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The Crystal Structure of *p*-Phenylenediamine Dihydrochloride

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p-Phenylenediamine Dihydrochloride의 結晶構造

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要 約

p-Phenylenediamine dihydrochloride의 結晶構造를 X-線 廻折法을 利用하여 解明하였다. 이 結晶은 三斜晶系에 屬하며, 空間群은 $C_i^1-P\bar{1}$이고, 格子常數는 $a=4.38\pm0.02$, $b=5.90\pm0.02$, $c=8.76\pm0.03$ Å, $\alpha=110\pm1$, $\beta=96\pm1$, $\gamma=101\pm1°$이다. 그리고 單位格子속에 들어있는 化學單位數, Z는 1이다. 各原子의 座標는 *a*, *b* 및 *c* 軸에 따른 二次元的인 電子密度의 投影 및 (F_o-F_c)合成에 依하여 얻었다. 이 結晶構造와 이미 硏究된 aliphatic diamine의 hydrogen halide들의 構造와를 比較하였다.

Abstract

The crystal structure of *p*-phenylenediamine dihydrochloride has been determined from X-ray oscillation and Weissenberg photographs. The crystal is triclinic, space group $C_i^1-P\bar{1}$, with cell dimensions $a=4.38\pm0.02$, $b=5.90\pm0.02$, $c=8.76\pm0.03$ Å, $\alpha=110\pm1$, $\beta=96\pm1$ and $\gamma=101\pm1°$. There is one molecule in the unit cell.

The atomic coordinates were found by means of two-dimensional Fourier projection and (F_o-F_c) projection along the *a*, *b* and *c* axes. The structure of *p*-phenylenediamine dihydrochloride is discussed in relation to the structures of hexamethylenediamine dihydrochloride, hexamethylenediamine dihydroiodide and ethylenediamine dihydrochloride.

Introduction

Among aliphatic diamine hydrogen halide salts, the crystal structures of hexamethylenediamine dihydrochloride[1], hexamethylenediamine dihydroiodide[2] and ethylenediamine dihydrochloride[3] have hitherto been determined by X-ray diffraction method. In these crystals, the modes of N—H···X (X: halogen) hydrogen bonding were provided; in the first crystal, one of its nitrogen atom within diamine residue forms three hydrogen bonds and the other nitrogen atom forms two hydrogen bonds. In the other two crystals, each of the nitrogen atoms within diamine residue form three hydrogen bonds respectively.

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The investigation have been undertaken in order to provide with the additional information concerning the mode of the hydrogen bonding.

Experimental

p-Phenylenediamine dihydrochloride was obtained in the form of reddish brown plate-like crystals from water solution in dark room. The crystals were reduced by slicing and dissolving to a cylinder about 0.1 mm. in diameter.

Samples were mounted along the three crystal axes, and oscillation and equi-inclination Weissenberg photographs were taken with Cu—K_α radiation for the zero layer lines and for all obtainable layer lines about *a*, *b* and *c* axes. Multiple-film techniques were employed. The relative intensities were estimated visually with the aid of a calibration strip produced with the X-ray set under carefully controlled conditions. The intensities were corrected for Lorentz and polarization factors.

Unit Cell and Space Group

The accurate unit cell dimensions were determined by Buerger's back-reflection method[9] using (h 0 0), (0 k 0) and (0 0 l) reflections. There were $a=4.38\pm0.02$, $b=5.90\pm0.02$, $c=8.76\pm0.03$ Å, $\alpha=110\pm1$, $\beta=96\pm1$ and $\gamma=101\pm1°$. The density of the crystal was determined by flotation to be 1.485 g/cm^3, which corresponds to one (calculated 0.977) molecule of the *p*-phenylenediamine dihydrochloride in the unit cell. The observed systematic extinctions restrict in space group to $P\bar{1}$ or $P1$. Choice of space group is fallen upon $P\bar{1}$ by structure factors calculation during interpretation of Patterson maps, and is justified by the resulting electron density maps projected along the *a*, *b* and *c* axes.

Determination of the Structure

Suitable rough structure was rather easily deduced; Patterson projections on (1 0 0), (0 1 0) and (0 0 1) showed prominent Cl—Cl peaks and other peaks which could be assigned to Cl—C and Cl—N vectors. Then, the x, y, z parameters are roughly determined from the consideration of the structure factors of certain (0 k l), (h k 0) and (h 0 l) reflections.

Fourier projections along the *a* and *b* axes showed clearly resolved view of the molecule. Parameters obtained from these projections did not greatly differ

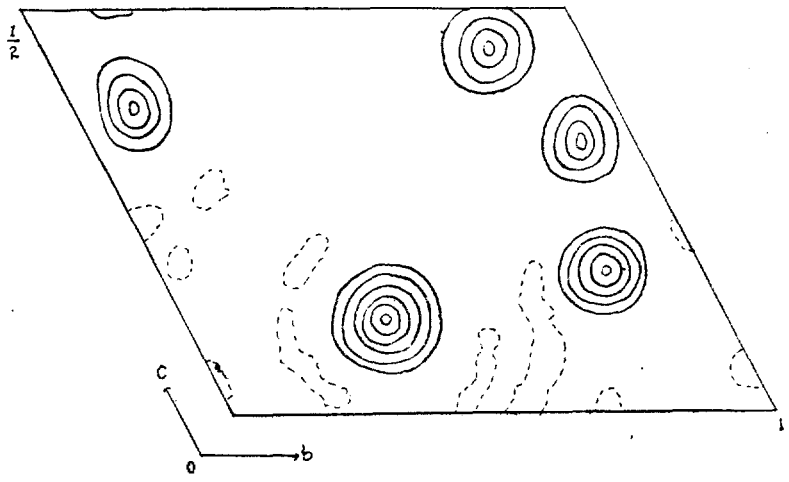

Fig. 1 Fourier projection of the electron density along the *a*-axis (arbitrary scale).

from the initial set and led to no change in sign of F_{0kl} and F_{h0l}. After five cycles of F_c and (F_o-F_c) syntheses the reliability factors, R, were 0.10, 0.15 and 0.14 for $0kl$, $h0l$ and $hk0$ reflections respectively, non-observed reflections being omitted.

The final electron density projections are shown in Fig. 1, Fig. 2 and Fig. 3. Final atomic parameters are given in Table I, and comparison of F_o and F_c is shown in Table Ⅱ.

Discussion of the Structure

The interatomic distances and bond angles are given in Table Ⅲ and the molecular dimensions are shown in Fig. 4.

The molecule is a *trans* type with a center of symmetry in it.

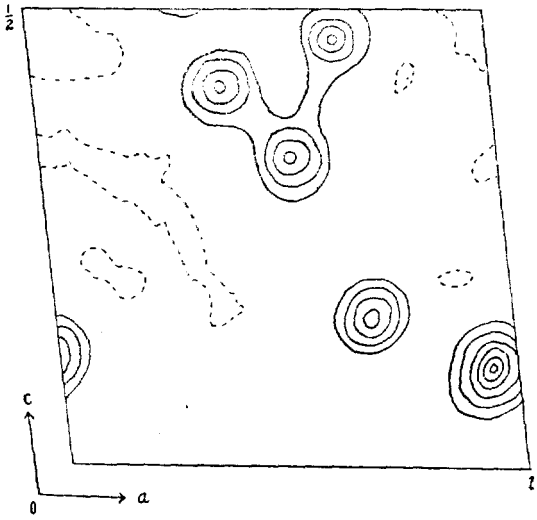

Fig. 2 Fourier projection of the electron density along the *b*-axis (arbitrary scale).

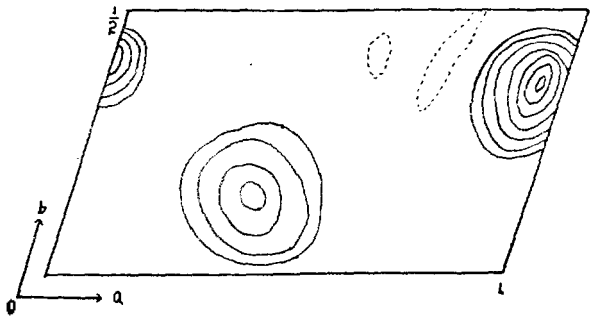

Fig. 3 Fourier projection of the electron density along the *c*-axis (arbitrary scale).

The three C—C distances are 1.39 and 1.40 Å, and all the three C—C—C angles are very close to 119° respectively. These values reasonable agree with those proviously found in the phenyl group. The C—N distance is in good agreement with the normal single bond distance of 1.475 Å.

Each nitrogen atom has three nearest chlorine neighbours, the N—H···Cl distances being 3.26, 3.29 and 3.30 Å. The N—H···Cl distances and the concerned

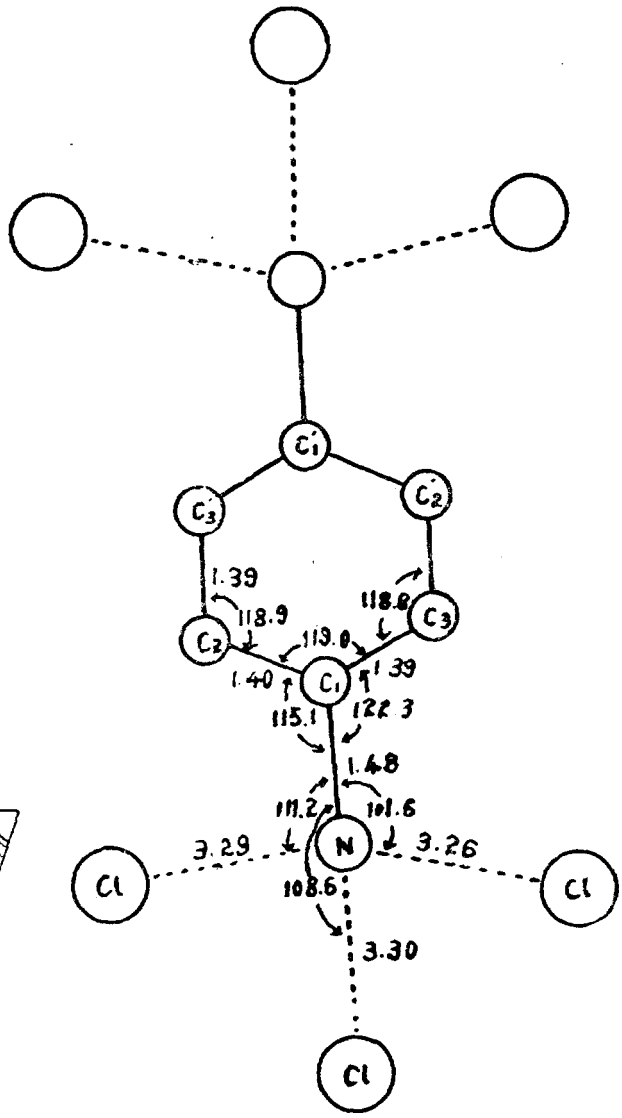

Fig. 4 Molecular dimensions of *p*-phenylenediamine dihydrochloride.

C—N—Cl angles are such that the bonds must be considered hydrogen bonds. Since both nitrogen atoms of the *p*-phenylenediamine residue of the molecule enter into three hydrogen bonding with neighbouring chlorine atoms, the formular of the salt can be shown as. $^{-}Cl\cdot{}^{+}H_3N\cdot C_6H_4\cdot NH_3^{+}\cdot Cl^{-}$.

The arrangement of the molecule in a unit cell is shown in Fig. 5.

The number of hydrogen bonds in the crystal are same with that of hexamethylenediamine dihydroiodide and ethylenediamine dihydrochloride. However, the hydrogen bonds in the crystal *p*-phenylenediamine dihydrochloride results in the formation of two dimensional network parallel to *b* and *c* axes, and along the *a*-axis molecules are bound by Van der Waals forces; on the other hand, the hydrogen bonds in

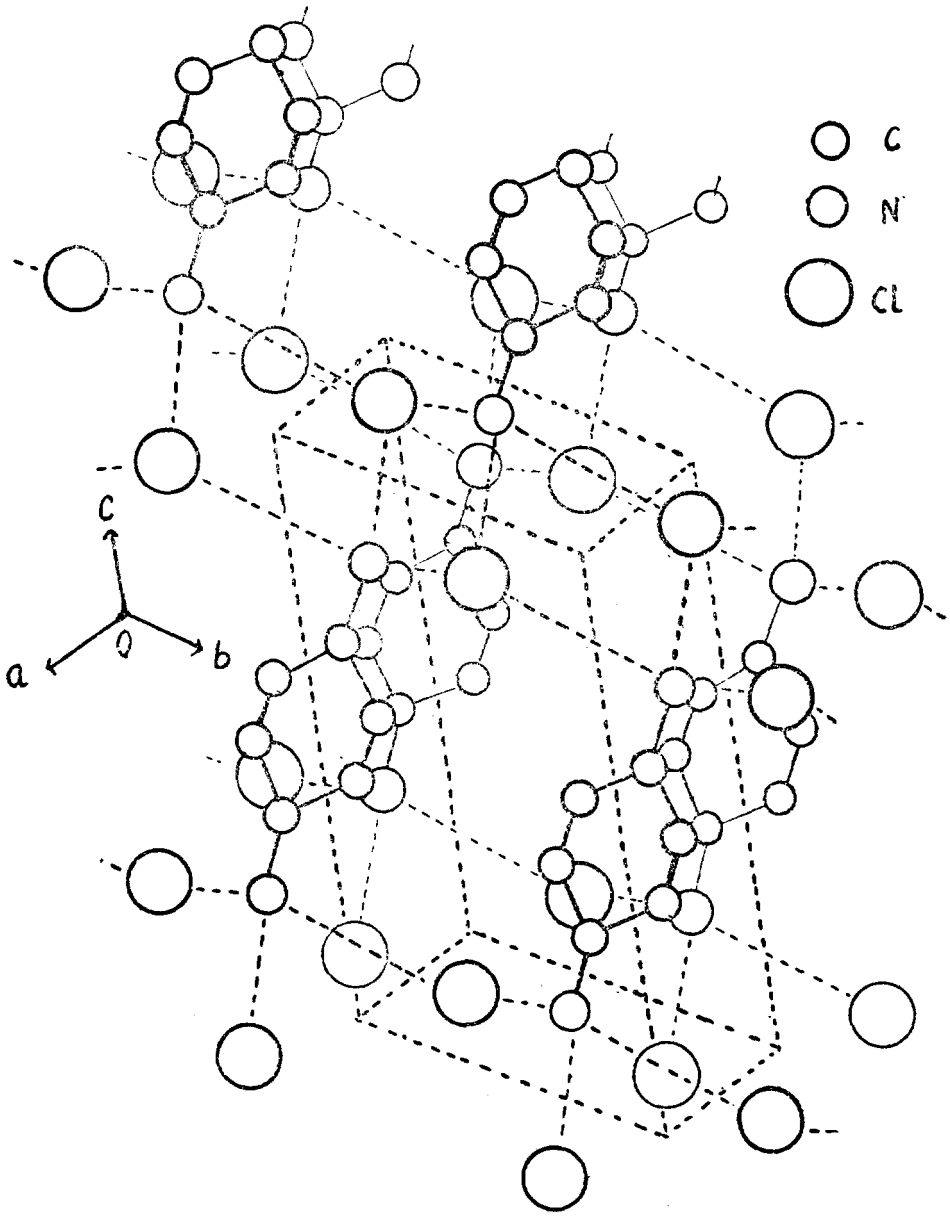

Fig. 5 The arrangement of the molecule in a unit cell.

Table Ⅰ Final Atomic Parameters.

	x	y	z
Cl	0.930	0.327	0.128
N	0.633	0.815	0.177
C_1	0.542	0.907	0.340
C_2	0.643	0.797	0.450
C_3	0.413	0.115	0.390

Table Ⅱ Comparison of F_o and F_c

hkl	F_o	F_c	hkl	F_o	F_c
010	5.80	4.31	$02\bar{1}1$	1.40	1.07
020	10.78	−10.64	$03\bar{1}$	8.34	7.82
030	3.30	2.59	$03\bar{2}$	1.39	−1.33
040	5.02	−5.09	$03\bar{3}$	2.87	−2.52
050	4.01	−4.03	$03\bar{4}$	12.20	−11.48
060	4.40	4.55	$03\bar{5}$	4.55	−5.21
001	2.51	1.76	$03\bar{6}$	0.69	0.49
002	1.69	−1.60	$03\bar{7}$	4.86	4.52
003	9.98	−9.91	$03\bar{8}$	9.90	9.36
004	13.50	−12.78	$03\bar{9}$	3.10	2.86
005	2.02	−1.98	$03\bar{1}0$	3.32	−2.77
006	3.70	2.82	$03\bar{1}1$	3.48	−3.85
007	4.37	4.23	$04\bar{1}$	6.21	6.50
088	3.57	3.33	$04\bar{2}$	10.00	10.10
009	2.35	2.32	$04\bar{3}$	6.15	5.80
0010	1.97	−1.30	$04\bar{4}$	0.00	−0.03
$01\bar{1}$	6.62	−7.08	$04\bar{5}$	4.76	−3.70
$01\bar{2}$	7.52	8.84	$04\bar{6}$	7.64	−7.82
$01\bar{3}$	10.55	12.32	$04\bar{7}$	2.79	−2.34
$01\bar{4}$	5.15	4.93	$04\bar{8}$	1.33	−0.92
$01\bar{5}$	1.20	−0.97	$04\bar{9}$	4.54	3.05
$01\bar{6}$	3.73	−3.96	$04\bar{1}0$	2.08	2.16
$01\bar{7}$	10.58	−11.48	$05\bar{1}$	4.94	−5.30
$01\bar{8}$	0.00	−0.82	$05\bar{2}$	1.87	−1.92
$01\bar{9}$	1.95	2.22	$05\bar{3}$	4.91	−5.28
$01\bar{1}0$	4.13	4.25	$05\bar{4}$	6.20	6.46
$02\bar{1}$	12.14	−15.65	$05\bar{5}$	5.69	6.45
$02\bar{2}$	12.06	−12.28	$05\bar{6}$	3.91	4.04
$02\bar{3}$	6.83	6.37	$05\bar{7}$	2.26	2.34
$02\bar{4}$	6.86	6.42	$05\bar{8}$	6.78	−6.69
$02\bar{5}$	10.53	8.80	$05\bar{9}$	5.95	−5.16
$02\bar{6}$	5.84	6.58	$05\bar{1}0$	3.46	−3.85
$02\bar{7}$	6.15	−6.17	$06\bar{1}$	2.56	2.21
$02\bar{8}$	0.00	−0.43	$06\bar{2}$	0.77	−0.95
$02\bar{9}$	5.78	−5.39	$06\bar{3}$	9.95	−9.54
$02\bar{1}0$	3.05	−3.05	$06\bar{4}$	1.63	−1.32
$06\bar{5}$	2.33	−2.34	100	3.16	−1.51
$06\bar{6}$	2.26	1.98	200	7.67	8.22
$06\bar{7}$	6.29	5.36	300	4.04	3.79
$06\bar{8}$	3.10	2.36	400	2.75	−3.42
$06\bar{9}$	0.00	0.82	500	0.67	−0.92
$07\bar{1}$	2.12	2.01	$10\bar{1}$	5.10	5.86
$07\bar{2}$	3.13	3.63	$10\bar{2}$	7.64	−7.02
$07\bar{3}$	2.72	3.23	$10\bar{3}$	2.00	−10.12
$07\bar{4}$	2.50	3.34	$10\bar{4}$	1.07	−1.73
$07\bar{5}$	2.25	−2.66	$10\bar{5}$	3.55	−4.07
$07\bar{6}$	5.27	−5.67	$10\bar{6}$	3.07	3.07
$07\bar{7}$	2.62	−3.35	$10\bar{7}$	3.31	3.14
011	10.33	−11.45	$10\bar{8}$	5.81	5.40
012	8.66	−8.47	$10\bar{9}$	0.69	0.77
013	0.55	−0.85	$10\bar{1}0$	0.80	−1.19
014	3.27	−0.80	$20\bar{1}$	0.80	0.54
015	8.20	8.35	$20\bar{2}$	6.46	−5.99
016	5.07	5.10	$20\bar{3}$	4.92	−5.70
017	4.68	3.84	$20\bar{4}$	9.12	−9.10
018	4.87	−4.85	$20\bar{5}$	0.90	1.27
019	4.09	−4.37	$20\bar{6}$	3.93	4.29
021	6.27	5.48	$20\bar{7}$	7.37	7.92
022	9.97	8.51	$20\bar{8}$	2.43	1.54
023	11.59	10.57	$20\bar{9}$	0.47	−0.7
024	2.34	2.73	$20\bar{1}0$	2.96	−3.02
025	3.75	−3.45	$30\bar{1}$	4.61	−5.15
026	6.20	−6.48	$30\bar{2}$	5.66	−6.54
027	2.87	−2.50	$30\bar{3}$	8.16	−7.74
028	2.00	−2.15	$30\bar{4}$	0.00	−0.35
031	8.62	7.20	$30\bar{5}$	4.52	3.87
032	0.72	0.48	$30\bar{6}$	6.16	5.82
033	4.25	−4.56	$30\bar{7}$	2.20	1.97
034	1.90	−2.22	$30\bar{8}$	0.49	0.27
035	7.78	−7.29	$30\bar{9}$	3.01	−2.70
036	0.74	−0.63	$40\bar{1}$	2.86	−3.68
037	3.18	3.63	$40\bar{2}$	4.35	−5.26
041	5.92	−6.68	$40\bar{3}$	1.88	−1.29
042	6.19	−5.44	$40\bar{4}$	2.97	3.42
043	5.08	−4.55	$40\bar{5}$	2.26	1.40
044	7.62	7.46	$40\bar{6}$	3.09	3.75
045	2.46	2.71	$40\bar{7}$	1.81	1.53
046	3.23	3.90	$40\bar{8}$	1.22	−1.31
051	1.63	1.29	$50\bar{1}$	2.89	−3.49
052	3.33	3.29	$50\bar{2}$	1.98	−2.11
053	1.83	2.18	$50\bar{3}$	0.62	0.18
054	4.30	4.86	$50\bar{4}$	0.81	−0.73
061	5.88	6.59	$50\bar{5}$	4.14	5.16
062	0.00	0.31	101	13.85	20.37

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
102	6.44	6.91	304	0.75	−1.21	$2\bar{3}0$	6.03	5.78	110	12.97	+14.93
103	3.64	−4.15	305	4.66	−3.47	$2\bar{4}0$	6.94	−5.40	120	11.24	−11.29
104	7.82	−6.63	306	4.36	−4.61	$2\bar{5}0$	0.76	−0.50	130	10.95	11.02
105	9.04	−7.72	307	1.72	1.68	$2\bar{6}0$	2.92	2.05	140	4.76	4.62
106	4.94	−4.47	401	3.20	3.57	$3\bar{1}0$	4.21	−3.31	150	3.87	−4.42
107	6.15	5.44	402	4.43	3.91	$3\bar{2}0$	8.09	6.10	160	3.44	3.52
108	4.50	4.18	403	5.66	5.85	$3\bar{3}0$	2.62	1.79	210	11.31	12.00
109	3.98	3.03	404	1.01	−0.74	$3\bar{4}0$	.724	−6.08	220	0.64	−1.42
201	3.61	4.30	405	1.97	−2.57	$3\bar{5}0$	5.71	5.46	230	4.60	3.87
202	4.46	2.93	501	0.56	−0.23	$3\bar{6}0$	4.92	3.94	240	0.75	−0.65
203	3.19	2.76	502	1.74	2.26	$4\bar{1}0$	7.83	−6.84	250	7.09	−8.77
204	4.43	−3.88	$1\bar{1}0$	9.48	−10.04	$4\bar{2}0$	6.12	6.36	310	2.74	1.90
205	4.95	−5.58	$1\bar{2}0$	7.99	5.11	$4\bar{3}0$	0.00	−0.10	320	11.00	−12.80
206	1.83	−1.49	$1\bar{3}0$	12.68	12.98	$4\bar{4}0$	8.45	−6.78	330	3.60	−2.90
207	4.93	−3.73	$1\bar{4}0$	6.54	−5.88	$4\bar{5}0$	3.42	2.40	340	4.40	5.37
208	5.14	4.18	$1\bar{5}0$	2.82	−2.33	$5\bar{1}0$	2.35	−2.57	410	4.40	5.35
301	5.83	6.80	$1\bar{6}0$	8.50	7.18	$5\bar{2}0$	6.08	4.79	420	0.000	−0.02
302	5.96	7.37	$2\bar{1}0$	15.53	−15.73	$5\bar{3}0$	2.49	−1.02	430	3.25	3.03
303	0.93	−1.12	$2\bar{2}0$	5.18	−2.71	$5\bar{4}0$	0.00	−0.25	510	5.13	6.54

Table 3 Interatomic Distances (Å) and Bond Angles (°).

Interatomic Distances		Bond Angles	
C_1—C_2	1.40	∠ C_1—C_2—C_3'	118.9
C_1—C_3	1.39	∠ C_2'—C_3—C_1	118.8
C_2—C_3'	1.39	∠ C_2—C_1—C_3	119.0
C_1—N	1.48	∠ C_3—C_1—N	122.3
C···C	3.79	∠ C_2—C_1—N	115.1
Cl···Cl	4.38, 4.56	∠ C_1—N—Cl	101.6, 108.6, 111.2
N—H···Cl	3.26, 3.29, 6.30		

hexamethylenediamine dihydrochloride, hexamethylenediamine dihydroiodide and ethylenediamine dihydrochloride form three dimensional network. The shortest intermolecular C—C distance, 3.79 Å, is reasonable as a value for Van der Waals contact of carbon atoms.

References

1) W. F. Binnie and J. Monteath Robertson, *Acta Cryst.* **2**, 180~186 (1949).
2) Kwan Sup Han, *This Journal*, **2**, 74 (1963).
3) Chung Hoe Koo, Moon Il Kim and Chung Soo Yoo, *ibid.* **7**, 293~298 (1963).
4) M. J. Buerger, *Z. Krist.* (A)**97**, 433~468 (1937).