Hydrogen Bond Studies

13. The Crystal Structure of Hydrazinium Perchlorate Hemihydrate, $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$

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The crystal structure of $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$ has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $C2/c$, with eight molecules in a unit cell with the dimensions: $a = 8.657$, $b = 7.484$, $c = 15.285$ Å, $\beta = 99.36°$.

The structure contains columns parallel to the b axis of alternating perchlorate and hydrazinium ions. The $N_2H_5^+$ ions form hydrogen bonds to ClO_4^- ions within a column, to ClO_4^- in neighbouring columns and to water molecules. The H_2O molecules lie on twofold axes in channels formed between hydrazinium perchlorate columns, and are linked to $N_2H_5^+$ ions by hydrogen bonds (lengths: 2.837, 2.897 Å). Each $N_2H_5^+$ ion is surrounded by at least eleven oxygen atoms at possible hydrogen bond distances. There is no hydrogen bonding between either the water molecules and the ClO_4^- ions, or between the $N_2H_5^+$ ions.

The crystal structure of hydrazinium perchlorate hemihydrate, $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$, (designated HPHH hereafter) has been reported earlier by Hoogsteen and Conant [1] and by Conant, Corrigan and Hoogsteen.[2] This study was based on two projections and because of overlap some of the parameters were uncertain. The value of the N—N distance, for example, in the $N_2H_5^+$ ion was 1.65 Å while the expected value is about 1.45 Å. It was found of interest to refine this structure to get more reliable bond distances and angles, as HPHH forms part of a series of hydrazinium salts studied by the present author. The structures of $(N_2H_5)_2SO_4$,[3] $N_2H_5H_2PO_4$,[4] and $N_2H_6(H_2PO_4)_2$[5] have been reported earlier.

The structure of HPHH was determined independently of the previous investigation. The same structure was found but after refinement the differences in some bond distances were as large as 0.25 Å.

EXPERIMENTAL

HPHH was prepared by mixing hydrazine hydrate (*pro analysi*) with perchloric acid (*pro analysi*). The product was recrystallized from dilute alcohol. The sample contained 22.64 % N_2H_4; calculated for $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$ 22.65 %. (Analyzed at the Central Analytical Laboratory at this Institute.)

The crystals decomposed when irradiated with X-rays. Two single crystals had to be used to collect the data. Equi-inclination Weissenberg photographs were recorded using CuK radiation and the multiple-film technique (five films) with the crystals rotating around the b axis. The layers $0 \leq k \leq 4$ were collected from crystal 1 (length 0.4 mm, cross section 0.22×0.26 mm) and layers $5 \leq k \leq 6$ from crystal 2 (length 0.3 mm, cross section 0.16×0.24 mm). The relative intensities were measured visually by comparison with a calibrated scale. The intensity range was 1 to 15 000. The data were corrected for the Lorentz and polarization effects. No absorption correction was performed. The linear absorption coefficient μ for $CuK\alpha$ radiation is 64.7 cm^{-1}.

As a result of radiation damage, the crystals seemed to split into small fragments, as very sharp powder lines could be registrated from such crystals. The same diffraction picture was obtained from a freshly-powdered sample.

The number of independent reflexions recorded was 688 from crystal 1, and 231 from crystal 2, a total of 919 reflexions. However, 113 of these were too weak to be measured. About 82 % of the reflexions within the Cu-reflexion sphere were thus recorded.

In order to obtain information about possible phase transformations, some single-crystal Weissenberg photographs were recorded at −188°C. These indicated the same structure as at room temperature. A slightly smaller unit cell and changes in intensities due to temperature effects were observed at −188°C.

The density of HPHH was determined by weighing the specimen in air and in *m*-xylene. The value obtained was 1.91 g·cm^{-3}.

UNIT CELL AND SPACE GROUP

The diffraction symmetry $2/m$ and systematic absences for hkl with $h + k \neq 2n$ and for $h0l$ with $l \neq 2n$ indicate the monoclinic space groups Cc or $C2/c$. As shown below, the structure can be described satisfactorily in $C2/c$ with 1 chlorine, 4 perchlorate oxygens, and 2 nitrogen atoms in the general eight-fold positions:

$$(0,0,0;\tfrac{1}{2},\tfrac{1}{2},0) + (x,y,z); (\bar{x},\bar{y},\bar{z}); (\bar{x},y,\tfrac{1}{2}-z); (x,\bar{y},\tfrac{1}{2}+z)$$

and the water oxygen in the special fourfold position e (on a 2-fold axis):

$$(0,0,0;\tfrac{1}{2},\tfrac{1}{2},0) + (0,y,1/4); (0,\bar{y},3/4).[6]$$

The dimensions of the monoclinic unit cell were determined from powder photographs recorded in a Guinier-Hägg focussing camera using $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) with silicon ($a = 5.43054$ Å at 25°C) as an internal standard. The cell parameters were calculated from a set of hkl and θ by the method of least squares based on 38 reflexions. The cell parameters with estimated standard deviations are:

$$a = 8.657 \pm 0.003, \; b = 7.484 \pm 0.003, \; c = 15.285 \pm 0.005 \; \text{Å}$$
$$\beta = 99.36 \pm 0.02°. \; \text{Unit cell volume} = 977.08 \; \text{Å}^3.$$

With eight formula units of $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$ the calculated density is 1.92 g·cm^{-3}. The observed density was 1.91 g·cm^{-3}.

The unit cell dimensions given above are in fair agreement with those reported by Conant *et al.*[2] The greatest difference is found in the c dimension, which was reported to be 15.409 ± 0.043 Å.

DETERMINATION OF THE ATOMIC COORDINATES

The position of the chlorine atom was determined from the Harker vectors in a three-dimensional Patterson synthesis based on the reflexions from crystal 1. Using the known chlorine position, an F_o synthesis was then calculated, from which the coordinates of the other atoms could be deduced. The structure found was the same as reported by Conant et al.[2]

The atomic parameters together with isotropic temperature factors and inter-layer scale factors were refined by full-matrix least-squares methods. In the first stage only the reflexions from crystal 1 were used. After a few cycles the R factor $\sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.112. The reflexions from crystal 2 were now included in the refinement. After two cycles the R value was 0.113 and all shifts in this run were at the most one standard deviation. The total number of parameters varied was 37.

A difference Fourier synthesis based on the reflexions with $\sin \theta / \lambda$ less than 0.5 Å^{-1} was calculated in order to locate the hydrogen atoms. However, no definite evidence for the location of these could be obtained. The difference maps indicated anisotropy in the thermal motions of the chlorine, oxygen, and nitrogen atoms.

The isotropic temperature factors were rather high; 3.8 Å^2 for chlorine and 4.5 to 5.2 Å^2 for the oxygen and nitrogen atoms. This, together with the difference Fourier, might indicate that the noncentrosymmetric space group Cc should be used instead of the centrosymmetric $C2/c$. Some cycles of least-squares calculations with the structure described in terms of Cc were now performed. However, no improvement was obtained, so the space group $C2/c$ was considered to be satisfactory.

Another reason for the high temperature factors could be disorder. If the atoms are disordered, reorientation to an ordered structure with a changed X-ray diffraction picture can be expected when cooling the crystals. A reorientation of the hydrogen atoms only would affect the X-ray data very little. However, the fact that the X-ray photographs recorded at room temperature and at −188°C were the same except for temperature factor effects, indicates that at least the heavy atoms are ordered.

The refinement was completed with some cycles of least-squares calculations using anisotropic temperature factors for all atoms. The atomic coordinates and an overall scale factor were also varied, making a total of 69 varied parameters. The relative inter-layer scale factors used were those from the last calculation with isotropic temperature factors. In the last cycle, the shifts in the parameters were less than one third of the corresponding standard deviations. The final R value was 0.080. A difference Fourier synthesis was calculated to find the hydrogen atoms, but these could not be located.

The least-squares calculations were based on F values, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights w were calculated as follows: $w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for a and c were 4.5 and 0.018, respectively. An analysis of the weighting scheme showed that the a and c values were satisfactory. Reflexions too weak to be measured were given zero weight in all calculations. The nine strongest reflexions (inaccurately measured) were also zero weighted in the refinement, which was thus based

Table 1. Atomic coordinates with estimated standard deviations.

Atom	x	y	z
Cl	0.2035 ± 0.0001	0.0719 ± 0.0002	0.1044 ± 0.0001
O(1)	0.0907 ± 0.0004	0.1714 ± 0.0006	0.0465 ± 0.0003
O(2)	0.1261 ± 0.0004	−0.0322 ± 0.0006	0.1642 ± 0.0003
O(3)	0.3146 ± 0.0004	0.1880 ± 0.0005	0.1548 ± 0.0003
O(4)	0.2845 ± 0.0005	−0.0470 ± 0.0005	0.0538 ± 0.0002
N(1)	0.1345 ± 0.0005	0.5634 ± 0.0006	0.1358 ± 0.0003
N(2)	0.3051 ± 0.0005	0.5787 ± 0.0007	0.1390 ± 0.0003
O(W)	0	0.3197 ± 0.0007	0.2500

Table 2. Anisotropic temperature factor parameters with estimated standard deviations, each multiplied by 10^4. The expression used is: $\exp[-(h^2\beta_{11} + hk\beta_{12} + ...)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	123 ± 2	162 ± 4	46 ± 1	9 ± 3	40 ± 1	0 ± 2
O(1)	156 ± 6	206 ± 11	65 ± 2	45 ± 11	9 ± 6	45 ± 7
O(2)	155 ± 5	226 ± 10	54 ± 2	−30 ± 11	74 ± 5	8 ± 6
O(3)	139 ± 5	199 ± 10	65 ± 2	−30 ± 11	14 ± 5	−28 ± 7
O(4)	170 ± 6	205 ± 9	54 ± 2	30 ± 11	78 ± 5	−24 ± 6
N(1)	100 ± 5	255 ± 12	59 ± 2	−12 ± 11	56 ± 6	6 ± 8
N(2)	105 ± 6	253 ± 13	56 ± 2	−24 ± 11	42 ± 6	11 ± 8
O(W)	144 ± 7	199 ± 13	55 ± 2	0	55 ± 7	0

Table 3. Root-mean-square components, R_i, of thermal vibration along principal axes of the ellipsoids of vibration, calculated from the β_{ij} values in Table 2.

Atom	R_1	R_2	R_3
Cl	0.20 Å	0.22 Å	0.23 Å
O(1)	0.21	0.25	0.29
O(2)	0.20	0.26	0.27
O(3)	0.22	0.24	0.28
O(4)	0.20	0.25	0.27
N(1)	0.18	0.26	0.27
N(2)	0.19	0.25	0.27
O(W)	0.22	0.24	0.26

on 797 observations. The final R value for all 919 observed reflexions was 0.086.

The atomic scattering factors used were those of neutral chlorine, oxygen, and nitrogen, respectively. Dispersion corrections for chlorine and oxygen were included.[7]

The atomic parameters are listed in Tables 1 and 2. The root-mean-square components of thermal vibration along principal axes of the ellipsoids of vibration are given in Table 3. The observed and calculated structure factors are compared in Table 4. Tables 5 to 7 list the bond distances and angles. The standard deviations in these were calculated from the standard deviations of the atomic coordinates. The errors in the cell dimensions were also considered. The distances listed are not corrected for thermal motion.

Computer programmes. All calculations were made on a CD 3600 computer with programmes already presented in the paper preceding this.

Table 4. Observed and calculated structure factors. Reflexions not included in the refinement are indicated with an asterisk: nine strong reflexions and those which were too weak to be measured. The F_o values for the latter are given as $\frac{1}{\sqrt{2}} F_{\min}$ for the reflexions in question. By mistake the reflexion (028) with $F_o = 11.5$ and $F_c = 10.5$ was not included in the refinement or in the table below.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	18	11.8	10.6
0	0	16	8.9	8.2
0	0	14	21.2	21.6
0	0	12	4.6	3.9
0	0	10	38.4	39.4
0	0	8	26.8	29.2
0	0	6	2.3	4.7
0	0	4	170.8	181.2 *
2	0	18	3.7	3.4
2	0	16	19.5	18.2
2	0	14	6.4	6.6
2	0	12	11.8	12.8
2	0	10	20.9	22.8
2	0	8	4.1	3.9
2	0	6	15.7	18.8
2	0	4	84.6	100.2
2	0	2	107.3	134.2 *
2	0	0	159.4	172.0 *
2	0	-2	43.1	50.0
2	0	-4	191.7	171.6 *
2	0	-6	14.3	12.5
2	0	-8	21.4	23.0
2	0	-10	11.5	12.1
2	0	-12	32.5	33.0
2	0	-14	15.4	15.5
2	0	-16	5.4	5.3
2	0	-18	18.6	16.2
4	0	16	8.1	7.6
4	0	14	1.9	1.7 *
4	0	12	34.1	33.4
4	0	10	21.7	22.1
4	0	8	43.6	47.4
4	0	6	76.0	82.0
4	0	4	32.1	31.5
4	0	2	10.1	4.5
4	0	0	16.5	10.7
4	0	-2	27.9	20.4
4	0	-4	16.0	11.3
4	0	-6	18.2	16.7
4	0	-8	93.5	93.3
4	0	-10	12.9	12.1
4	0	-12	51.5	52.9
4	0	-14	24.5	24.7
4	0	-16	18.3	17.2
4	0	-18	9.6	8.0
6	0	14	3.2	2.2
6	0	12	18.5	17.4
6	0	10	4.2	3.9
6	0	8	50.8	56.9
6	0	6	17.5	18.2
6	0	4	43.0	47.1
6	0	2	14.4	11.1
6	0	0	22.5	23.4
6	0	-2	48.2	51.2
6	0	-4	6.5	7.0
6	0	-6	14.6	14.4
6	0	-8	46.4	43.8
6	0	-10	9.6	8.4
6	0	-12	57.6	56.7
6	0	-14	7.6	7.8
6	0	-16	17.1	14.3
6	0	-18	8.7	9.1
8	0	10	5.8	4.1
8	0	8	14.4	13.3
8	0	6	1.9	1.0 *
8	0	4	26.5	28.5
8	0	2	5.8	3.3
8	0	0	19.7	18.9
8	0	-2	26.5	25.4
8	0	-4	10.4	11.0
8	0	-6	23.7	22.4
8	0	-8	12.8	13.0
8	0	-10	20.2	20.4
8	0	-12	16.2	14.5
8	0	-14	1.6	0.7 *
10	0	4	4.8	4.6
10	0	2	6.2	6.9
10	0	0	28.9	26.3
10	0	-2	19.9	18.4
10	0	-4	29.9	24.8
10	0	-6	30.4	27.3
10	0	-8	12.7	12.1
10	0	-10	8.1	8.2
1	1	18	15.9	13.2
1	1	17	1.7	1.3 *
1	1	16	20.8	16.5
1	1	15	22.0	19.5
1	1	14	16.6	15.4
1	1	13	1.9	3.3 *
1	1	12	24.1	22.6
1	1	11	12.7	12.0
1	1	10	22.0	22.2
1	1	9	13.0	13.8
1	1	8	13.6	13.3
1	1	7	9.2	10.2
1	1	6	7.8	7.6
1	1	5	50.9	44.5
1	1	4	96.4	96.3
1	1	3	3.5	3.5
1	1	2	94.0	99.4 *
1	1	-3	23.5	31.0
1	1	-4	45.4	48.1
1	1	-5	92.7	93.7
1	1	-6	36.7	32.8
1	1	-7	6.9	8.0
1	1	-8	31.3	35.2
1	1	-9	3.4	2.5
1	1	-10	6.7	7.5
1	1	-11	9.5	10.0
1	1	-12	32.4	32.6
1	1	-13	8.5	9.2
1	1	-14	1.9	1.9 *
1	1	-15	5.6	5.1
1	1	-16	32.9	33.1
1	1	-17	1.8	1.3 *
1	1	-18	5.8	5.4
1	1	-19	8.1	8.0
3	1	17	4.3	3.8
3	1	16	1.7	0.4 *
3	1	15	8.5	7.9
3	1	14	14.4	12.6
3	1	13	2.7	2.5
3	1	12	6.3	6.1
3	1	11	31.9	30.8
3	1	10	17.0	15.1
3	1	9	1.8	2.6 *
3	1	8	49.7	50.4
3	1	7	1.6	1.6 *
3	1	6	1.5	2.9 *
3	1	5	1.4	0.9 *
3	1	4	83.0	81.8
3	1	3	5.4	4.6
3	1	2	55.9	52.9
3	1	1	38.4	38.6
3	1	0	65.5	63.3
3	1	-1	16.9	16.0
3	1	-2	23.3	24.2
3	1	-3	104.7	97.3
3	1	-4	4.6	4.2
3	1	-5	41.4	39.0
3	1	-6	37.8	40.0
3	1	-7	35.0	35.9
3	1	-8	12.7	11.0
3	1	-9	46.8	45.7
3	1	-10	40.9	43.4
3	1	-11	5.9	7.1
3	1	-12	25.7	27.9
3	1	-13	1.9	1.9 *
3	1	-14	25.3	28.0
3	1	-15	1.9	2.4 *
3	1	-16	18.1	18.9
3	1	-17	5.4	4.7
3	1	-18	4.0	2.0
3	1	-19	2.1	1.7
5	1	15	2.4	2.3
5	1	14	3.4	2.7
5	1	13	3.6	3.9
5	1	12	2.6	2.4
5	1	11	7.1	7.0
5	1	10	20.0	19.8
5	1	9	1.9	1.5 *
5	1	8	30.9	33.1
5	1	7	29.1	30.8
5	1	6	18.4	17.3
5	1	5	4.9	5.6
5	1	4	70.9	69.5
5	1	3	4.8	4.8
5	1	2	10.8	11.2
5	1	1	23.5	22.9
5	1	0	23.5	21.4
5	1	-1	13.1	12.6
5	1	-2	17.7	15.8
5	1	-3	9.9	8.0
5	1	-4	42.7	40.6
5	1	-5	2.2	3.2
5	1	-6	34.2	33.7
5	1	-7	49.0	44.8
5	1	-8	45.0	45.4
5	1	-9	6.7	5.7
5	1	-10	61.3	63.3
5	1	-11	10.7	11.1
5	1	-12	10.8	12.1
5	1	-13	11.4	11.6
5	1	-14	20.0	22.6
5	1	-15	6.4	5.6
5	1	-16	5.1	4.6
5	1	-17	3.3	1.7
5	1	-18	1.3	1.0 *
7	1	12	1.9	2.2
7	1	11	1.7	1.7 *
7	1	10	11.2	11.4
7	1	9	2.6	3.1
7	1	8	7.6	7.3
7	1	7	7.6	8.5
7	1	6	21.1	21.7
7	1	5	1.9	2.1 *
7	1	4	18.7	20.0
7	1	3	36.1	37.1
7	1	2	8.9	8.7
7	1	1	5.3	6.3
7	1	0	29.9	31.9
7	1	-1	14.9	15.3
7	1	-2	4.9	4.4
7	1	-3	13.2	13.7
7	1	-4	46.2	43.8
7	1	-5	8.8	10.1
7	1	-6	9.3	8.6
7	1	-7	1.9	2.7 *
7	1	-8	53.6	54.5
7	1	-9	1.9	1.3 *
7	1	-10	17.4	17.5
7	1	-11	13.5	15.0
7	1	-12	17.0	18.2
7	1	-13	1.8	0.4 *
7	1	-14	10.1	9.9
7	1	-15	7.0	6.6
7	1	-16	1.4	0.3 *
9	1	8	4.1	4.9
9	1	7	2.9	2.5
9	1	6	6.6	6.9
9	1	5	6.3	6.5
9	1	4	1.8	2.0 *
9	1	3	8.9	8.5
9	1	2	16.1	15.4
9	1	1	4.9	4.8
9	1	0	9.1	8.2
9	1	-1	20.7	20.5
9	1	-2	19.7	19.1
9	1	-3	1.8	1.2 *
9	1	-4	26.5	27.7
9	1	-5	4.5	3.3
9	1	-6	11.5	10.8
9	1	-7	4.9	3.4
9	1	-8	20.2	19.9
9	1	-9	5.4	4.3
9	1	-10	2.5	2.9
9	1	-11	1.7	1.9 *
9	1	-12	7.6	6.6
9	1	-13	1.2	0.1 *
11	1	-2	11.5	13.6
11	1	-3	2.0	2.1
11	1	-4	2.5	2.1
11	1	-5	6.1	6.7
0	2	18	6.6	7.2
0	2	17	11.3	10.5
0	2	16	3.7	3.6
0	2	15	1.8	1.0 *
0	2	14	9.6	10.1
0	2	13	5.7	5.4
0	2	12	5.6	5.0
0	2	11	30.6	27.8
0	2	10	19.3	16.6
0	2	9	12.5	12.5
0	2	7	39.4	35.7
0	2	6	7.1	6.0
0	2	5	68.6	63.8
0	2	4	107.5	96.6 *
0	2	3	110.0	126.3 *
2	2	17	6.6	7.3
2	2	16	3.0	2.8
2	2	15	5.2	3.8
2	2	14	1.8	1.4 *
2	2	13	28.7	29.8
2	2	12	1.9	1.8 *
2	2	11	13.3	12.0
2	2	10	1.8	3.1 *
2	2	9	11.7	12.6
2	2	8	9.2	10.0
2	2	7	32.1	28.2
2	2	6	88.0	89.5
2	2	5	10.1	10.6
2	2	4	68.7	64.0
2	2	3	15.9	11.5
2	2	2	108.2	99.9
2	2	1	27.1	21.9
2	2	0	109.7	98.1 *
2	2	-1	135.0	131.9 *
2	2	-2	42.7	39.2
2	2	-3	64.3	64.3
2	2	-4	51.6	39.2
2	2	-5	100.2	95.6
2	2	-6	4.5	4.5
2	2	-7	87.0	90.9
2	2	-8	7.1	4.4
2	2	-9	24.5	27.5
2	2	-10	8.9	8.6
2	2	-11	10.6	11.6
2	2	-12	17.4	18.2
2	2	-13	1.9	1.3 *
2	2	-14	24.9	28.4
2	2	-15	3.7	5.9
2	2	-16	5.8	5.7
2	2	-17	4.0	3.7
2	2	-18	7.7	8.7
4	2	16	6.1	6.0
4	2	15	8.6	8.5
4	2	14	1.8	1.4 *
4	2	13	17.6	17.2
4	2	12	5.2	4.2
4	2	11	8.5	9.2
4	2	10	10.1	10.1
4	2	9	39.0	40.6
4	2	8	17.7	18.3
4	2	7	5.5	7.1
4	2	6	42.4	41.6
4	2	5	12.3	13.9
4	2	4	9.8	9.1
4	2	3	2.9	3.0
4	2	2	78.7	77.2
4	2	1	17.0	15.8
4	2	0	7.7	6.3
4	2	-1	3.5	5.0
4	2	-2	5.6	4.0
4	2	-3	13.0	12.0
4	2	-4	11.3	8.4
4	2	-5	80.9	73.8
4	2	-6	4.2	3.7
4	2	-7	39.8	38.7
4	2	-8	1.6	5.0 *
4	2	-9	18.3	16.6
4	2	-10	9.9	9.4
4	2	-11	32.1	33.9
4	2	-12	33.2	34.1
4	2	-13	2.7	2.1
4	2	-14	12.2	14.0
4	2	-15	8.3	9.7
4	2	-16	9.3	8.6
4	2	-17	1.7	2.1 *
4	2	-18	8.5	9.5
6	2	14	3.1	3.4
6	2	13	5.8	6.6
6	2	12	14.6	14.2
6	2	11	12.6	12.3
6	2	10	1.8	0.2 *
6	2	9	11.0	12.9
6	2	8	16.8	16.9
6	2	7	16.7	18.5
6	2	6	7.4	6.8
6	2	5	37.5	40.0
6	2	4	17.2	17.4
6	2	3	12.4	12.0
6	2	2	7.4	7.9
6	2	1	25.1	23.7
6	2	0	5.5	4.5
6	2	-1	9.4	9.6
6	2	-2	12.6	10.8
6	2	-3	5.5	5.8
6	2	-4	4.9	5.9
6	2	-5	2.5	2.3
6	2	-6	15.8	16.0
6	2	-7	17.8	18.5
6	2	-8	30.9	32.5
6	2	-9	19.0	17.9
6	2	-10	10.8	12.0
6	2	-11	17.6	19.3
6	2	-12	16.5	18.1
6	2	-13	10.1	10.2
6	2	-14	5.5	5.5
6	2	-15	21.3	20.6
6	2	-16	7.1	7.0
6	2	-17	6.1	7.2
8	2	10	5.1	5.7
8	2	9	4.0	3.7
8	2	8	12.2	12.4
8	2	7	12.1	11.7
8	2	6	5.2	4.6
8	2	5	11.4	14.0
8	2	4	1.8	0.6 *
8	2	3	12.1	12.4
8	2	2	1.9	3.4 *
8	2	1	32.3	34.9
8	2	0	3.3	2.6
8	2	-1	1.9	1.0 *
8	2	-2	8.2	8.1
8	2	-3	11.0	10.3
8	2	-4	1.9	0.5 *
8	2	-5	7.3	6.9
8	2	-6	34.4	34.5
8	2	-7	2.6	1.5
8	2	-8	7.3	7.7
8	2	-9	5.2	4.7
8	2	-10	13.7	14.3
8	2	-11	4.8	3.6
8	2	-12	10.2	9.7
8	2	-13	18.8	18.2
8	2	-14	1.4	1.1 *
8	2	-15	4.3	6.4
10	2	4	4.4	5.4
10	2	3	5.9	7.0
10	2	2	1.4	1.3 *
10	2	1	11.2	13.1
10	2	0	6.8	6.5
10	2	-1	4.9	3.9
10	2	-2	9.1	10.0
10	2	-3	20.1	20.5
10	2	-4	12.5	12.4
10	2	-5	1.6	0.3 *
10	2	-6	13.4	13.2
10	2	-7	12.8	12.3
10	2	-8	3.7	4.2
10	2	-9	5.1	5.3
10	2	-10	7.2	10.2
1	3	17	1.4	1.5 *
1	3	16	5.0	3.5
1	3	15	20.3	19.9
1	3	14	1.7	2.2 *
1	3	13	13.4	14.3
1	3	12	6.9	7.3
1	3	11	45.1	43.9
1	3	10	4.7	5.0
1	3	9	44.5	45.7
1	3	8	33.4	30.4
1	3	7	40.8	39.8
1	3	6	6.3	4.9
1	3	5	35.9	40.9
1	3	4	26.4	27.0
1	3	3	37.7	39.0
1	3	2	54.4	54.1
1	3	1	16.6	14.0
1	3	0	12.4	15.5
1	3	-1	10.3	8.5
1	3	-2	59.9	57.1
1	3	-3	6.0	4.5
1	3	-4	0.9	2.8 *
1	3	-5	55.8	57.1
1	3	-6	17.8	16.4
1	3	-7	14.9	15.3
1	3	-8	1.4	0.2 *
1	3	-9	61.8	67.2
1	3	-10	6.7	6.1
1	3	-11	24.6	27.5
1	3	-12	23.5	26.6
1	3	-13	20.6	24.2
1	3	-14	3.0	2.7
1	3	-15	17.0	19.5
1	3	-16	7.1	7.9
1	3	-17	5.7	6.0
1	3	-18	1.3	0.6 *
3	3	16	1.9	1.8
3	3	15	12.6	12.3
3	3	14	5.7	6.1
3	3	13	1.7	1.3 *
3	3	12	4.3	5.0
3	3	11	23.1	24.5
3	3	10	2.5	3.3
3	3	9	13.9	16.7
3	3	8	1.7	0.6 *
3	3	7	27.9	27.6
3	3	6	7.3	6.1
3	3	5	25.2	26.2
3	3	4	85.1	80.0
3	3	3	25.8	21.1
3	3	2	21.4	21.8
3	3	1	55.5	57.3
3	3	0	17.3	17.9
3	3	-1	16.5	14.9
3	3	-2	2.5	2.3
3	3	-3	83.0	81.0
3	3	-4	10.9	9.3
3	3	-5	44.8	38.0
3	3	-6	59.7	55.9
3	3	-7	43.8	42.4
3	3	-8	5.9	5.8
3	3	-9	34.8	35.0
3	3	-10	13.5	17.3
3	3	-11	4.6	2.4
3	3	-12	7.7	8.8
3	3	-13	16.8	18.5
3	3	-14	8.8	11.1
3	3	-15	6.3	6.5
3	3	-16	10.7	12.1
3	3	-17	9.3	10.5
3	3	-18	2.4	2.0
5	3	14	2.6	2.5
5	3	13	5.0	5.1
5	3	12	1.7	0.7 *
5	3	11	7.8	7.8
5	3	10	4.9	5.7
5	3	9	2.5	2.3
5	3	8	7.3	6.9
5	3	7	10.6	10.9
5	3	6	1.7	0.4 *
5	3	5	21.2	22.4
5	3	4	11.5	4.6
5	3	3	36.6	35.2
5	3	2	3.1	4.1
5	3	1	62.5	62.9
5	3	0	33.7	31.3
5	3	-1	44.2	41.6
5	3	-2	3.7	2.5
5	3	-3	100.6	91.3
5	3	-4	1.5	1.8 *
5	3	-5	18.2	17.1
5	3	-6	17.2	15.8
5	3	-7	46.9	46.1
5	3	-8	13.0	14.1
5	3	-9	4.9	2.3
5	3	-10	5.0	4.0
5	3	-11	13.4	14.5
5	3	-12	3.5	3.5
5	3	-13	4.2	4.7
5	3	-14	7.2	8.6
5	3	-15	4.8	4.7
5	3	-16	3.1	1.3
5	3	-17	8.2	10.8
7	3	11	1.2	1.4 *
7	3	10	8.0	8.8
7	3	9	4.0	4.1
7	3	8	1.7	0.4 *
7	3	7	9.2	9.8
7	3	6	5.2	5.4
7	3	5	2.4	0.8
7	3	4	1.8	1.8 *
7	3	3	29.2	30.2
7	3	2	5.6	5.6
7	3	1	22.2	21.9
7	3	0	7.9	8.2
7	3	-1	45.9	43.8
7	3	-2	3.5	3.2
7	3	-3	36.8	35.4
7	3	-4	31.5	30.6
7	3	-5	25.5	24.6
7	3	-6	5.0	4.4
7	3	-7	28.5	26.6
7	3	-8	19.7	18.7
7	3	-9	12.4	12.4
7	3	-10	8.1	8.2
7	3	-11	16.0	16.4
7	3	-12	6.4	6.4
7	3	-13	1.6	1.0 *
7	3	-14	7.1	6.8
7	3	-15	10.5	12.9
9	3	7	2.9	3.2
9	3	6	4.2	4.9
9	3	5	10.1	12.0
9	3	4	3.1	2.7
9	3	3	14.2	12.7
9	3	2	5.2	5.7
9	3	1	7.0	7.6
9	3	0	1.7	0.4 *
9	3	-1	17.3	15.0
9	3	-2	4.2	3.6
9	3	-3	4.9	3.5
9	3	-4	4.9	3.9
9	3	-5	15.0	12.0
9	3	-6	2.9	2.9
9	3	-7	7.4	8.5
9	3	-8	13.7	12.5
9	3	-9	10.8	9.1
9	3	-10	1.4	1.3 *
9	3	-11	13.6	15.2
0	4	17	1.2	1.8 *
0	4	16	1.5	1.1 *
0	4	15	4.0	3.9
0	4	14	4.1	3.7
0	4	13	18.1	16.5
0	4	12	5.6	4.3
0	4	11	40.5	34.8
0	4	10	11.3	8.8
0	4	9	4.9	4.7
0	4	8	15.1	13.1
0	4	7	96.8	92.2
0	4	6	17.4	15.3
0	4	5	23.6	26.5
0	4	4	4.6	4.8
0	4	3	13.4	17.8
0	4	2	5.4	8.4
2	4	16	3.0	2.6
2	4	15	1.5	1.2 *
2	4	14	4.6	3.9
2	4	13	12.4	12.2
2	4	12	5.2	4.9
2	4	11	20.1	18.0
2	4	10	16.7	14.5
2	4	9	31.5	31.7

Table 4. Continued.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	4	8	1.6	0.8 *
2	4	7	43.4	38.7
2	4	6	4.4	4.5
2	4	5	14.4	13.8
2	4	4	5.0	5.8
2	4	3	76.6	66.7
2	4	2	9.2	9.0
2	4	1	9.3	9.5
2	4	0	3.4	2.3
2	4	-1	29.0	31.5
2	4	-2	4.4	2.2
2	4	-3	21.1	23.4
2	4	-4	40.4	44.7
2	4	-5	52.7	58.6
2	4	-6	8.5	7.9
2	4	-7	32.3	34.8
2	4	-8	17.2	18.0
2	4	-9	11.7	11.9
2	4	-10	1.6	2.7 *
2	4	-11	35.1	37.7
2	4	-12	1.7	1.7 *
2	4	-13	5.2	6.0
2	4	-14	1.7	2.6 *
2	4	-15	6.4	6.3
2	4	-16	1.6	0.4 *
2	4	-17	7.1	8.1
4	4	13	1.3	0.5 *
4	4	13	17.5	15.7
4	4	12	7.0	6.7
4	4	11	5.3	4.2
4	4	10	1.6	1.4 *
4	4	9	9.5	9.1
4	4	8	4.8	5.0
4	4	7	1.7	0.7 *
4	4	6	1.6	1.2 *
4	4	5	32.9	31.3
4	4	4	4.5	3.8
4	4	3	18.3	14.2
4	4	2	5.6	4.6
4	4	1	36.9	33.9
4	4	0	14.2	10.3
4	4	-1	85.3	76.7
4	4	-2	16.4	16.2
4	4	-3	11.6	8.9
4	4	-4	20.6	18.3
4	4	-5	37.0	32.6
4	4	-6	10.6	8.7
4	4	-7	21.5	21.6
4	4	-8	12.1	12.0
4	4	-9	8.1	7.6
4	4	-10	2.4	2.1
4	4	-11	9.2	9.3
4	4	-12	4.4	2.1
4	4	-13	5.5	4.8
4	4	-14	4.4	2.2
4	4	-15	17.7	17.8
4	4	-16	3.2	2.0
4	4	-17	2.2	2.9
6	4	12	1.1	0.9 *
6	4	11	10.8	10.4
6	4	10	3.1	1.8
6	4	9	9.6	8.8
6	4	8	4.1	3.0
6	4	7	12.8	12.1
6	4	6	1.7	1.0 *
6	4	5	7.7	6.3
6	4	4	7.1	6.6
6	4	3	3.8	3.1
6	4	2	14.0	14.3

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
6	4	1	38.1	39.1
6	4	0	1.7	0.2 *
6	4	-1	21.3	22.2
6	4	-2	9.9	8.3
6	4	-3	17.5	17.3
6	4	-4	1.7	0.4 *
6	4	-5	36.1	35.8
6	4	-6	1.7	0.9 *
6	4	-7	6.7	6.3
6	4	-8	1.7	1.3 *
6	4	-9	2.4	1.6
6	4	-10	2.9	2.9
6	4	-11	13.6	13.8
6	4	-12	6.4	5.7
6	4	-13	7.9	8.3
6	4	-14	3.7	2.3
6	4	-15	10.6	12.8
8	4	8	1.1	0.9 *
8	4	7	9.3	10.6
8	4	6	1.5	0.6 *
8	4	5	10.8	11.5
8	4	4	7.9	7.9
8	4	3	9.3	8.5
8	4	2	4.4	4.6
8	4	1	10.3	11.8
8	4	0	7.1	7.2
8	4	-1	4.7	4.7
8	4	-2	4.4	4.6
8	4	-3	14.8	16.9
8	4	-4	0.9	0.9 *
8	4	-5	8.5	9.7
8	4	-6	3.3	3.9
8	4	-7	2.9	3.3
8	4	-8	1.6	1.0 *
8	4	-9	17.9	18.1
8	4	-10	1.5	1.5 *
8	4	-11	1.3	1.3 *
8	4	-12	4.5	4.5
8	4	-13	10.4	14.0
10	4	-1	2.6	2.3
10	4	-2	1.0	0.2 *
10	4	-3	4.2	6.6
10	4	-4	1.0	1.5 *
10	4	-5	2.6	2.9
1	5	15	4.6	5.1
1	5	14	9.9	8.6
1	5	13	4.7	3.7
1	5	12	16.0	15.9
1	5	11	28.1	26.0
1	5	10	1.7	0.1 *
1	5	9	24.9	24.9
1	5	8	46.3	44.5
1	5	7	21.5	20.9
1	5	6	2.5	1.7
1	5	5	29.4	31.7
1	5	4	26.7	26.3
1	5	3	7.9	7.0
1	5	2	2.3	3.9
1	5	1	16.6	21.3
1	5	0	5.1	7.4
1	5	-1	2.3	2.9
1	5	-2	12.0	17.1
1	5	-3	12.7	6.3
1	5	-4	18.0	20.4
1	5	-5	24.7	27.1
1	5	-6	17.0	18.0
1	5	-7	1.5	2.8 *
1	5	-8	24.2	23.4

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	5	-9	49.3	48.7
1	5	-10	7.7	8.0
1	5	-11	15.8	15.0
1	5	-12	25.2	23.4
1	5	-13	12.6	11.4
1	5	-14	1.7	1.5 *
1	5	-15	12.1	10.2
1	5	-16	6.7	7.3
3	5	14	2.7	2.3
3	5	13	1.6	0.5 *
3	5	12	7.7	7.2
3	5	11	11.4	10.5
3	5	10	6.9	6.4
3	5	9	5.7	5.1
3	5	8	14.0	14.8
3	5	7	15.5	14.0
3	5	6	4.0	1.4
3	5	5	4.2	5.3
3	5	4	42.5	40.1
3	5	3	9.3	9.5
3	5	2	9.9	11.6
3	5	1	35.5	37.4
3	5	0	23.1	24.4
3	5	-1	3.9	3.3
3	5	-2	24.7	27.5
3	5	-3	33.9	38.1
3	5	-4	15.4	16.2
3	5	-5	25.6	25.3
3	5	-6	5.1	5.3
3	5	-7	26.2	27.3
3	5	-8	2.9	2.0
3	5	-9	17.8	17.4
3	5	-10	11.7	10.3
3	5	-11	1.7	1.3 *
3	5	-12	7.2	5.8
3	5	-13	13.1	12.1
3	5	-14	2.9	2.9
3	5	-15	3.8	3.2
3	5	-16	12.0	11.3
5	5	12	1.2	0.6 *
5	5	11	6.3	6.3
5	5	10	1.7	0.7 *
5	5	9	1.7	1.3 *
5	5	8	5.8	5.3
5	5	7	2.1	0.7 *
5	5	6	6.9	6.2
5	5	4	17.6	17.2
5	5	3	20.0	20.0
5	5	2	9.9	9.1
5	5	1	32.1	30.8
5	5	0	50.6	48.0
5	5	-1	24.2	24.6
5	5	-2	12.8	12.3
5	5	-3	58.6	59.2
5	5	-4	29.4	30.1
5	5	-5	5.1	3.8
5	5	-6	13.1	12.2
5	5	-7	19.8	19.8
5	5	-8	15.7	14.9
5	5	-9	2.4	1.7
5	5	-10	2.4	1.7
5	5	-11	3.2	6.6
5	5	-12	1.7	0.3 *
5	5	-13	1.7	0.9 *
5	5	-14	4.1	4.0
5	5	-15	4.1	4.2
7	5	8	2.6	3.0
7	5	8	1.3	0.3 *

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
7	5	7	7.5	7.6
7	5	6	1.6	0.6 *
7	5	5	1.7	0.5 *
7	5	4	9.8	9.0
7	5	3	16.0	14.6
7	5	2	4.3	4.3
7	5	1	10.2	9.1
7	5	0	17.0	16.8
7	5	-1	29.6	28.0
7	5	-2	1.7	0.3 *
7	5	-3	17.7	17.0
7	5	-4	28.6	26.6
7	5	-5	14.1	13.3
7	5	-6	1.8	1.4 *
7	5	-7	16.2	14.8
7	5	-8	15.3	13.0
7	5	-9	6.2	5.1
7	5	-10	9.3	7.5
7	5	-11	7.8	6.2
7	5	-12	8.4	7.3
7	5	-13	1.0	0.4 *
9	5	1	4.5	5.1
9	5	0	3.1	2.2
9	5	-1	7.1	6.2
9	5	-2	3.9	3.3
9	5	-3	1.4	0.9 *
9	5	-4	5.7	6.4
9	5	-5	7.3	6.4
9	5	-6	1.7	1.5
9	5	-7	1.9	2.0
0	6	16	8.1	12.8
0	6	15	1.8	1.1 *
0	6	14	5.4	5.5
0	6	13	2.1	1.9 *
0	6	12	7.2	4.1
0	6	11	21.0	9.7
0	6	10	23.0	23.8
0	6	9	2.1	1.1 *
0	6	8	20.6	19.1
0	6	7	18.9	19.1
0	6	6	20.0	19.3
0	6	5	15.6	15.5
0	6	4	36.7	39.8
0	6	3	12.8	14.5
0	6	2	6.8	7.1
0	6	1	5.7	7.1
0	6	0	10.8	10.0
2	6	13	10.8	10.8
2	6	12	6.2	5.2
2	6	11	6.1	4.9
2	6	10	10.2	11.3
2	6	9	6.4	6.4
2	6	8	3.6	0.9
2	6	7	5.0	5.0
2	6	6	33.2	37.6
2	6	5	1.9	1.0 *
2	6	4	18.2	18.0
2	6	3	6.2	6.2
2	6	2	19.6	21.5
2	6	1	4.7	4.9
2	6	0	37.3	38.9
2	6	-1	19.1	19.3
2	6	-2	9.9	9.4
2	6	-3	10.9	12.7
2	6	-4	17.6	18.2
2	6	-5	23.8	22.7
2	6	-6	3.8	2.7
2	6	-7	22.7	24.7
2	6	-8	26.7	26.9

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	6	-9	11.7	9.9
2	6	-10	7.3	7.1
2	6	-11	3.8	3.8
2	6	-12	15.0	10.8
2	6	-13	2.1	1.5 *
2	6	-14	16.5	12.9
2	6	-15	4.0	2.3
4	6	12	6.8	7.7
4	6	11	1.8	1.1 *
4	6	10	6.5	5.6
4	6	9	9.1	8.9
4	6	8	11.1	11.2
4	6	7	5.7	5.1
4	6	6	9.0	10.6
4	6	5	2.1	1.8 *
4	6	4	3.6	3.7
4	6	3	16.5	16.9
4	6	2	31.1	34.5
4	6	1	7.9	8.6
4	6	0	13.5	13.4
4	6	-1	11.6	12.1
4	6	-2	15.8	16.8
4	6	-3	3.4	3.1
4	6	-4	22.3	22.7
4	6	-5	21.3	22.0
4	6	-6	7.1	6.6
4	6	-7	7.2	7.6
4	6	-8	9.4	8.3
4	6	-9	3.0	2.2
4	6	-10	6.2	3.2
4	6	-11	6.1	3.8
4	6	-12	20.3	15.1
4	6	-13	1.9	0.9 *
4	6	-14	11.1	8.4
6	6	9	3.2	3.2
6	6	8	8.3	8.5
6	6	7	5.5	5.5
6	6	6	5.5	4.5
6	6	5	8.6	8.6
6	6	3	9.7	10.3
6	6	2	3.1	3.9
6	6	1	6.9	7.9
6	6	0	10.6	11.3
6	6	-1	6.1	5.1
6	6	-2	6.8	5.6
6	6	-3	6.1	6.2
6	6	-4	3.1	4.3
6	6	-5	3.1	1.5
6	6	-6	10.2	8.7
6	6	-7	16.3	14.1
8	6	3	2.7	2.7
8	6	2	1.7	3.6
8	6	1	10.6	11.0
8	6	0	7.5	8.5
8	6	-1	1.8	0.8 *
8	6	-2	4.5	5.3
8	6	-3	2.6	2.2
8	6	-4	3.6	3.2
8	6	-5	1.7	0.4 *
8	6	-6	14.5	14.9
8	6	-7	1.5	1.1 *
8	6	-8	3.9	4.9

DISCUSSION OF THE STRUCTURE

The structure of HPHH can be described as composed of columns parallel to the b axis of alternating $N_2H_5^+$ and ClO_4^- ions (Fig. 1). The $N_2H_5^+$ ions are nearly parallel to the a axis. These ions are hydrogen bonded to ClO_4^- ions within and in neighbouring columns and to water molecules. The H_2O molecules lie on twofold axes in channels formed between the hydrazinium perchlorate columns, and are linked by hydrogen bonds to the $N_2H_5^+$ ions but not to the ClO_4^- ions. The environment of the $N_2H_5^+$ ions is quite complicated; the number of oxygen neighbours within possible hydrogen bond distances is at least eleven (Table 6, Figs. 2, 4, and 5). Each water molecule is surrounded by four nitrogen neighbours in a roughly tetrahedral arrangement (Table 7, Figs. 2 and 3). Details of the structure will be described below.

The perchlorate ion

The perchlorate ion forms a nearly regular tetrahedron (Table 5). The uncorrected Cl—O distances are somewhat shorter than values found in the literature, for example in H_3OClO_4.[8] (Consult this paper for further references.) The corrected distances in the latter case were: 1.445, 1.478, 1.465, and 1.468 Å
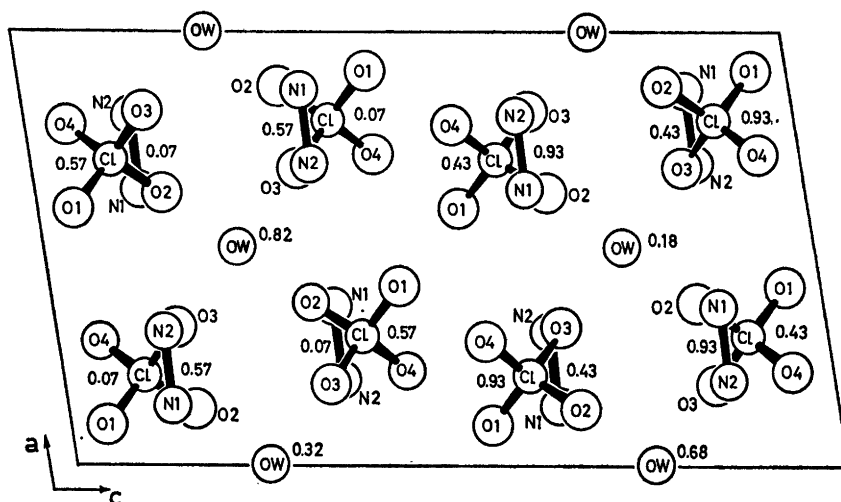
Fig. 1. The structure of $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$ projected along the b axis. The y coordinates are given for the chlorine atoms and for the centres of the N—N bonds. This and all other figures were drawn with the programme OR TEP.
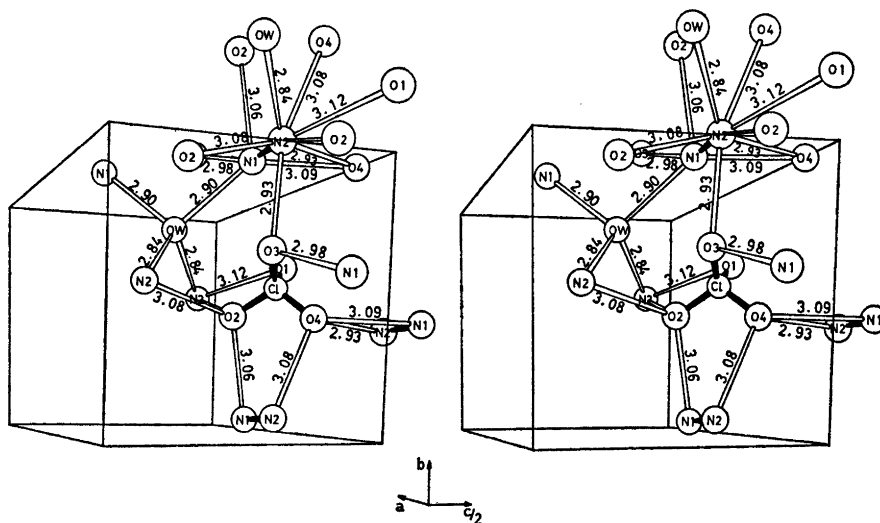

Fig. 2. Stereoscopic pair of figures showing part of the structure. All neighbours to the different atoms at distances less than 3.13 Å are drawn. Some bond distance labels are omitted to avoid overlap.

(standard deviations about ± 0.006 Å). However, if a correction for thermal motion is made in the present case, assuming riding motion (oxygen on chlorine) the agreement with the literature values is better. The corrected
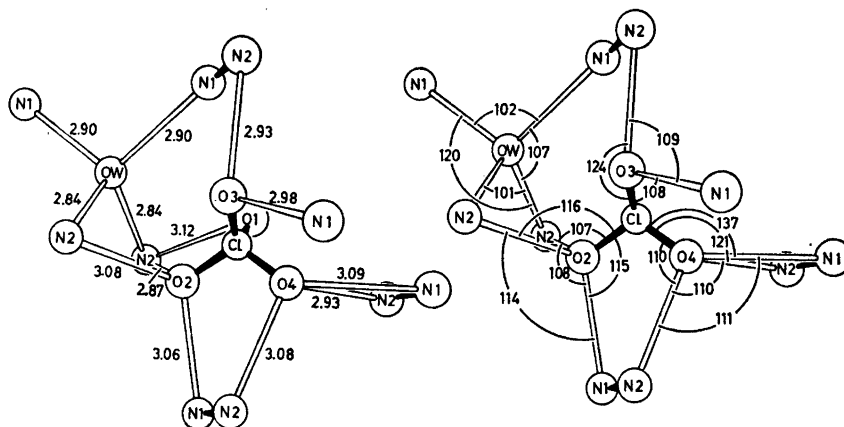
Fig. 3. Bond distances and angles around the perchlorate and water oxygen atoms. (Oxygen O(1) is omitted in the right part.) The orientation is the same as in the right part of Fig. 2.

Table 5. The ClO_4^- ion: Interatomic distances and angles with estimated standard deviations (*cf.* Figs. 2 and 3). All contacts less than 3.19 Å are listed.

1. Within ClO_4^-

Cl	—O(1)	1.418 ± 0.004 Å	O(1)—Cl—O(2)	109.5 ± 0.2°
	—O(2)	1.445 ± 0.004	—O(3)	110.7 ± 0.2
	—O(3)	1.426 ± 0.004	—O(4)	109.6 ± 0.2
	—O(4)	1.435 ± 0.004	O(2)—Cl—O(3)	109.2 ± 0.2
			—O(4)	108.9 ± 0.2
			O(3)—Cl—O(4)	108.9 ± 0.2

2. Around the perchlorate oxygens

O(1)—N(2)	3.120 ± 0.006 Å	Cl—O(1)—N(2)	96.7 ± 0.2°
O(2)—N(1)	3.060 ± 0.007 Å	Cl—O(2)—N(1)	114.8 ± 0.2°
—N(2)	2.865 ± 0.006	—N(2)	107.4 ± 0.2
—N(2)′	3.083 ± 0.006	—N(2)′	115.8 ± 0.2
		N(1)—O(2)—N(2)	108.2 ± 0.2
		—N(2)′	113.5 ± 0.2
		N(2)—O(2)—N(2)′	94.7 ± 0.2
O(3)—N(1)	2.980 ± 0.005 Å	Cl—O(3)—N(1)	108.2 ± 0.2°
—N(2)	2.934 ± 0.006	—N(2)	123.8 ± 0.2
		N(1)—O(3)—N(2)	108.5 ± 0.2
O(4)—N(1)	3.093 ± 0.006 Å	Cl—O(4)—N(1)	137.4 ± 0.2°
—N(2)	2.933 ± 0.006	—N(2)	121.3 ± 0.2
—N(2)″	3.083 ± 0.006	—N(2)″	109.6 ± 0.2
		N(1)—O(4)—N(2)	28.2 ± 0.2
		—N(2)″	110.7 ± 0.2
		N(2)—O(4)—N(2)″	109.8 ± 0.2

Cl—O distances are: 1.438, 1.458, 1.442, and 1.448 Å. (Given in the same order as in Table 5.)

The environment of the perchlorate oxygens is illustrated in Figs. 2 and 3, and some bond distances and angles are listed in Table 5. The number of nitrogen neighbours within 3.12 Å is one for O(1), two for O(3) and three for O(2) and O(4), respectively. All other neighbouring atoms are at distances greater than 3.19 Å. Hydrogen bonding between the water molecules and the perchlorate oxygens can thus be excluded.

The Cl—O—N angles where O—N represents a possible hydrogen bond are in the range 97—124°, except Cl—O(4)—N(1) which is 137°. The N—O—N angles are distributed between 95 to 114° except one, N(1)—O(4)—N(2), which is 28°.

The hydrazinium ion

The N—N distance of 1.474 ± 0.006 Å is somewhat longer than usually found for this type of bond, namely 1.44—1.45 Å.[3,4] (Further references are given in papers 3 and 4.)

The hydrazinium ion in this structure is a singly charged $N_2H_5^+$ ion. This has five hydrogen atoms and one lone pair available for hydrogen bonding. The nitrogen atom which belongs to the NH_3^+ end can thus be engaged in three hydrogen bonds as the donor of hydrogen, while the NH_2 nitrogen atom can donate two hydrogens but can accept one (or possibly more) to its lone pair.
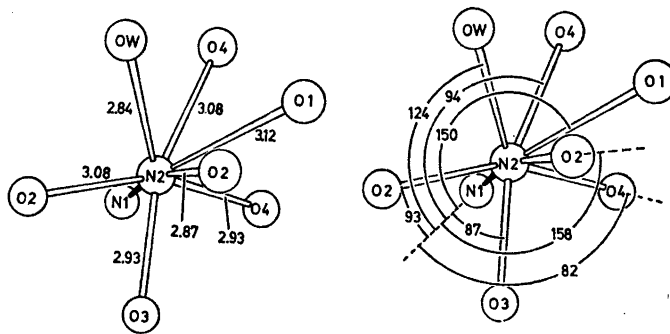

Fig. 4. Bond distances and N—N—O angles around N(2). Orientation as in Fig. 2, right part.
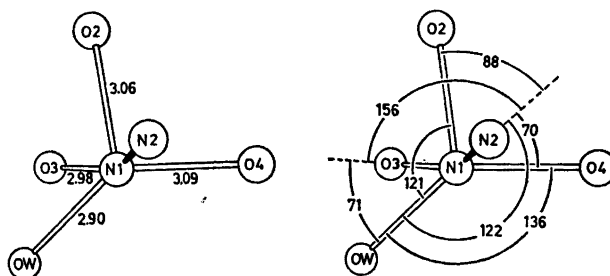

Fig. 5. Bond distances and N—N—O and O(W)—N—O angles around N(1). Orientation as in Fig. 2, right part.

The N—H···O bonds from the NH_3^+ end can be expected to be shorter than those from the NH_2 end. It is thus reasonable to suppose that N(1) is part of the NH_2 group and N(2) of the NH_3^+ group (see Table 6, Figs. 4 and 5.)

Hydrogen bonding from the NH_3^+ group. The nitrogen atom N(2) has one water oxygen at 2.837 Å and six perchlorate oxygen neighbours at 2.865— 3.120 Å (Table 6, Fig. 4). Two of these contacts, N(2)—O(3) at 2.934 Å and N(2)—O(4) at 3.083 Å, are with ClO_4^- ions within a hydrazinium perchlorate column; the rest are to neighbouring columns. The N—N—O angles subtended at N(2) show considerable variation as can be seen in Table 6. The number of oxygen neighbours at possible hydrogen bond distances is thus greater than the number of hydrogen atoms at N(2). This situation is not unusual and was found for example in $(N_2H_5)_2SO_4$,[3] where six atoms (two nitrogens and four oxygens) surrounded a NH_3^+ group at distances from 2.761 to 3.143 Å.

The hydrogen bonding at N(2) is thus quite complicated and no definite conclusion about the positions of the hydrogen atoms can be made from consideration of the N—O distances. One hydrogen atom was assumed to be engaged in a N(2)—H···O(W) bond (distance 2.837 Å). When this hydrogen atom was fixed, approximate positions of the other two were calculated, assuming that the angles N—N—H and H—N—H are 109°, and the N—H distance 1.03 Å. The latter two hydrogen atoms were located in regions where they each might exert an attraction on three oxygen atoms; one hydrogen atom on two O(2) atoms and one O(3), the other one on O(1) and two O(4) (Table 6, Figs. 2 and 4). Of these, the angles N(1)—N(2)—O(2) (158°) and

Table 6. The $N_2H_5^+$ ion: Bond distances and some selected angles with estimated standard deviations (*cf.* Figs. 2, 4, and 5). All contacts less than 3.25 Å are listed.

Around N(1)		Around N(2)	
N(1)—N(2)	1.474 ± 0.006 Å		
N(1)—O(W)	2.897 ± 0.006	N(2)—O(W)	2.837 ± 0.006 Å
—O(3)	2.980 ± 0.005	—O(2)	2.865 ± 0.006
—O(2)	3.060 ± 0.007	—O(4)	2.933 ± 0.006
—O(4)	3.093 ± 0.006	—O(3)	2.934 ± 0.006
—O(4)′	3.194 ± 0.006	—O(4)′	3.083 ± 0.006
—O(3)′	3.204 ± 0.006	—O(2)′	3.083 ± 0.006
—O(1)	3.233 ± 0.006	—O(1)	3.120 ± 0.006
N(2)—N(1)—O(W)	121.8 ± 0.3°	N(1)—N(2)—O(W)	124.4 ± 0.3°
—O(3)	156.1 ± 0.3	—O(2)	157.9 ± 0.4
—O(2)	88.0 ± 0.3	—O(4)	82.0 ± 0.3
—O(4)	69.9 ± 0.3	—O(3)	86.6 ± 0.3
—O(4)′	156.2 ± 0.3	—O(4)′	93.9 ± 0.3
—O(3)′	66.1 ± 0.3	—O(2)′	92.6 ± 0.3
—O(1)	97.6 ± 0.3	—O(1)	149.9 ± 0.3
O(W)—N(1)—O(3)	70.6 ± 0.1	O(W)—N(2)—O(2)	68.6 ± 0.1
—O(2)	121.1 ± 0.2	—O(4)	133.4 ± 0.2
—O(4)	135.6 ± 0.2	—O(3)	125.4 ± 0.2
—O(4)′	68.0 ± 0.1	—O(4)′	70.3 ± 0.2
—O(3)′	68.3 ± 0.2	—O(2)′	65.6 ± 0.1
—O(1)	69.6 ± 0.2	—O(1)	72.0 ± 0.1

N(1)—N(2)—O(1) (150°) are rather unfavourable for N—H···O bonding. These latter oxygen atoms lie near the extension of the N—N axis. Similar contacts were also found in $(N_2H_5)_2SO_4$[3] (2.919 and 2.939 Å) and in $N_2H_5H_2PO_4$[4] (3.037 Å).

No significant peaks could be found in the difference Fourier maps on or near the predicted hydrogens positions, or on other reasonable places around the hydrazinium ion. A possible reason may be that the hydrogen atoms are disordered.

Hydrogen bonding at the NH_2 group. The nitrogen atom N(1) has one O(W) at 2.897 Å, which contact is assumed to represent an O—H···N bond. The perchlorate oxygen neighbours are now one O(2) at 3.060 Å (part of a ClO_4^- ion within a column); one O(3) at 2.980 Å and one O(4) at 3.093 Å (Figs. 2 and 5). The latter two N—O contacts are to ClO_4^- ions in neighbouring hydrazinium perchlorate columns. There are also some oxygen atoms at about 3.20 Å (Table 6).

Possible hydrogen positions were derived making the same assumptions as above, and assuming that the angle *lone pair*—N—H is 109°. The O—H···N bond is then assumed to be linear, the hydrogen atom pointing at the lone pair on N(1). According to this one hydrogen atom is situated so that it may form a bent N—H···O(2) bond (length 3.060 Å) and possibly also interact weakly with O(3). However, the N—N—O(3) angle is large, namely 156° (compare with the NH_3^+ group). The other hydrogen atom may exert a weak interaction on O(4), but the N—N—O(4) angle is again unfavourable, being only about 70°. There are some additional oxygen neighbours at about 3.20 Å, which also may interact weakly with the hydrogens at N(1).

The water molecule

The water oxygen atom and the nearest nitrogen neighbours form a roughly tetrahedral arrangement; the N—O distances are 2.837 and 2.897 Å (two of each kind as the oxygens lie on twofold axes); the N—O(W)—N angles are between 101 to 120° (Figs. 2 and 3, Table 7).

The assumption was made earlier, that N(2) corresponds to the nitrogen in the NH_3^+ group, which means that the O(W)—N contacts of 2.837 Å are N(2)—H···O(W) bonds. Consequently, the remaining O(W)—N contacts (2.897 Å) are O(W)—H···N(1) bonds.

Table 7. The water molecule. Bond distances and angles with estimated standard deviations (*cf.* Figs. 2 and 3). All contacts less than 3.39 Å are given. Note that O(W) lies on a twofold axis.

O(W)—N(2)	2.837 ± 0.006 Å	N(1)—O(W)—N(1)	101.9 ± 0.3°
—N(1)	2.897 ± 0.006	—N(2)	107.4 ± 0.1
—O(2)	3.212 ± 0.006	—N(2)	120.2 ± 0.1
		N(2)—O(W)—N(2)	101.0 ± 0.3

COMPARISON WITH THE EARLIER REPORTED RESULTS

The earlier reported investigation of HPHH was based on two projections and because of overlap some parameters were unreliable, which was pointed out by the authors.[1,2] In the discussion of the present structure, no reference to the earlier reported results has been made, as there are discrepancies as a consequence of uncertain parameters. The interpretation of the hydrogen bonding system made by Conant et al.[1,2] and by the present author is principally the same.

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Received February 6, 1967.