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p-Phenylenediamine Dihydroperchlorate의 결정 및 분자구조

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The Crystal and Molecular Structure of *p*-Phenylenediamine Dihydroperchlorate

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요 약. *p*-Phenylenediamine dihydroperchlorate의 세포상수는 $a=4.79\pm0.02$, $b=9.03\pm0.02$, $c=7.12\pm0.03$Å, $\alpha=109.4\pm0.2$, $\beta=79.6\pm0.2$, $\gamma=104.6\pm0.2°$, $Z=1$이며 空間群은 $P\bar{1}$이다. 구조는 Patterson 및 Fourier법으로 해석하였으며 block diagonal 최소자승법으로 정밀화하였다. 等傾斜 Weissenberg 사진들에서 얻은 387개의 관측된 反射에 대하여 R값은 0.13이었다. 이 물질의 결정구조에서 수소결합은 아미노기와 과염소산 이온 사이에서 이루어져 있으며 2가지 형이 있다. 첫째것은, 한개의 三枝型 N···O 수소결합이고, 둘째것은, 보통형의 2개의 N···O 수소 결합이다. 한개의 *p*-phenylenediamine 그룹은 실험오차 내에서 평면이며 12개의 과염소산이온에 결합되어 있다. 그중 10개의 과염소산이온은 수소결합으로 연결되어 있으며 2개는 van der Waals힘들로 접촉되어 있다. 한개의 과염소산이온은 6개의 *p*-phenylenediamine과 4개의 과염소산이온에 의하여 둘러싸여 있다. 6개의 *p*-phenylenediamine 그룹 중 5개는 수소결합이 되어있고 나머지는 van der Waals힘으로 접촉되어 있다.

ABSTRACT. *p*-Phenylenediamine dihydroperchlorate, $C_6H_4N_2H_4\cdot2HClO_4$, crystallizes in space group $P\bar{1}$ with $a=4.79\pm0.02$, $b=9.03\pm0.02$, $c=7.12\pm0.03$ Å, $\alpha=109.4\pm0.2$, $\beta=79.6\pm0.2$, $\gamma=104.6\pm0.2°$, $Z=1$.

The structure has been solved by the Patterson and Fourier methods. The refinement by block-diagonal least-squares cycles gives $R=0.13$ for 387 observed reflexions collected on equi-inclination Weissenberg photographs with Cu$K\alpha$ radiation.

There are two different types of five hydrogen bonds. The first type consists of one trifurcated N···O hydrogen bond and the second of two normal N···O hydrogen bonds, both of which exist between the amino group and the perchlorate groups. A *p*-phenylenediamine group is approximately planar within an experimental error and bonded to twelve perchlorates: ten perchlorates forming hydrogen bonds and two being contacted with the van der Waals forces. A perchlorate group is surrounded by six *p*-phenylenediamines and four perchlorates; among the six *p*-phenylenediamines, five of them are hydrogen-bonded, and the rest contacted with the van der Waals force.

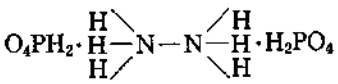
INTRODUCTION

The crystal structure of *p*-phenylenediamine dihydroperchlorate has been determined as a part of a systematic structural investigation concerning amine salts in solid state. The previous research connected with this program has concerned the following X-ray structural determinations:

Ethylendiamine dihydrochloride,[1]

$$ClH\cdot H_2N\cdot H_2C\cdot CH_2\cdot NH_2\cdot HCl$$

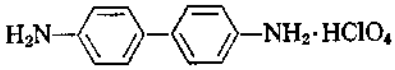
Hydrazonium diphosphate,[2]



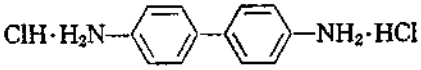
p-Phenylenediamine dihydrobromide,[3]

p-Phenylenediamine dihydrochloride,[4]

Benzidine perchlorate,[5]



Benzidine dihydrochloride,[6]



Monoethanolamine hydrochloride,[7]

$$HO\cdot CH_2\cdot CH_2\cdot NH_2\cdot HCl$$

Monoethanolamine hydrobromide,[8]

$$HO\cdot CH_2\cdot CH_2\cdot NH_2\cdot HBr\cdot$$

The present research has centred its interest on the hydrogen bonding scheme and packing of the *p*-phenylenediamine dihydroperchlorate molecules in solid state.

EXPERIMENTAL

Crystals of *p*-phenylenediamine dihydroperthlorate were prepared in the form of rough violet plates by concentrating the solution obtained by dissolving *p*-phenylenediamine in aqueous perchloric acid at room temperature. The crystals chosen for data collection were approximately cylindrical, 0.2 mm in diameter and 1.0 mm in length.

The three-dimensional X-ray data were collected from equi-inclination integrated Weissenberg photographs about the *a*, *b* and *c*-axes by the multiple-film technique and estimated by visual comparison with an intensity scale constructed from one of the reflexions. A total of 387 independent reflexions was recorded. The unit-cell dimensions were measured from aluminum-superimposed zero-layer Weissenberg photographs, using Cu $K\alpha$ radiation (λ=1.5418 Å).

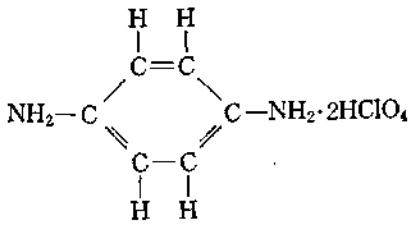
The density measured by the flotation method in a mixture of carbon tetrachloride and methyliodide agrees with the value calculated for one molecule in a unit cell into the equation

$$D_c=\frac{Z\times M.W.}{V\times N}$$

where Z is the number of formular units in the unit cell; M.W. is the molecular weight; V is the volume of the unit cell; N is Avogadro's number. Although the diffraction pattern and the measured density suggest the possibility of $P\bar{1}$ or $P1$ in space group, the shape of the molecule implies that the center of symmetry of the molecule may coincide with the origin in the space group $P\bar{1}$ assumed. This choice of the space group was justified by the results of the structure determination.

Crystal data

Compound: *p*-phenylenediamine dihydroperchlorate



Formula weight: 309.08.

Unit cell parameters:

$a=4.79\pm0.02$ Å	$\alpha=109.4\pm0.2^0$
$b=9.03\pm0.02$	$\beta=79.6\pm0.2$
$c=7.12\pm0.03$	$\gamma=104.6\pm0.2$
$V=276.5$ Å^3	$Z=1$.
$D_c=1.8_6$	$D_m=1.8_3$ g·cm^{-3}

Space group: $P\bar{1}$.

The data were corrected for Lorentz and polarization effects, and for spot-shape differences. No absorption correction was applied. Inter-layer scale factors connecting each layer were obtained by using the common reflexions. Then these structure factors were placed on an absolute scale by Wilson's method[10] (1942) to give an overall temperature factor of 1.51 Å^2 and a scale factor of 1.57. The structure factors were converted into normalized structure factors, $E(hkl)$, by the formula

$$E(hkl)=\frac{K\cdot F(hkl)\cdot k}{(\varepsilon_j\sum n_j f_j^2)^{1/2}\ \exp(-B(\frac{\sin\theta}{\lambda})^2)}$$

where K is the over-all scale factor; $F(hkl)$ is the observed structure factor; k is the weighting factor for a class of even or odd indices which is introduced if necessary to make the average of E^2 values approximately equal to one; ε is the weighting factor for a zone of reflection; n_j is the number of jth kind of atoms in the unit cell; f_j is the atomic scattering factor of jth atomic kind for a reflection (hkl); B is the overall temperature factor; θ is the Bragg angle; λ is the wave length used.

All the calculation were performed on the FACOM 230-25 computer, using the programs written by Shiono[11] (1968).

STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional sharpend Patterson function was synthesized with $E(hkl)^2$ as coefficients. The coordinates of a chlorine atom were easily deduced from the Patterson map and refined to an R value of 0.49 for all reflexions, using an overall temperature factor, where R is given by

$$R=\frac{\sum||F_0|-|F_c||}{\sum|F_0|}$$

Then a chlorine-phased Fourier synthesis was computed. The approximate atomic parameters for all the remaining non-hydrogen atoms were derived from this synthesis. With all atomic parameters and individual isotropic temperature factors calculated, two cycles of the block-diagonal least-squares refinement were carried out and reduced the R factor to 0.13. The function minimized was $\sum w(|F_0|-F_c|)^2$. The weighting scheme, w, was calculated according to the equation proposed by Cruickshank[12], $w=(a+b|F_0|+c|F_0|^2)^{-1}$, where $a=2.0\times F_{min}=0.738$, $b=1.0$ and $c=2.0/F_{max}=0.042$. The atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography[13] (1969).

The final positional and thermal parameters of the atoms with their estimated standard deviations are given in *Table* 1. *Table* 2 gives the observed and calculated structure factors.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 is a schematic drawing of the *p*-

Table 1. Final positional and isotropic thermal parameters in *p*-phenylenediamine dihydroperchlorate. The e. s. d.'s are given in parentheses in units of the last decimal place.

Atom	x	y	z	b(Å^2)
C (1)	0.443 (10)	0.388 (5)	0.310 (6)	3.0 (7)
C (2)	0.584 (9)	0.350 (4)	0.434 (6)	1.7 (6)
C (3)	0.624 (10)	0.461 (5)	0.628 (6)	1.8 (7)
N	0.664 (8)	0.200 (4)	0.366 (5)	2.1 (6)
O (1)	−0.047 (9)	0.211 (4)	0.660 (5)	5.0 (9)
O (2)	0.289 (7)	6.110 (4)	0.729 (4)	4.0 (7)
O (3)	−0.192 (8)	0.015 (4)	0.826 (5)	4.4 (7)
O (4)	0.032 (9)	0.278 (4)	0.987 (5)	4.6 (8)
Cl	0.022 (2)	0.155 (1)	0.805 (1)	1.6 (1)

Table 2. Observed and calculated structure factors.

h	k	l	F_0	F_c	h	k	l	F_0	F_c	h	k	l	F_0	F_c	h	k	l	F_0	F_c
0	0	1	15.02	14.33	0	6	3	14.51	21.00	0	6	−2	40.09	29.94	1	1	2	56.37	49.13
0	0	2	70.80	65.44	0	6	5	17.04	17.90	0	6	−3	32.74	39.71	1	1	3	25.78	19.98
0	0	3	21.92	14.53	0	7	0	16.41	15.41	0	6	−4	4.78	12.95	1	1	4	25.47	27.49
0	0	5	34.45	35.41	0	7	1	39.19	34.64	0	6	−5	27.68	29.21	1	1	6	20.15	26.37
0	0	6	21.19	20.23	0	7	3	7.86	19.80	0	6	−8	13.59	15.73	1	1	8	13.76	13.18
0	0	7	7.67	9.49	0	8	0	7.25	8.59	0	6	−6	11.39	16.26	1	2	0	66.99	68.11
0	0	8	11.39	11.79	0	8	1	13.84	16.19	0	7	−1	12.57	14.22	1	2	2	37.47	34 74
0	1	0	38.45	46.81	0	9	0	7.51	8.05	0	7	−2	19.59	23.12	1	2	3	28.96	28.88
0	1	1	84.95	92.13	0	10	0	7.74	11.15	0	7	−3	25.55	23.44	1	2	4	27.66	29.08
0	1	2	22.55	17.09	0	1	−1	15.63	17.65	0	7	−4	30.11	26.90	1	2	5	10.39	16.01
0	1	3	68.01	64.60	0	1	−2	87.76	92.20	0	7	−5	28.96	27.01	1	2	6	17.29	15.92
0	1	4	10.00	11.09	0	1	−4	19.68	22.13	0	7	−7	12.19	13.74	1	3	0	50.99	52.02
0	1	5	6.94	8.34	0	1	−5	17.43	18.12	0	7	−8	2.31	7.13	1	3	1	10.65	13.78
0	1	6	23.35	25.98	0	1	−7	18.66	17.42	0	8	−1	15.19	12.12	1	3	2	46.05	43.68
0	2	0	41.54	41.38	0	2	−1	102.93	97.82	0	8	−2	25.84	25.32	1	3	3	22.66	20.23
0	2	1	84.23	82.48	0	2	−2	22.88	32.26	0	8	−4	29.66	37.48	1	3	4	14.90	15.64
0	2	2	7.61	0.10	0	2	−4	12.74	18.94	0	8	−6	16.31	15.16	1	3	7	10.21	7.60
0	2	3	52.96	49.77	0	2	−5	20.86	25.42	0	9	−1	24.21	25.90	1	4	1	49.60	47.42
0	2	4	27.55	29.56	0	2	−6	15.80	10.35	0	9	−3	17.41	16.92	1	4	2	11.92	10.84
0	2	7	14.84	18.68	0	2	−7	11.74	10.88	0	9	−6	18.17	22.56	1	4	3	19.43	21.80
0	3	0	46.90	45.59	0	3	−2	51.50	44.49	0	10	−3	17.84	17.92	1	4	4	21.19	22.90
0	3	1	35.78	30.57	0	3	−4	8.57	19.12	0	10	−5	19.00	19.98	1	4	5	11.25	9.53
0	3	2	56.01	48.13	0	3	−5	14.43	18.42	0	10	−6	12.25	6.51	1	4	6	12.98	16.19
0	3	5	21.21	22.75	0	3	−6	20.98	20.25	0	11	−2	10.39	13.69	1	5	0	18.00	11.34
0	3	7	19.12	18.10	0	3	−7	29.02	30.41	0	11	−4	9.21	12.44	1	5	1	37.86	39.37
0	4	0	25.10	17.10	0	4	−1	43.64	33.65	1	0	0	54.41	53.13	1	5	2	37.11	33.35
0	4	1	14.53	10.65	0	4	−2	45.27	43.95	1	0	1	80.15	81.85	1	5	4	12.65	16.75
0	4	2	21.59	20.94	0	4	−3	14.33	23.79	1	0	2	44.98	39.64	1	5	6	8.98	4.09
0	4	3	18.96	21.78	0	4	−4	48.47	48.31	1	0	3	36.37	38.96	1	6	0	38.43	32.02
0	5	0	28.19	21.70	0	4	−6	25.76	23.71	1	0	4	23.84	19.30	1	6	2	41.31	47.71
0	5	1	36.47	27.72	0	5	−2	10.43	19.93	1	0	5	41.09	46.04	1	6	4	10.21	11.78
0	5	2	37.35	39.16	0	5	−3	39.23	37.99	1	0	6	17.55	17.88	1	7	0	35.15	39.77
0	5	3	15.74	18.83	0	5	−4	40.80	45.94	1	0	7	14.00	14.21	1	7	3	14.96	15.96
0	5	6	10.51	7.41	0	5	−6	28.35	26.48	1	0	8	10.10	12.53	1	8	0	11.29	7.78
0	6	0	35.23	28.59	0	5	−8	16.57	10.85	1	1	0	74.50	75.19	1	8	1	22.39	23.24
0	6	1	18.74	22.59	0	6	−1	40.02	34.55	1	1	1	52.64	56.40	1	8	3	12.86	13.52

1	9	0	12.74	12.72	1	−8	4	12.21	8.59	1	−2	−5	24.64	31.90	3	0	0	47.84	49.95
1	9	2	7.80	12.16	1	−8	5	17.82	23.91	1	−2	−6	14.43	18.94	3	0	1	5.82	1.68
1	10	0	9.47	12.52	1	−8	6	13.94	13.89	1	−3	−1	26.29	24.82	3	0	2	4.35	5.42
1	−1	0	65.93	65.62	1	−8	7	22.55	23.61	1	−3	−2	44.00	39.36	3	0	3	9.21	9.26
1	−1	1	59.54	54 32	1	−8	8	12.23	7.30	1	−3	−3	20.21	16.50	3	0	4	22.82	24.36
1	−1	2	70.33	69.89	1	−9	0	12.76	14.70	1	−3	−4	12.53	14.01	3	0	5	27.96	29.69
1	−1	3	22.06	34.85	1	−9	1	11.70	15.28	1	−3	−5	18.37	18.54	3	0	6	14.27	14.63
1	−1	4	57.78	53.47	1	−9	2	14.14	13.95	1	−4	−1	22.88	22.30	3	0	7	12.43	8.70
1	−1	5	22.88	22.12	1	−9	3	18.72	17.90	1	−4	−2	14.49	14.02	3	1	0	16.47	15.28
1	−1	7	21.59	21.17	1	−9	4	19.29	18.45	1	−4	−3	40.70	45.29	3	2	0	31.27	32.45
1	−2	0	31.82	33.32	1	−9	5	24.70	20.70	1	−5	−1	30.84	25.37	3	3	0	35.17	37.44
1	−2	1	97.75	92.47	1	−10	0	11.12	11.16	1	−5	−3	14.27	11.04	3	4	0	12.12	7.03
1	−2	2	43.37	45.02	1	−10	2	14.37	14.00	1	−5	−4	20.92	20.87	3	6	0	13.55	15.49
1	−2	3	20.23	28.26	1	−10	5	01.94	10.30	1	−6	−1	21.84	22.45	3	7	0	7.23	9.34
1	−2	4	37.60	46.06	1	−10	6	9.10	8.82	1	−6	−2	31.86	36.86	3	8	0	16.47	15.65
1	−2	5	12.08	16.94	1	−11	1	11.06	13.43	1	−6	−3	11.74	10.74	3	−1	0	12.76	10.25
1	−2	6	54.19	56.15	1	0	−1	55.41	59.20	1	−6	−4	16.00	13.72	3	−2	0	31.47	30.87
1	−2	8	11.35	9.33	1	0	−2	3.22	3.06	1	−7	−1	22.23	22.16	3	−3	0	55.11	54.09
1	−3	0	27.35	21.26	1	0	−3	16.80	18.93	1	−7	−3	16.31	18.99	3	−4	0	16.25	14.21
1	−3	1	31.68	33.34	1	0	−4	15.29	8.59	1	−8	−1	20.66	18.36	3	−5	0	8.41	10.53
1	−3	3	71.76	78.57	1	0	−5	22.66	20.02	1	−8	−2	13.08	13.68	3	−6	0	20.31	12.29
1	−3	2	16.65	26.56	1	0	−6	15.74	19.09	1	−8	−3	10.94	8.55	3	−7	0	20.41	13.31
1	−3	4	11.12	17.25	1	0	−7	14.88	11.94	1	−10	−1	13.65	12.55	3	−8	0	7.31	14.51
1	−3	5	27.90	28.04	1	1	−1	123.99	124.40	2	0	0	49.09	52.63	3	−9	0	10.37	8.95
1	−3	8	15.10	19.98	1	1	−2	20.15	23.97	2	0	1	3.16	0.32	3	−10	0	12.70	12.81
1	−4	0	23.47	27.37	1	1	−3	8.02	4.19	2	0	2	5.10	10.26	3	0	−1	4.98	3.80
1	−4	1	17.49	18.62	1	1	−4	20.17	19.34	2	0	3	15.90	15.32	3	0	−2	33.09	31.39
1	−4	2	24.08	21.58	1	1	−5	21.02	23.92	2	0	4	9.25	10.20	3	0	−3	2.37	2.48
1	−4	3	43.76	49.55	1	1	−6	13.02	10.93	2	0	5	28.11	25.95	3	0	−4	21.33	20.63
1	−4	5	28.11	29.84	1	2	−1	6.33	12.71	2	0	6	15.00	19.10	3	0	−5	19.26	18.47
1	−4	6	16.51	13.44	1	2	−2	8.14	12.57	2	0	7	5.08	7.30	3	0	−6	1.69	5.32
1	−4	7	24.00	23.13	1	3	−1	45.15	38.79	2	0	8	18.27	16.59	4	0	0	25.31	21.04
1	−5	0	19.92	14.76	1	3	−2	55.64	46.18	2	1	0	31.45	32.72	4	0	1	32.27	37.75
1	−5	1	20.57	15.35	1	3	−3	10.80	19.32	2	2	0	32.57	37.88	4	0	3	23.92	27.73
1	−5	4	36.70	40.29	1	4	−1	67.05	62.04	2	3	0	15.84	19.79	4	0	4	6.20	9.79
1	−5	6	24.66	22.84	1	4	−2	27.62	31.81	2	4	0	10.29	6.91	4	0	5	3.86	4.83
1	−5	8	13.53	14.57	1	5	−1	34.04	38.47	2	5	0	11.74	11.38	4	0	6	14.06	14.94
1	−6	3	49.19	39.39	1	5	−2	10.00	0.88	2	6	0	18.04	17.98	4	1	0	8.14	9.62
1	−6	4	13.33	13.76	1	5	−4	38.45	39.62	2	8	0	5.39	5.59	4	2	0	23.74	18.65
1	−6	5	28.08	22.05	1	5	−3	31.06	29.16	2	9	0	18.84	19.75	4	3	0	24.25	19.06
1	−6	6	13.02	19.24	1	6	−3	33.53	35.55	2	−1	0	2.06	4.74	4	4	0	18.00	16.70
1	−6	7	13.55	6.47	1	7	−2	24.96	27.21	2	−2	0	56.54	56.23	4	5	0	11.63	11.13
1	−6	8	16.31	16.98	1	8	−2	13.49	16.36	2	−3	0	25.31	28.50	4	6	0	10.10	14.45
1	−7	0	17.82	16.59	1	9	−1	14.33	14.45	2	−4	0	41.37	35.13	4	−1	0	22.82	26.72
1	−7	2	11.06	10.90	1	9	−2	13.78	1.55	2	−5	0	6.90	1.22	4	−2	0	3.02	3.87
1	−7	3	24.15	29.84	1	10	−2	18.49	22.26	2	−6	0	12.94	11.09	4	−3	0	8.08	4.71
1	−7	4	34.11	31.78	1	−1	−1	73.19	74.96	2	−7	0	21.96	28.10	4	−4	0	18.00	10.83
1	−7	5	34.84	31.15	1	−1	−2	17.47	19.86	2	−9	0	17.92	14.55	4	−5	0	17.98	14.29
1	−7	6	11.57	1.27	1	−1	−3	17.88	17.72	2	−10	0	25.47	23.26	4	−6	0	5.31	2.61
1	−7	7	13.19	10.01	1	−1	−4	15.90	19.61	2	0	−1	31.41	24 62	4	−7	0	24.08	21.86
1	−7	8	9.78	14.59	1	−1	−6	13.55	15.73	2	5	−2	13.61	13.84	4	−8	0	14.90	13.45
1	−8	0	6.27	8.39	1	−2	−1	50.27	48.12	2	0	−4	6.67	7.95	4	0	−1	5.49	3.99
1	−8	1	27.25	24.12	1	−2	−2	7.61	13.38	2	0	−0	21.33	24.24	4	0	−2	26.45	25.72
1	−8	2	19.12	18.84	1	−2	−3	22.59	22.31	2	0	−6	2.94	4.20	4	0	−4	12.86	15.03
1	−8	3	14.25	15.48	1	−2	−4	26.39	25.18	2	0	−7	6.10	8.11	4	0	−5	11.45	14.32

5	0	0	18.23	19.67	5	1	0	6.59	9.04	5	−3	0	2.37	2.88	5	0	−2	11.61	13.43
5	0	1	10.43	12.38	5	2	0	11.47	12.12	5	−4	0	15.16	17.24	5	0	−3	6.20	8.72
5	0	2	3.61	4.06	5	3	0	9.78	11.09	5	−6	0	11.12	8.58	6	−1	0	8.47	12.83
5	0	3	17.59	16.60	5	4	0	2.45	3.86	5	−7	0	11.23	15.41	6	−3	0	12.74	14.89
5	0	4	15.45	14.63	5	−1	0	20.63	17.65	5	−8	0	3.18	10.67	6	−4	0	2.65	4.14
5	0	5	18.72	18.53	5	−2	0	7.16	8.50	5	0	−1	2.16	4.12					

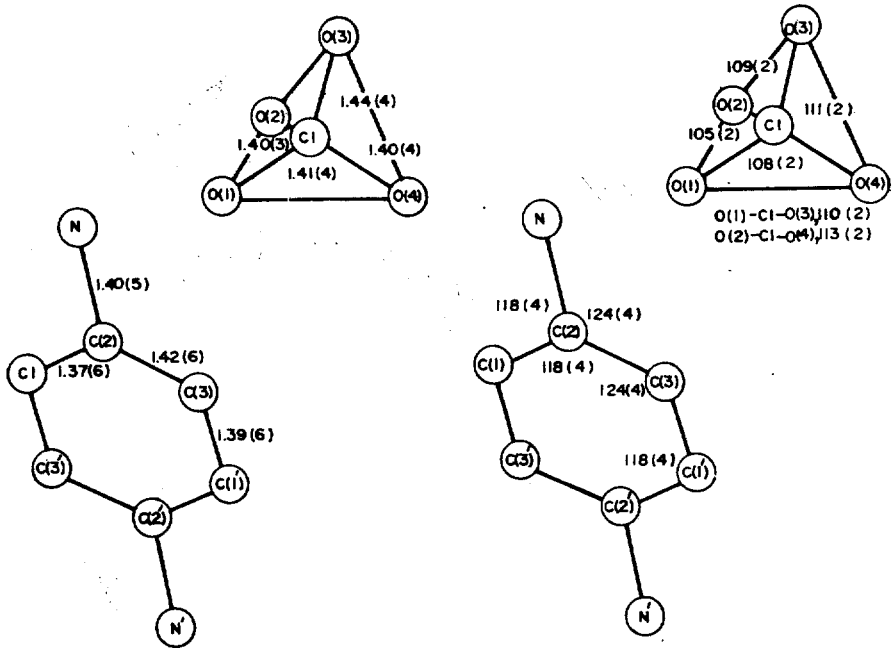


Fig. 1. A schematic drawing of the *p*-phenylenediamine dihydroperchlorate showing the labelling of the atoms and the intramolecular bond lengths (Å) and angles (°).

Table 3. Intramolecular bond distances and angles in *p*-phenylenediamine dihydroperchlorate. The e.s.d.'s are given in parentheses in units of the last decimal place.

A. P-Phenylene diamine	C(1)-C(2)	1.37(6)Å	C(1)-C(2)-C(3)	118(4)°
	C(2)-C(3)	1.42(6)	C(1)-C(2)-N	118(4)
	C(3)-C(1′)	1.39(6)	C(2)-C(3)-C(1′)	124(4)
	C(2)-N	1.40(5)	C(3)-C(1′)-C(2′)	118(4)
			C(3)-C(2)-N	124(4)
B. Perchlorate	Cl-O(1)	1.41(4)	O(1)-Cl-O(2)	105(2)
	Cl-O(2)	1.40(3)	O(1)-Cl-O(3)	110(2)
	Cl-O(3)	1.44(4)	O(1)-Cl-O(4)	108(2)
	Cl-O(4)	1.40(4)	O(2)-Cl-O(3)	109(2)
			O(2)-Cl-O(4)	113(2)
			O(3)-Cl-O(4)	111(2)

phenylenediamine dihydroperchlorate molecule showing the labelling of non-hydrogen atoms and the intramolecular bond lengths and angles with estimated standard deviations. *Table* 3

also gives these bond lengths and angles.

The *p*-Phenylenediamine. The mean bond length and angle in the benzene ring are 1.39 (6) Å and 120(4)° respectively, and the C(2)—N bond length of 1.40(5) Å is in agreement with the C—N bond of 1.41 Å in sulfaguanidine monohydrate[14]. The deviations of atoms from the best plane of a *p*-phenylenediamine are given in *Table* 4. From *Table* 4 it is seen that the *p*-phenylenediamine is planar within an experimental error.

The Perchlorate. The average bond length 1.41(4) Å of Cl—O and the average bond angle 109(2)° of O—Cl—O lie close to Boer's values[15] 1.426(2) Å and 109.5(2)°, respectively, which are reported in *N, N, N', N'*-tetramethyl-*p*-diaminobenzene perchlorate.

The Hydrogen Bond. The projections of *p*-phenylenediamine dihydroperchlorates along the *a* and *b*-axes are given in *Fig.* 2, in which the hydrogen bonds are shown by broken lines. *Fig.* 3 also shows the formation of the hydrogen bonds surrounding a amino group in the *p*-phenylenediamine dihydroperchlorate. *Table* 5 gives the interatomic distances between molecules.

Table 4. Deviations of the atoms from the least-squares plane in *p*-phenylenediamine. The equation of the plane is expressed in the from $Ax+By+Cz=D$, where x, y and z are in Å.

Atoms included in plane	Distances from the best plane	Constants
C (1)	−0.03	$A=6.744$
C (2)	0.01	$B=0.348$
C (3)	−0.03	$C=-0.388$
C (1′)	0.03	$D=1.975$
C (2′)	−0.01	
C (3′)	0.03	
N	0.01	
N (′)	−0.01	

Between the amino group and perchlorates, there are two types of the N···O hydrogen bonds: the first is one trifurcated hydrgen bond and the second two normal ones. One of the two hydrogen atoms in the amino group are involved in a trifurcated hydrogen bond to the oxygen atoms O(4*g*), O(2*e*) and O(3*d*) in three symmetry related perchlorate groups; the lengths of the three hydrogen bonds are N···O (4*g*) = 3.13, N···O(2*e*) = 2.72 and N···O(3*d*) = 2.81 Å, and the angles around the nitrogen

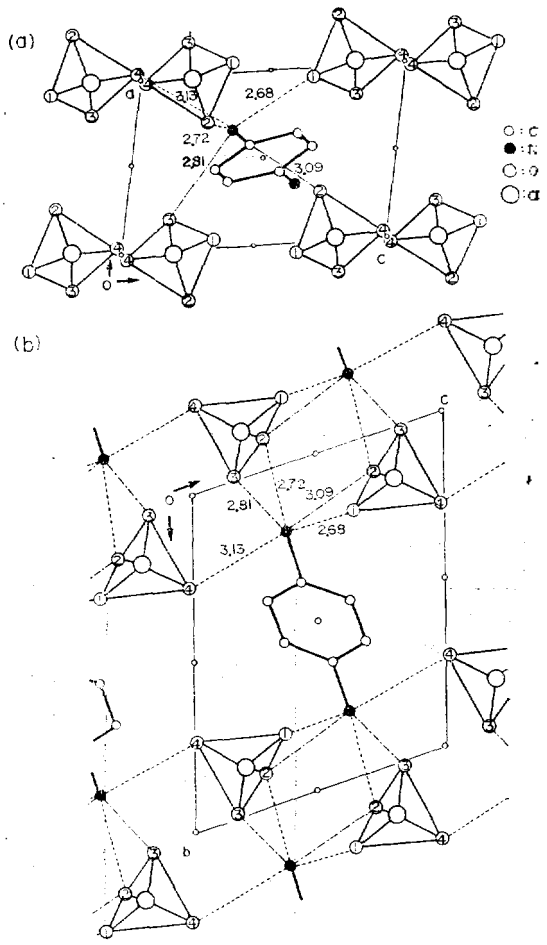


Fig. 2. Projections of *p*-phenylenediamine dihydroperchlorates along the (a) *b*-axis and (b) *a*-axis. In (a), the hydrogen bonds towards upper perchlorates are shown in heavy broken lines, and those towards lower ones in chain lines.

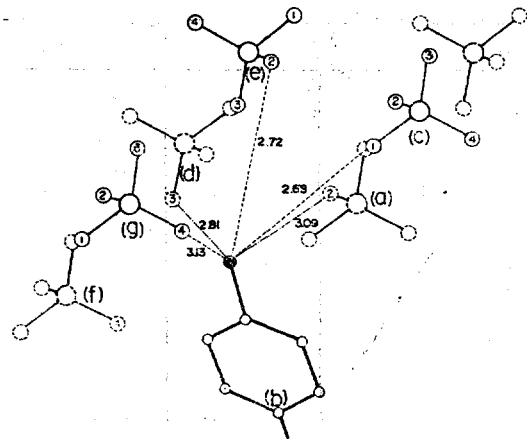


Fig. 3. The formation of the hydrogen bonds surrounding the amino group. Alphabetical letters show symmetry code.

Table 5. Interatomic distances in *p*-phenylenediamine dihydroperchlorate.

Hydrogen bonds		
N···O (1c)	2.68 Å	
N···O (2a)	3.09	
N···O (4g)	3.13	trifurcated
···O (2e)	2.72	
···O (3d)	2.81	
Other short contacts		
C (1)···O (4*f*)	3.05	
C (3)···O (1*c*)	3.15	
O (2*a*)···O (3*c*)	3.09	
O (2*a*)···O (1*c*)	3.08	

Symmetry code:

a	*x*,	*y*,	*z*
b	$-x$,	$-y$,	$-z$
c	$1+x$,	*y*,	*z*
d	$-1-x$,	$-1-y$,	$-z$
e	$-x$,	$-1-y$,	$-z$
f	*x*,	*y*,	$1-z$
g	$1+x$,	*y*,	$1-z$.

atom are O(4*g*)···N···O(2*e*)=98.3, O(4*g*)···N···O(3*d*)=97.6 and O(2*e*)···N···O(3*d*)=67.8°.

Table 6. Interatomic hydrogen bonds reported in other compounds.

A. N···O		
Ammonium sulfate	2.99,	2.90Å
Urea	3.03,	2.99
Dimethylglyoxime	2.77	
Hydroxylammonium perchlorate[18]	2.752~3.155	
3-Methyl-3-pyrazolin-5-one[19]	2.627,	2.713
B. N···O (trifurcated)		
Ammonium sulfate	3.33	3.06
	3.19	3.05
	3.19	3.05

On the other hand, two normal N···O hydrogen bonds are formed with the distances, N···O (1*c*)=2.68 and N···O(2*a*)=3.09 Å, in which the nitrogen atom would act both as a donor of a hydrogen atom in one hydrogen bond and as an acceptor of a hydrogen atom in another. Thus, the amino group exists as a NH_3^+ ion. Some related types of the N···O hydrogen bonds reported in other compounds are listed in *Table*[16] 6 for comparison.

Four short intermolecular distances less than 3.20 Å are observed and given in *Table* 5. Considering van der Waals radii[17] are 1.57 and 1.40 Å for carbon and oxygen atoms respectively, these intermolecular distances appear to be the limit of the van der Waals contact.

Judging from the results so far available, the *p*-phenylenediamine dihydroperchlorates are linked through three-dimensional intermolecular hydrogen bonds as well as the van der Waals interactions. The hydrogen bonding scheme in a *p*-phenylenediamine dihydroperchlorate is different, due to the fact that it contains a trifurcated hydrogen bond, from those found in other amine salts. Comparison is given in *Table* 7[1~8].

Table 7. Hydrogen bonding schemes in amine salts.

Compounds	Space group	Lattice constants		Types	Distances
Ethylenediamine dihydrochloride	$P2_1/c$	a=4.44(2) Å b=6.88(2) c=9.97(2)	β=92(1)°	N—H···Cl	3.14 Å 3.16 3.22
Hydrazonium diphosphate	$P2_1/c$	a=4.52(2) b=8.06(3) c=10.74(3)	β=100.0(5)	N—H···O	2.89 2.62 2.79
p-Phenylenediamine dihydrobromide	$P\bar{1}$	a=4.52(2) b=6.13(2) c=8.88(3)	α=111(1) β=97(1) γ=101(1)	N—H···Br	3.33 3.38 3.41
p-Phenylenediamine dihydrochloride	$P\bar{1}$	a=4.38(2) b=5.90(2) c=8.76(3)	α=110(1) β=96(1) γ=101(1)	N—H···Cl	3.26 3.29 3.30
Benzidine perchlorate	P_{mnn}	a=7.48 b=22.42 c=10.23		N—H···O N—H···N	2.96 2.78
Benzidine dihydrochloride	$P\bar{1}$	a=4.38(1) b=5.76(1) c=12.82(2)	α=101.5(2) β=99.5(2) γ=99.5(2)	N—H···Cl	3.21 3.19 3.24
Monoethanolamine hydrochloride	$P\bar{1}$	a=4.24(2) b=7.44(2) c=7.48(2)	α=102.4(3) β=91.1(3) γ=77.2(3)	N—H···Cl N···H···O O—H···Cl	3.15 3.24 3.28 2.90 3.14
Monoethanolamine hydrobromide	$P\bar{1}$	a=4.54(3) b=7.45(3) c=7.76(4)	α=102.5(2) β=93.6(2) γ=78.7(2)	N···Br N···O O···Br	3.39 3.40 3.40 2.93 3.29

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