	932	122	+
7	3456	3458	195	-
8	1938	2064	162	-
9	33	171	111	+
10	2231	2365	177	+
11	2716	2740	127	-
12	256	350	120	+
13	3537	3711	223	+
14	269	193	122	-
15	679	632	111	-
16	447	446	75	-
17	371	306	103	-
18	236	127	69	+
19	18	52	91	-
*** H 4 5 ***				
0	6318	6053	190	-
1	3445	3352	178	-
2	2193	2375	151	+
3	22	0	94	+
4	48	150	100	+
5	208	123	98	+
6	105	109	108	+
7	305	309	115	-
8	1309	1404	149	-
9	769	667	123	-
10	367	235	119	-
11	56	163	118	+
12	34	0	115	-
13	1869	1598	159	+
14	570	444	134	+
15	46	120	101	+
16	24	0	99	-
17	758	791	79	-
18	50	0	95	+
*** H 5 5 ***				
1	452	409	103	-
2	365	408	106	+
3	103	35	94	+
4	290	245	105	-
5	493	551	116	+
6	6	131	104	-
7	298	216	117	-
8	210	119	113	+
9	28	61	111	+

H	CALC	OBS	SIG	
*** H 5 5 ***				
10	8	5	110	+
11	402	368	121	-
12	887	1018	147	-
13	2278	2390	188	+
14	757	828	114	+
15	1210	1176	89	-
16	38	129	97	-
17	86	87	69	-
*** H 6 5 ***				
0	5505	5590	198	-
1	54	13	101	-
2	225	334	105	+
3	1156	1189	133	+
4	454	423	112	+
5	9	19	106	-
6	580	363	119	+
7	5	5	103	-
8	26	137	111	-
9	12	16	110	+
10	178	64	115	+
11	357	184	125	+
12	1	0	119	+
13	1466	1634	129	-
14	252	281	105	+
15	374	427	106	-
16	183	181	70	-
17	1920	1868	135	+
*** H 7 5 ***				
1	2	61	106	-
2	3902	3881	211	+
3	9	0	103	-
4	550	495	121	-
5	3609	3578	207	+
6	1	0	106	+
7	2	235	111	-
8	17	110	111	+
9	424	399	126	-
10	0	58	110	+
11	431	595	125	+
12	482	535	109	-
13	660	724	111	+
14	88	0	103	+
15	9	21	67	-
16	30	37	96	+
*** H 8 5 ***				
0	246	301	109	+
1	547	617	123	-
2	613	521	124	-
3	369	470	121	-
4	1	0	107	+
5	86	272	114	-
6	198	312	116	+
7	106	100	115	+
8	8028	7850	260	-
9	59	0	119	+
10	1	0	74	-
11	15	0	99	+
12	360	263	74	+
13	400	377	106	+
14	4	40	67	-
15	301	334	100	-
16	0	18	95	-
*** H 9 5 ***				
1	607	675	125	-
2	913	646	127	-
3	407	427	118	+
4	47	231	115	+
5	1631	1515	157	+
6	749	658	132	+
7	344	433	120	-
8	1740	1845	114	-
9	1206	1183	122	-
10	287	276	104	-
11	327	242	104	+
12	2113	2144	142	+
13	99	55	68	-
14	3	55	97	-
*** H 10 5 ***				
0	23	80	112	+
1	479	490	121	+
2	1168	1079	145	-
3	22	0	113	-
4	1007	729	137	+
5	323	386	80	-
6	157	184	99	+
7	660	789	110	+
8	697	743	80	-
9	20	97	97	-
10	7	13	102	-
11	274	271	71	-
12	494	568	111	+
13	125	230	97	+
*** H 11 5 ***				
1	354	355	104	-
2	364	504	102	+
3	13	0	97	+
4	14	0	98	+
5	885	912	85	+
6	49	120	99	-
7	249	123	98	+
8	37	105	69	+
9	1303	1402	92	-
10	54	39	98	+
11	925	774	119	+
*** H 12 5 ***				
0	1	4	66	-
1	31	8	95	+
2	59	114	96	-
3	72	8	99	+
4	1494	1632	98	+
5	13	132	69	+
6	42	0	69	-
7	244	311	99	-
8	9	23	98	-
9	372	435	104	+
*** H 13 5 ***				
1	495	590	107	-
2	154	164	97	-
3	721	660	112	+
4	53	96	101	-
5	432	293	103	-
6	2	34	96	+
*** H 0 6 ***				
0	13121	12758	387	-
1	955	1089	125	-
2	2012	2113	151	-
3	6094	6487	223	+
4	1603	1911	150	+
5	2908	3099	186	-
6	197	379	115	+

H	CALC	OBS	SIG	
*** H 0 6 ***				
7	5978	6444	225	-
8	1065	923	145	-
9	8559	9073	304	+
10	53	142	127	+
11	148	273	125	+
12	79	0	125	-
13	1568	1876	180	-
14	3159	3139	139	-
15	665	669	85	+
16	8	52	72	-
17	270	94	74	-
18	20	0	102	-
*** H 1 6 ***				
1	16	85	88	+
2	550	509	106	+
3	4	40	94	+
4	831	1188	129	+
5	356	367	112	+
6	1077	1094	135	-
7	182	222	117	-
8	3360	3710	213	-
9	103	98	122	-
10	6806	6838	242	+
11	956	768	149	+
12	675	633	140	-
13	686	831	151	+
14	23	0	111	+
16	519	523	112	-
17	568	560	80	-
18	190	323	101	+
*** H 2 6 ***				
0	7	9	85	+
1	311	116	93	-
2	312	380	161	+
3	4559	4429	143	+
4	140	151	104	+
5	1590	1814	151	-
6	0	227	110	-
7	341	446	123	+
8	6	10	117	+
9	1095	1100	149	-
10	1801	1854	172	-
11	592	588	140	+
12	5	0	123	+
13	246	323	134	+
14	1232	1310	126	+
15	1007	994	90	-
16	263	128	106	+
17	160	164	72	-
18	49	0	98	-
*** H 3 6 ***				
1	286	268	98	+
2	976	946	120	+
3	14	0	99	+
4	85	152	102	+
5	284	364	115	+
6	23	87	109	-
7	58	179	116	-
8	1065	1072	146	-
9	234	204	121	-
10	605	870	140	+
11	164	337	127	-
12	0	0	123	-
13	146	185	86	+
14	152	31	108	+
15	985	926	120	+
16	823	852	83	-
17	5	44	100	-
18	7	0	97	+
*** H 4 6 ***				
0	7	185	97	-
1	10	0	96	-
2	18	0	99	-
3	128	120	103	+
4	21	14	103	+
5	149	0	114	+
6	565	497	119	+
7	3310	3176	197	-
8	260	217	125	-
9	120	58	118	+
10	6	22	121	-
11	2453	2659	195	+
12	1313	1251	166	+
13	134	305	110	-
14	7	0	106	-
15	1218	1394	128	-
16	559	487	78	-
17	579	421	110	+
*** H 5 6 ***				
1	7792	7280	248	-
2	9445	8667	267	+
3	921	983	134	+
4	5160	5047	185	-
5	243	183	113	+
6	607	598	125	-
7	498	519	126	-
8	1140	964	139	+
9	25	0	116	+
10	161	87	123	-
11	80	216	120	-
12	1102	1215	128	+
13	604	515	126	-
14	327	13	109	-
15	523	523	79	-
16	137	152	103	-
17	117	31	101	-
*** H 6 6 ***				
0	192	305	112	-
1	5637	5464	177	+
2	348	498	121	+
3	254	306	113	+
4	371	335	120	+
5	1692	1526	152	-
6	292	221	120	-
7	530	540	128	+
8	53	192	118	-
9	642	586	132	-
10	106	39	122	+
11	119	234	113	+
12	739	645	116	+
13	263	124	109	+
14	245	319	76	+
15	962	860	86	-
16	242	182	104	-
*** H 7 6 ***				
1	272	322	117	+
2	297	192	116	-
3	247	132	117	-
4	1087	1091	140	+
5	453	516	124	+
6	39	37	114	+
7	84	0	119	+
8	724	662	139	-
9	1182	1156	153	-

H	CALC	CHS	SIG	
*** H 7 6 ***				
10	14	0	107	-
11	367	71	118	-
12	2031	2098	145	+
13	528	473	79	+
14	2221	2159	112	-
15	370	335	103	+
*** H 8 6 ***				
0	24	0	114	+
1	1819	1924	166	+
2	183	151	113	+
3	473	546	128	-
4	15	53	113	+
5	419	262	122	+
6	6	0	116	+
7	350	229	127	-
8	12	108	105	-
9	33	0	104	+
10	65	0	105	-
11	181	211	103	-
12	12	58	71	-
13	857	983	117	+
14	371	370	104	+
*** H 9 6 ***				
1	24[illegible]	139	119	-
2	64	21	115	+
3	155	199	120	+
4	126	103	118	-
5	69	20	103	+
6	281	617	110	-
7	21	15	103	+
8	337	190	75	+
9	8	0	100	-
10	283	200	73	-
11	[illegible]	21	70	+
12	1072	1170	122	+
13	[illegible]	123	100	+
*** H 10 6 ***				
0	2358	2426	117	-
1	55	77	104	+
2	522	679	111	-
3	31	0	102	+
4	378	426	109	+
5	10	11	72	+
6	0	0	100	+
7	924	898	121	-
8	411	415	75	-
9	615	718	79	+
10	46	0	100	+
11	[illegible]	52	98	+
*** H 11 6 ***				
1	26	5	97	+
2	40	231	98	-
3	54	182	100	+
4	1360	1224	91	+
5	127	72	71	+
6	1002	1[illegible]2	88	-
7	134	201	103	-
8	44	217	99	+
9	68	68	99	-
*** H 12 6 ***				
	132	0	99	+
1	398	621	107	-
2	9	0	99	-
3	94	101	98	-
4	17	65	99	-
5	1379	1322	129	+
6	176	156	101	+
*** H 1 7 ***				
1	5[illegible]	0	103	-
2	136	157	105	+
3	184	185	110	+
4	80	249	111	+
5	1026	1115	140	-
6	254	435	124	+
7	376	223	130	+
8	21	227	127	+
9	387	519	141	+
10	47	0	130	-
11	3242	3422	228	-
12	530	365	131	-
13	273	349	121	+
14	274	284	116	-
15	2[illegible]2	339	79	+
16	7	182	107	+
17	224	321	109	-
*** H 2 7 ***				
0	67	100	99	-
1	147	19	100	+
2	110	136	105	+
3	355	351	113	+
4	3077	2932	188	-
5	252	236	118	+
6	181	167	122	+
7	0	0	121	+
8	1	27	126	+
9	290	324	133	-
10	2288	2279	191	-
11	163	253	139	-
12	3	207	116	+
13	4	0	112	+
14	825	1060	125	+
15	39	37	78	+
16	1517	1137	131	-
*** H 3 7 ***				
1	861	844	126	-
2	838	705	121	-
3	5024	4892	241	+
4	1009	1035	132	-
5	241	319	121	+
6	1	0	116	+
7	962	986	145	-
8	384	331	133	+
9	2217	2352	193	+
10	34	140	130	+
11	204	60	124	-
12	166	247	120	+
13	737	756	128	+
14	12	0	78	-
15	61	24	77	-
16	55	0	107	-
*** H 4 7 ***				
0	10227	9856	323	-
1	60	188	113	-
2	2367	2366	173	+
3	163	216	114	-
4	651	776	130	+
5	0	52	113	+
6	437	432	129	-
7	59	155	121	-
8	94	120	125	-

H	CALC	OBS	SIG	
*** H 4 7 ***				
9	75	0	130	-
10	114	200	91	+
11	50	58	117	+
12	191	2	81	+
13	473	470	114	+
14	87	219	78	+
15	216	304	109	+
16	773	605	122	-
*** H 5 7 ***				
1	85	0	114	-
2	91	46	113	-
3	2	26	113	+
4	9	0	113	-
5	211	113	85	+
6	341	336	130	+
7	17	0	122	+
8	2	198	126	-
9	67	60	87	-
10	53	141	119	-
11	458	553	92	-
12	23	5	111	-
13	2569	2456	123	+
14	53	0	111	-
15	855	894	121	-
*** H 6 7 ***				
0	548	507	124	-
1	42	31	111	+
2	38	83	116	+
3	80	189	123	+
4	96	0	119	-
5	70	0	119	+
6	496	308	131	+
7	307	170	131	+
8	525	704	132	-
9	7	3	114	-
10	19	124	80	+
11	935	776	123	-
12	653	678	86	-
13	18	35	76	-
14	211	335	106	+
*** H 7 7 ***				
1	81	0	124	+
2	40	0	121	-
3	1359	1413	154	-
4	91	0	124	+
5	245	163	130	+
6	102	0	118	+
7	92	183	118	-
8	0	159	114	+
9	906	905	90	-
10	95	92	112	-
11	116	329	77	-
12	61	141	76	-
13	334	310	111	+
*** H 8 7 ***				
0	32	0	67	-
1	867	749	99	-
2	4	249	119	-
3	900	1172	133	-
4	1367	1531	143	+
5	6	144	115	+
6	555	643	129	+
7	18	0	79	+
8	733	776	119	-
9	57	31	75	+
10	188	166	77	+
11	50	168	107	+
12	354	359	113	+
*** H 9 7 ***				
1	670	553	129	-
2	14	0	78	-
3	228	125	83	+
4	116	129	78	-
5	1320	1301	132	+
6	86	141	109	+
7	1079	1188	92	-
8	4	94	73	-
9	457	352	114	-
10	182	105	110	-
11	2514	2746	161	+
*** H 10 7 ***				
0	657	661	82	+
1	224	252	107	-
2	1010	977	89	-
3	16	46	72	-
4	203	327	75	+
5	66	81	73	+
6	1072	1119	94	+
7	87	125	106	+
8	1099	853	121	-
9	6	75	102	+
*** H 11 7 ***				
1	65	0	100	-
2	61	122	103	-
3	23	226	102	+
4	128	99	105	+
5	17	104	105	-
6	171	116	105	+
*** H 0 8 ***				
0	1827	1446	149	-
1	6	238	119	+
2	120	103	119	+
3	6352	6470	232	+
4	537	659	139	+
5	2681	3342	213	-
6	1536	1781	176	+
7	8	107	138	-
8	1682	2118	195	+
9	639	644	90	+
10	850	979	97	-
11	286	297	88	-
12	256	203	85	+
13	491	483	92	-
14	1130	876	136	+
15	669	501	120	+
*** H 1 8 ***				
1	583	759	126	-
2	40	80	114	-
3	292	291	125	+
4	353	350	127	+
5	87	83	126	+
6	112	150	122	-
7	531	416	143	-
8	559	560	153	-
9	3	18	122	-
10	3182	3294	184	+
12	1024	880	134	-
13	453	577	91	+
14	1	0	116	+
15	11	145	116	-

H	CALC	OBS	SIG	
*** H 2 8 ***				
0	999	1087	132	-
1	1895	2311	168	-
2	83	89	111	+
3	208	277	119	+
4	330	422	131	+
5	135	104	125	+
6	215	72	130	+
7	802	1105	165	-
8	3250	3225	156	-
9	32	0	121	-
10	135	420	135	-
11	279	331	122	+
12	426	246	87	+
13	91	111	84	+
14	3	0	114	+
*** H 3 8 ***				
1	285	277	119	-
2	16	79	112	+
3	301	239	123	+
4	216	296	129	-
5	322	455	135	+
6	63	0	129	+
7	674	707	151	-
8	247	246	120	-
9	942	1237	136	-
10	5	0	82	-
11	1	5	114	-
12	166	170	85	+
13	677	582	125	+
14	369	607	132	+
*** H 4 8 ***				
0	2647	2440	182	-
1	72	0	116	+
2	1	0	115	-
3	60	0	122	+
4	1088	958	151	+
5	349	159	130	-
6	308	390	95	-
7	278	296	123	+
8	1	0	119	+
9	161	41	86	-
10	0	74	117	+
11	375	349	86	+
12	18	20	84	-
13	1	45	114	-
*** H 5 8 ***				
1	3	0	122	+
2	3811	3555	218	+
3	360	400	132	-
4	278	387	133	-
5	2740	2772	135	+
6	76	148	120	-
7	1181	1237	139	+
8	152	168	85	+
9	270	262	121	-
10	91	0	117	-
11	226	214	84	+
12	8	40	115	-
13	177	313	120	+
*** H 6 8 ***				
0	213	295	91	+
1	1130	1284	140	+
2	258	193	122	-
3	208	238	134	-
4	10	31	117	-
5	3	383	119	-
6	206	245	85	+
7	19	0	119	+
8	1130	1076	137	-
9	43	64	83	+
10	44	158	83	-
11	6	0	116	+
12	267	437	121	+
*** H 7 8 ***				
1	550	822	130	-
2	24	0	121	-
3	1556	1447	107	+
4	100	0	85	-
5	18	0	114	+
6	189	222	119	+
7	635	554	89	-
8	34	111	80	-
9	158	108	117	-
10	1027	1020	133	-
11	2	238	116	+
*** H 8 8 ***				
0	0	87	81	-
1	218	109	119	+
2	189	228	119	-
3	563	317	125	-
4	422	266	84	+
5	10	54	81	+
6	32	112	80	-
7	94	34	79	+
8	309	364	117	-
9	187	293	117	-
*** H 9 8 ***				
1	175	250	81	-
2	217	500	84	-
3	27	88	80	-
4	250	300	115	+
5	268	221	116	+
6	82	125	113	-
7	64	112	114	+
*** H 10 8 ***				
1	246	176	111	+
2	2	124	109	+
3	29	145	109	+
4	135	274	110	+
*** H 1 9 ***				
1	114	69	104	+
2	1	13	[illegible]	+
3	20	32	100	+
4	29	162	105	-
5	1	0	108	-
6	753	846	87	+
8	11	0	116	+
9	0	0	84	+
10	1221	1279	105	-
11	496	287	130	-
12	231	426	130	+
*** H 2 9 ***				
0	10	62	74	-
1	169	209	107	-
2	1387	1571	134	+
3	385	696	112	-
4	26	0	109	-
5	1398	1392	136	+

H	CALC	OBS	SIG	
*** H 2 9 ***				
6	61	0	113	-
7	3	0	114	-
8	219	128	119	+
9	775	735	100	-
10	31	34	87	-
11	128	0	127	+
12	42	428	126	+
*** H 3 9 ***				
1	1471	1399	136	-
2	197	141	112	+
3	299	300	113	+
4	887	718	122	-
5	114	64	80	-
6	48	98	117	-
7	3	16	115	-
8	881	748	98	+
9	121	389	89	+
10	120	289	124	-
11	1056	843	142	-
*** H 4 9 ***				
0	1855	1822	111	-
1	1121	1286	135	+
2	280	284	117	+
3	137	218	80	-
4	10	0	80	-
5	444	504	124	-
6	2	103	116	-
7	133	106	85	+
8	0	152	86	-
9	53	0	124	+
10	155	153	126	+
11	85	327	124	-
*** H 5 9 ***				
1	50	0	118	-
2	304	99	121	-
3	58	0	117	+
4	44	0	117	+
5	54	10	119	+
6	227	259	95	+
7	105	248	125	-
8	1	0	120	-
9	62	0	125	+
10	183	309	126	-
*** H 6 9 ***				
0	10	11	86	+
1	51	0	121	-
2	191	169	86	+
3	202	104	87	-
4	38	0	86	-
5	705	812	95	+
6	78	20	86	+
7	88	152	121	+
8	59	0	122	-
9	72	334	123	-
*** H 7 9 ***				
1	285	498	92	+
2	1325	1305	108	-
3	25	96	88	-
4	78	0	126	+
5	189	112	123	+
6	341	501	129	+
7	0	242	122	+
*** H 8 9 ***				
0	193	236	123	-
1	133	0	125	-
2	514	466	131	-
3	126	155	124	-
4	27	279	123	+
*** H 0 10 ***				
0	236	0	95	-
1	823	846	134	-
2	0	8	78	-
3	486	599	91	+
4	1212	1120	98	-
5	633	644	126	+
6	712	695	125	+
7	57	0	116	-
8	95	153	125	-
*** H 1 10 ***				
1	255	86	78	-
2	113	49	78	-
3	637	808	92	+
4	4	182	81	+
5	44	291	83	+
6	18	0	118	+
7	36	181	119	-
8	0	87	122	+
*** H 2 10 ***				
0	2760	2626	131	-
1	328	230	87	-
2	391	408	84	+
3	23	159	82	+
4	1044	997	96	+
5	153	0	124	-
6	241	106	123	-
7	8	0	122	-
8	110	263	127	-
*** H 3 10 ***				
1	162	248	85	-
2	59	225	84	-
3	132	155	84	+
4	73	0	120	-
5	725	422	131	+
6	7	0	125	+
7	261	287	127	-
*** H 4 10 ***				
0	78	216	123	-
1	112	0	125	+
2	36	0	124	-
3	11	0	121	-
4	111	149	127	+
5	47	0	122	-
6	468	568	130	+
*** H 5 10 ***				
1	2	26	122	+
2	23	54	125	+
3	831	698	143	-
4	29	317	127	+
*** H 6 10 ***				
0	256	515	134	+
1	9	201	127	+

than the value 2·437 Å reported for the unsubstituted compound. The hydrogen atom appears to be, within experimental error, equidistant from the two oxygen atoms. Assessment of the full significance of this apparent centering of the hydrogen bond involves consideration of the thermal motion of the crystal, and discussion of this matter will be deferred to a later section.

The chloromaleate ion as a whole is not quite plane: calculation of the least-squares best plane by the method of Hamilton (1961) shows the average deviation of the 11 atoms from the plane to be 0·076 Å, with extremes to the two sides of 0·19 Å for O(3) and 0·16 Å for O(1). These deviations are shown in Fig. 5. The ethylenic group, however, is quite closely plane; the extreme deviations from a least-squares best plane through the six atoms of this group are 0·03 Å for H(2) and 0·01 Å for C(4). Similarly, there are but small departures from planarity at each carbon atom: the largest of the six dihedral angles formed by the 4 planes that are defined by C(4) and its three nearest neighbors is 1·6°; the corresponding quantities for the others are 0·9° for C(1), 0·6° for C(2) and 0·1° for C(3) (standard errors are 0·3°).

The largest deviations from planarity of the ion correspond to rotations of the carboxyl groups about the C–C single bonds. As measures of these rotations, we give the conformation angles* C(3)–C(2)–C(1)–O(2), −8·5° ± 0·3°, and C(2)–C(3)–C(4)–O(3), +9·0° ± 0·3°. For comparison, the conformation angle about the double bond, C(1)–C(2)–C(3)–C(4), is 1·9° ± 0·3°. It is somewhat puzzling that the carboxyl groups are rotated in the sense that displaces O(2) and O(3) to the same side of the mean plane of the ion.

All of the bond lengths are close to expected values. The dimensions of the two carboxyl groups are almost identical, indicating that the bonding is similar.

The bond lengths in the hydrogen chloromaleate ion are very similar to those reported (Darlow & Cochran, 1961) for the unsubstituted ion. The greatest difference, that in the length of the C(3)–H(2) bond, 1·088 ± 0·004 Å (this study) *vs* 0·96 ± 0·02 Å, may be attributed to a systematic discrepancy which frequently occurs in the location of hydrogen atoms by X-ray diffraction. Other differences are in the length of the C(1)–C(2) single bond adjacent to the chlorine atom, which is greater in the present case by 0·018 ± 0·004 Å, and in the C(1)–O(2) · · · O(3) angle, greater by 2·2 ± 0·3°. The foregoing errors are the combined precision measures from both determinations. As in the unsubstituted ion, both of the C–C–C angles show considerable strain (Darlow, 1961), and the considerations of strain energy presented there are also applicable to the hydrogen chloromaleate ion.

Ionic packing

Fig. 3 shows the ionic contacts between one hydrogen chloromaleate ion and its potassium ion neighbors. It is seen that three of the four oxygen atoms and the chlorine atom have potassium ion neighbors at significant contact distances. The absence of an ionic contact with O(2) provides an environmental dissimilarity between the two carboxyl groups which makes their dimensional similarity all the more noteworthy.

The overall packing arrangement can best be appreciated by examining the environment of the potassium ions, which occur in infinite sheets parallel to the **b** − **c** planes of the crystal, separated by the distance *a*/2. One type, K(1), is surrounded by six oxygen atoms at the vertices of a distorted octahedron possessing a diad axis of symmetry. The other, K(2), is surrounded by six oxygen atoms and four chlorine atoms at the vertices of a 14-sided polyhedron also possessing a diad axis. One polyhedron of each type is illustrated in Fig. 4, which shows the structure viewed nearly along

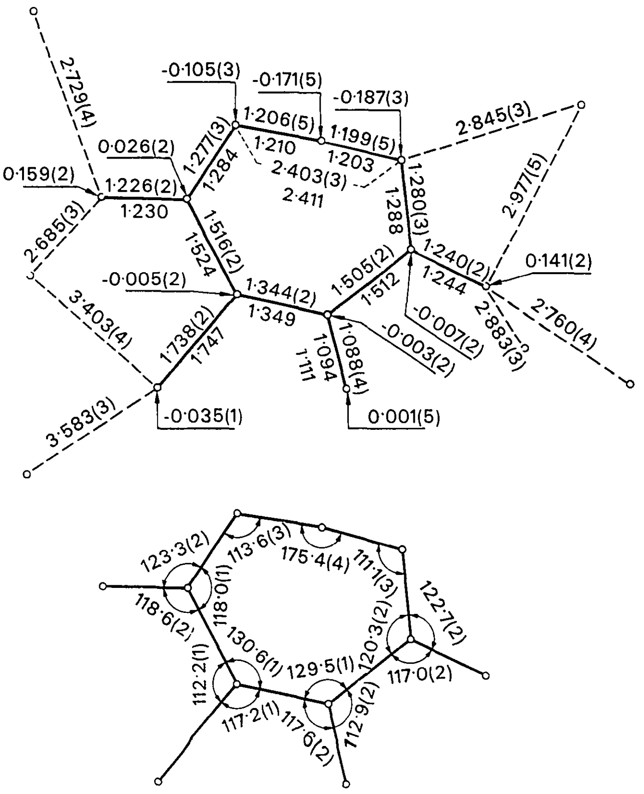

Fig. 5. Distances and angles in potassium hydrogen chloromaleate. The atoms may be identified by comparison with Fig. 3. Top diagram: two sets of interatomic distances. The upper number of each pair is the distance (Å) with its least-squares standard error (Å × 10^{-3}) in parenthesis, computed directly from the atomic parameters of Table 1. The lower number is the distance (Å) corrected for the effects of thermal motion as described in the text. Numbers with underline are the deviations (Å) from the least-squares best plane through the 11 atoms of the anion, with standard errors (Å × 10^{-3}) in parenthesis. Bottom diagram: bond angles (degrees) with least-squares standard errors (degrees × 10^{-1}) in parenthesis.

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* Conformation angle *A*−*B*−*C*−*D* is defined to be the azimuth of *CD* with respect to *BA* about the vector *BC* as polar axis of a right-handed system; that is, the clockwise angle from the projection of *BA* to the projection of *CD* viewed in the direction *BC*. An equivalent definition was given by Brown & Levy (1963).

the *c* axis. The polyhedra are linked into infinite sheets by sharing edges.

Thermal motion

In Figs. 3 and 4 the atoms are represented by the ellipsoids for thermal displacement including 50% probability. The figures suggest that the observed displacements can be accounted for as resulting mainly from rigid body oscillation and libration. An analysis on this basis by the method of Cruickshank (1956) did not yield a highly satisfactory fit, as the motions of some atoms were significantly overestimated and others were underestimated. It is plausible that the disagreement is due to neglect of internal modes of vibration, such as librations about the carbon–carbon single bonds (the largest discrepancies are for displacements out of the plane of the ion). Nevertheless, the analysis yields parameters that are plausible and are probably roughly correct. The principal root-mean-square values of the angular displacements resulting from this calculation (H and K atoms omitted, center of motion at center of mass of anion) are 5·3°, 3·5° and 3·0°. The first principal axis is within 5° of the C(1)–C(4) direction and the second is within 4° of the normal to the plane of the ion. This result is not greatly changed if the hydrogen atoms are included, nor if the center of motion is moved as much as 0·1 Å from the center of mass.

Corrected bond distances

The libration amplitudes just described were used to estimate thermal corrections to the bond distances, according to the formula (Busing & Levy, 1964)

$$S=S_0[1+0\cdot5\sum_{i=1}^{3}(\overline{\varphi_i^2}\sin^2\psi_i)]$$

in which S is the estimate of the mean separation, S_0 the uncorrected bond distance, and $\overline{\varphi_i^2}$ a mean-square amplitude of libration about a principal axis i making angle ψ_i with the bond direction. These corrected distances are shown in Fig. 5. In the case of the C(3)–H(2) bond, special treatment is required because the rigid-body model of thermal motion underestimates the thermal amplitudes of H(2), and the discrepancy clearly arises from bending of the C–H bond. Hence, an additional correction to the C–H bond length was made, using these excess thermal amplitudes and the 'riding' model discussed by Busing & Levy (1964). The results are as follows: uncorrected 1·088 Å, corrected for libration only $1{\cdot}09_4$ Å, corrected for both libration and bending $1{\cdot}11_1$ Å. We feel the accuracy of the corrected values to be of the order of 0·01 Å.

The bridging hydrogen atom

We consider now possible interpretations of the apparent central location of atom H(1) along the O · · · H · · · O bridge. The neutron diffraction analysis has determined the mean position to be at the center, in the sense of an average position over the lattice as well as over time. We ask whether the component of mean-square displacement of H(1) in the direction of the O · · · O bridge, as given by the thermal tensor, is to be ascribed to thermal oscillation about a single equilibrium point, or whether a part of this quantity should be ascribed to the existence of equilibrium positions displaced from the center and occupied at random throughout the lattice. The Bragg reflection data, of course, give no direct information on this question.

We shall discuss this question in the same way as was done by McGaw & Ibers (1963) and Ibers (1964) for the analogous question in the bifluoride ion; that is, we compare the mean-square amplitude of stretching of the O–H links in the bridge as deduced from the diffraction data with that to be expected from spectroscopic considerations. For the former, a satisfactory approximation may be taken to be the difference between the mean-square component of displacement of H(1) and the average of those for O(2) and O(3). For the latter, the mean-square displacement of a harmonic oscillator with the reduced mass of a hydrogen atom and a characteristic frequency $\nu=1600$ cm^{-1} is chosen. We neglect the effect of oscillations in which O(2) and O(3) move symmetrically and H(1) is stationary, since the effective mass and the rigidity of the ring structure would both tend to make such contributions small. The frequency 1600 cm^{-1} is the upper limit of the region of the infrared spectrum of potassium hydrogen maleate (not chlorinated) which is sensitive to replacement of H by D (Cardwell, Dunitz & Orgel, 1953) and is a value to be attributed to a very strong O · · · H · · · O bond (Rundle & Parasol, 1952). We obtain 0·017 ± 0·002 Å^2 from the diffraction data *vs.* 0·010 Å^2 from the expression $\bar{z}^2=h/(8\pi^2 c\nu m)$, given by harmonic oscillator theory. The difference is not a large one and is plausibly accounted for by some departure of the hydrogen atom potential function from a single parabolic minimum. For example, if a double minimum well is assumed, the square of the displacement of an equilibrium point from the center must be of the order of 0·007 Å^2, the difference between the above two values (the effects of displaced equilibrium and thermal amplitude are additive in the total mean-square displacement), and is thus less than the predicted thermal mean-square displacement of 0·010 Å^2. In other words, an excursion having the r.m.s. magnitude of 0·1 Å from one of the (assumed) displaced equilibrium points would bring the hydrogen atom to within this distance of the second equilibrium point; this situation would imply a low barrier, probably not greater than the zero-point vibrational level. In view of this comparison, the notion of a static displacement of the equilibrium position, involving a barrier much higher than the zero-point energy, can hardly be maintained. We therefore conclude that the hydrogen atom is effectively centered in a substantially symmetric potential well.

The stretching amplitude of the C–H Bond

Considerations similar to the foregoing may also be applied to the stretching amplitude of the C(3)–H(2) bond. Under similar assumptions, the diffraction analysis yields 0·0048 ± 0·0018 Å^2 as compared with a theoretical value of 0·0055 Å^2 for $\nu = 3020$ cm^{-1} (Herzberg, 1945). This very satisfactory agreement lends confidence to the reality of the thermal parameters determined by diffraction methods, and to the correctness of their interpretation.

The Fourier syntheses were computed with the program of A. Zalkin of Lawrence Radiation Laboratory. The least-squares refinements utilized a modification of the Busing, Martin & Levy (1962) program, prepared in part by W. C. Hamilton and J. A. Ibers of Brookhaven National Laboratory and by C. K. Johnson of this Laboratory. Distances, angles, and other derived quantities were computed with C. K. Johnson's modification of the Busing, Martin & Levy (1964) function and error program. The best-plane computation utilized a program written by W. C. Hamilton. The rigid-body thermal analysis program was that of Gantzel, Coulter & Trueblood (1961). The program for stereoscopic illustrations was prepared at this Laboratory by C. K. Johnson (1965); that for preparation of Table 2 by G. M. Brown and K. O. Martin of this Laboratory. The crystal specimen was grown by Dr S. W. Peterson, formerly of this Laboratory.

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