

## Crystal Structure of *p*-Phenylenediamine Dihydrochloride\*

BY R. CHANDRASEKARAN

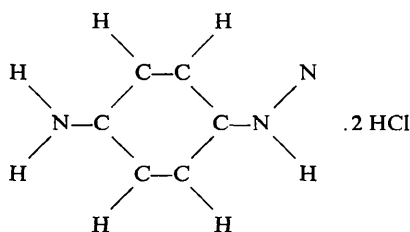
Centre of Advanced Study in Physics, University of Madras, Madras 25, India

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Crystals of *p*-phenylenediamine dihydrochloride are triclinic,  $a=8.75$ ,  $b=5.87$ ,  $c=4.34$  Å,  $\alpha=99^\circ 47'$ ,  $\beta=95^\circ 34'$ ,  $\gamma=111^\circ 10'$ ,  $Z=1$ , space group  $P\bar{1}$ . The structure has been determined in two projections. Three-dimensional X-ray intensity data were used to refine the positional and thermal parameters  $c'$  of the atoms by the least-squares method. All the hydrogen atoms in the molecule were located from an ( $F_o-F_c$ ) synthesis; the final  $R$  value is 0.106. The molecules in the lattice are held together by a system of hydrogen bonds of the type  $N-H \cdots Cl^-$ . The  $C-NH_3^+$  bond length of 1.49 Å in this structure is very close to the mean value of 1.487 Å observed in accurately determined structures of  $\alpha$ -amino acids.

### Introduction

The structure determination of the *p*-phenylenediamine dihydrochloride was undertaken as one of many similar studies in this laboratory on structures containing the amino group. The chemical formula of this compound is



It was of interest to determine whether the two amino groups become protonated, so that the chlorine atoms exist as chloride ions in the lattice. In such a case, purely from symmetry considerations one would expect the chloride ions to take symmetrical positions about the two  $-NH_3^+$  groups to facilitate hydrogen bonding. Conformational features of the amino group in such an aromatic ring system would be of interest for comparison with their features in other structures, such as in amino acids.

### Experimental

Good needle-shaped crystals were chosen from a commercially available pure sample. The crystals were colourless, but they slowly turned black on exposure to air and light. It was therefore necessary to seal the crystal in a Lindemann capillary tube. The outer surface of the tube surrounding the crystal was smeared with ink to minimize the amount of light reaching the specimen.

Rotation, Weissenberg and precession photographs were taken for the crystal about both the  $c$  and the  $b$  axes, with nickel filtered  $Cu K\alpha$  radiation. The photographs did not indicate any systematic absences of reflexions and showed that the crystal belonged to the triclinic system. The crystallographic data are summarized below:

Molecular formula:  $C_6H_8N_2 \cdot 2HCl$ ;  $M=181$   
 Triclinic;  $a=8.75$ ;  $b=5.87$ ;  $c=4.34$  Å;  
 $\alpha=99^\circ 47'$ ;  $\beta=95^\circ 34'$ ;  
 $\gamma=111^\circ 10'$ .  
 $P\bar{1}$

Space group:

$U=201.4$  Å<sup>3</sup>

$D_m=1.51$  (floatation in benzene-carbon-tetrachloride),  
 $Z=1$ .

$D_x=1.508$  g.cm<sup>-3</sup>

Absorption coefficient for X-rays,  $\mu(Cu K\alpha)=67$  cm<sup>-1</sup>

In view of the symmetry of the molecule, the space group was assumed to be  $P\bar{1}$  with half the molecule forming the asymmetric unit, the centre of inversion of the molecule occupying a centre of inversion of the space group. In fact, this choice of the space group was amply supported by the good agreement between the  $F_o$ 's and  $F_c$ 's at the end of the structure analysis.

The intensities of the  $hkl$  reflexions for the layers  $L=0$  to 3 and  $h0l$  reflexions were recorded with  $Cu K\alpha$  radiation using the multiple-film normal beam and equi-inclination Weissenberg techniques. During exposure for the higher layers, the film cassette was shifted through a small distance at regular intervals, the actual shift being determined by the length of the smallest spot as estimated from a trial photograph. By this technique (Stanley, 1955) all the spots were slightly drawn out, thereby causing a linear integration of the intensity. The peak intensities were estimated visually by comparison with a standard set of spots, recorded with the same crystal. In spite of the one-dimensional integration for the higher layers, the spot shapes on one half of the film were elongated at low angles. Therefore, Lorentz and polarization factors with the correction of

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Phillips (1962) were applied to reflexions on this half of the film. The reflexions on the other half appeared to have almost uniform spot size and hence Lorentz and polarization factors alone were applied to these. Some of the reflexions recorded on both halves of the film were then used to bring the intensities measured on the two halves of the film on to the same relative scale. The average thickness of the crystal used was less than 0.1 mm and no absorption correction was applied. The intensities measured on the various levels were placed on a common scale by comparison with the cross layer data and then on the absolute scale by Wilson's (1942) method.

### Structure analysis

The approximate coordinates of the chlorine atom were determined from the two Patterson projections down the *c* and *b* axis as 0.378, 0.183, 0.067. Since the Patterson map down the *c* axis contained sharply resolved peaks, a minimum function map (Buerger, 1951) was drawn. This map yielded the structure in this projection without ambiguity. An attempt to determine the structure in the projection down the *b* axis by the application of the minimum function method was only partly successful. This map clearly indicated the approximate orientation of the molecule and also the positions of the chlorine and the nitrogen atoms, but there was considerable overlap in the region of the carbon atoms. Hence, a chlorine-phased electron density function was calculated for this projection and the positions of all the atoms were then determined.

Preliminary structure factor calculations were carried out including all these atoms. The *R* values for the projections down the *c* and the *b* axes were calculated to be 0.23 and 0.21 respectively. The coordinates of the atoms were refined by successive two-dimensional difference-Fourier syntheses until the *R* values were reduced to 0.143 and 0.153 respectively for these two

projections. In the above calculations, the value of the thermal parameter *B* was 1.6 Å<sup>2</sup> as determined from the Wilson plots.

Initial three-dimensional least-squares refinement of the structure with the block-diagonal approximation was carried out on the CDC 3600 computer with a program written by the author for the space group *P* $\bar{1}$ . Special care was taken to take into account the possible interaction between the scale factor *k* for the *F*<sub>o</sub>'s and the thermal parameter *B*. The three-dimensional data consisting of 625 reflexions, including 60 unobserved reflexions were used in the refinement. The unobserved reflexions were assigned half the value of the locally observed minimum |*F*<sub>o</sub>|. Two cycles of refinement of

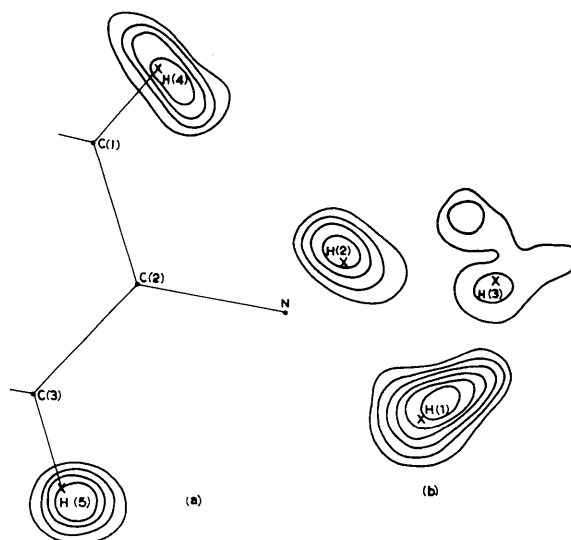


Fig. 1. Sections of the difference-Fourier map through (a) the plane of the molecule and (b) the plane expected to contain the hydrogen atoms bonded to the nitrogen atom. The contours are from 0.4 e.Å<sup>-3</sup> at increments of 0.1 e.Å<sup>-3</sup>.

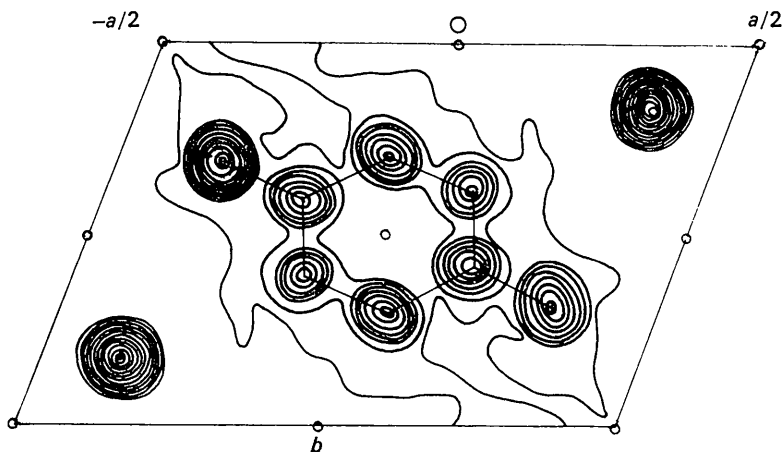


Fig. 2. Final electron-density map, projection down the *c* axis. Contours are drawn from zero level at intervals of 1 e.Å<sup>-2</sup>. At chlorine, contours are drawn at intervals of 2 e.Å<sup>-2</sup>.

the positional parameters with a single overall thermal parameter  $B$  for the atoms brought the  $R$  value from 0.17 to 0.142. Further refinement after switching to individual isotropic thermal parameters for each of the atoms reduced the  $R$  value to 0.118.

At this stage, a full-matrix least-squares program of Gantzel, Sparks & Trueblood (1961) for the CDC 3600 computer became available. This program was used to refine the positional parameters of the atoms, anisotropic thermal parameters of the chlorine atom individual isotropic thermal parameters for the rest, and the layerwise scale factors. Three cycles of refinement brought the  $R$  value down to 0.112.

In all the above refinements, a unit weighting scheme for  $F_o$ 's was employed and the function  $\Sigma (F_o - F_c)^2$  was minimized. The atomic scattering factors were adopted from *International Tables for X-ray Crystallography* (1962). The estimated standard deviations were calculated in the program from the residuals and the diagonal elements of the inverse matrix of the normal equations.

A three-dimensional difference-Fourier synthesis was now computed\* with a view to locating the hydrogen atoms. Sections of the difference Fourier map

\* The author is extremely grateful to the referee for computational help.

through the plane of the molecule, and the plane expected to contain the hydrogen atoms bonded to the nitrogen atom, are shown in Fig. 1. The positions of all five hydrogen atoms in the asymmetric unit were determined from this map.

Least-squares refinement was then continued, adjusting the positional parameters of all the atoms including the hydrogens, anisotropic thermal parameters of the chlorine atom, isotropic thermal parameters of the remaining non-hydrogen atoms and the layerwise scale factors. The hydrogen atoms were assigned a constant value of  $B = 2.5 \text{ \AA}^2$ . The weighting function used was  $W = 1/(A + |F_o| + C|F_c|^2)$  (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) with  $A = 2.6$  and  $C = 0.05$ . After two cycles of full-matrix refinement the  $R$  value converged to 0.106. The final shifts were much less than the corresponding standard deviations.

### Results and discussion

The final electron density distributions down the  $c$  and  $b$  axes are shown in Fig. 2 and 3 respectively. The final positional parameters of the atoms with their standard deviations and thermal parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2.

Table 1. Final atomic coordinates (fractional), standard deviations ( $\text{\AA}$ ) and thermal parameters

	$x$	$y$	$z$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$B(\text{\AA}^2)$
Cl	0.3718	0.1743	0.0695	0.002	0.002	0.002	—
C(1)	0.1129	0.3854	0.5714	0.009	0.009	0.011	2.74
C(2)	0.1561	0.5900	0.4384	0.008	0.009	0.010	2.58
C(3)	0.0481	0.7045	0.3594	0.009	0.009	0.010	2.26
N	0.3266	0.6829	0.3584	0.008	0.008	0.010	2.56
H(1)	0.3523	0.5509	0.2825		Mean		2.50
H(2)	0.3467	0.8450	0.2302		$\sigma(x) = 0.13$		2.50
H(3)	0.4101	0.7478	0.5385		$\sigma(y) = 0.14$		2.50
H(4)	0.1897	0.3169	0.6160		$\sigma(z) = 0.15$		2.50
H(5)	0.0819	0.8709	0.2669				2.50
$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$		
0.011422	0.022528	0.035859	0.017284	0.009782	0.018248		

$$\text{Temperature factor} = \exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)].$$

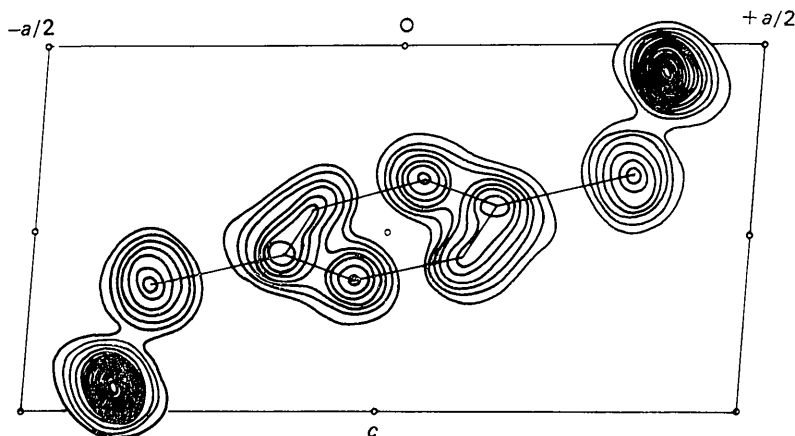


Fig. 3. Final electron-density map, projection down the  $b$  axis. Contours are drawn as in Fig. 2.

Table 2. Observed and calculated structure factors for phenylenediamine dihydrochloride

The column headings are  $h$ ,  $10|F_o|$  and  $10F_c$ .

$h$	$10 F_o $	$10F_c$	$h$	$10 F_o $	$10F_c$	$h$	$10 F_o $	$10F_c$	$h$	$10 F_o $	$10F_c$	$h$	$10 F_o $	$10F_c$	$h$	$10 F_o $	$10F_c$	
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1	53	-46	2	100	-103	3	86	87	4	58	-58	5	68	68	6	91	85	
2	27	-27	3	173	175	4	10	10	5	1	-1	6	32	-32	7	140	133	
3	191	203	4	94	-96	5	113	-117	6	74	-65	7	5	-8	8	64	-71	
4	246	-281	5	0	0	6	104	102	7	29	23	8	5	5	9	46	-45	
5	33	34	6	75	69	7	123	-111	8	49	50	9	5	5	10	58	56	
6	59	56	7	130	-134	8	6	5	9	34	-36	10	5	5	11	48	-48	
7	48	-57	8	44	40	9	30	30	10	7	80	11	5	5	12	117	-122	
8	53	95	9	10	-14	10	8	85	11	2	70	-80	12	5	13	66	-64	
9	27	-29	10	53	-49	11	9	50	12	3	62	72	13	5	14	34	-34	
10	27	-25	11	28	32	12	10	41	13	4	10	-15	14	5	15	54	-48	
11	1	0	12	0	0	13	36	-28	14	5	36	-28	15	5	16	142	144	
0	91	-105	13	0	0	14	1	1	15	5	33	-46	16	5	17	153	-152	
1	175	-218	14	84	-82	15	0	76	16	6	1	1	17	5	18	45	48	
2	169	165	15	33	31	16	29	29	17	6	43	42	18	5	19	16	18	
3	9	-9	16	93	-79	17	43	44	18	6	0	172	157	19	5	20	-33	-33
4	46	44	17	112	-99	18	198	-221	19	6	1	1	69	-69	20	6	75	-80
5	128	130	18	105	98	19	4	73	20	6	2	82	-82	21	6	80	-70	-70
6	81	-75	19	68	-59	20	5	5	21	6	3	96	-56	22	6	87	-79	-66
7	51	51	20	35	34	21	6	73	22	6	4	69	-67	23	6	94	-96	-93
8	50	47	21	100	88	22	7	128	143	2	179	174	24	6	101	159	-140	-140
9	57	-41	22	83	-72	23	8	20	-22	3	5	77	83	25	6	108	129	-9
10	2	0	23	60	43	24	9	10	-15	4	6	27	-28	26	6	115	42	-38
11	2	0	24	0	0	25	10	88	-66	5	7	68	62	27	6	122	67	67
12	188	-221	25	0	0	26	0	224	-219	6	8	69	62	28	6	129	126	126
13	91	-94	26	33	-30	27	1	83	30	7	9	62	-6	29	6	136	70	-75
14	148	158	27	153	-152	28	0	30	30	8	10	77	71	30	6	143	62	62
15	167	-184	28	63	-57	29	2	119	119	9	11	88	-82	31	6	150	75	-75
16	328	335	29	27	-27	30	3	52	54	10	12	99	-80	32	6	157	80	-80
17	57	48	30	47	30	31	4	10	16	11	13	110	-175	33	6	164	104	-104
18	81	-82	31	94	-96	32	5	89	96	12	14	121	-90	34	6	171	167	-172
19	27	28	32	51	-37	33	6	75	-80	13	15	132	-81	35	6	178	172	172
20	22	-21	33	5	-3	34	7	5	4	14	16	143	-92	36	6	185	31	52
21	3	0	34	0	0	35	8	5	7	15	17	154	-80	37	6	192	44	-44
22	47	-49	35	38	-28	36	9	58	-49	16	18	165	-70	38	6	200	57	57
23	134	113	36	60	43	37	10	67	58	17	19	176	-60	39	6	207	70	-70
24	5	-11	37	40	-43	38	11	63	69	18	20	187	-51	40	6	214	83	-83
25	66	-65	38	49	38	39	12	65	-74	19	21	198	-42	41	6	221	96	-96
26	27	30	39	53	-34	40	13	68	-88	20	22	209	-33	42	6	228	109	-109
27	91	-92	40	48	-35	41	14	68	-62	21	23	220	-24	43	6	235	122	-122
28	6	-9	41	107	73	42	15	68	62	22	24	231	-15	44	6	242	135	-135
29	45	33	42	57	-42	43	16	68	62	23	25	242	-6	45	6	249	148	-148
30	4	0	43	0	0	44	17	63	63	24	26	253	-26	46	6	256	161	-161
31	84	-78	44	53	-55	45	18	5	10	25	27	264	-17	47	6	263	174	-174
32	95	92	45	63	-63	46	19	57	-51	26	28	275	-8	48	6	270	187	-187
33	91	-92	46	71	-71	47	20	65	-51	27	29	286	-7	49	6	277	200	-200
34	68	66	47	86	-86	48	21	63	-63	28	30	297	-6	50	6	284	213	-213
35	47	93	48	18	-18	49	22	63	-63	29	31	308	-5	51	6	291	226	-226
36	25	-23	49	26	30	50	23	63	-63	30	32	319	-4	52	6	298	239	-239
37	42	38	50	62	55	51	24	63	-63	31	33	330	-3	53	6	305	252	-252
38	5	0	51	57	66	52	25	62	-57	32	34	341	-2	54	6	312	265	-265
39	59	57	52	30	36	53	26	62	-57	33	35	352	-1	55	6	319	278	-278
40	13	18	53	36	36	54	27	62	-57	34	36	363	0	56	6	326	291	-291
41	40	-38	54	39	-39	55	28	62	-57	35	37	374	0	57	6	333	304	-304
42	25	21	55	35	-28	56	29	62	-57	36	38	385	0	58	6	340	317	-317
43	66	-54	56	25	-21	57	30	62	-57	37	39	396	0	59	6	347	330	-330
44	6	0	57	0	0	58	31	62	-57	38	40	407	0	60	6	354	343	-343
45	68	53	58	9	10	59	32	61	-56	39	41	418	0	61	6	361	356	-356
46	98	-77	59	30	33	60	33	61	-56	40	42	429	0	62	6	368	369	-369
47	1	0	60	62	55	61	34	61	-56	41	43	440	0	63	6	375	382	-382
48	1	0	61	44	-39	62	35	61	-56	42	44	451	0	64	6	382	395	-395
49	124	-147	62	24	34	63	36	61	-56	43	45	462	0	65	6	389	408	-408
50	151	-145	63	0	0	64	37	61	-56	44	46	473	0	66	6	396	421	-421
51	228	227	64	1	1	65	38	61	-56	45	47	484	0	67	6	403	434	-434
52	87	-85	65	0	0	66	39	61	-56	46	48	495	0	68	6	410	447	-447
53	20	-22	66	68	-71	67	40	61	-56	47	49	506	0	69	6	417	460	-460
54	55	-52	67	393	-472	68	41	61	-56	48	50	517	0	70	6	424	473	-473
55	149	-176	68	145	141	69	42	61	-56	49	51	528	0	71	6	431	486	-486
56	5	6	69	66	67	70	43	61	-56	50	52	539	0	72	6	438	499	-499
57	26	24	70	132	-134	71	44	61	-56	51	53	550	0	73	6	445	512	-512
58	57	-44	71	158	147	72	45	61	-56	52	54	561	0	74	6	452	525	-525
59	-2	0	72	71	-75	73	46	61	-56	53	55	572	0	75	6	459	538	-538
60	237	301	73	86	-90	74	47	61	-56	54	56	583	0	76	6	466	551	-551
61	233	-265	74	92	94	75	48	61	-56	55	57	594	0	77	6	473	564	-564
62	141	-113	75	0	0	76	49	61	-56	56	58	605	0	78	6	480	577	-577
63	117	120	76	1	1	77	50	61	-56	57	59	616	0	79	6	487	590	-590
64	152	-169	77	188	186	78	51	61	-56	58	60	627	0	80	6	494	603	-603
65	105	114	78	120	100	79	52	61	-56	59	61	638	0	81	6	501	616	-616
66	91	94	79	224	-244	80	53	61	-56	60	62	649	0	82	6	508	629	-629
67	5	-4	80	102	96	81	54	61	-56	61	63	660	0	83	6	515	642	-642
68	75	76	81	108	-111	82	55	61	-56	62	64	671	0	84	6	522	655	-655
69	43	-35	82	61	-61	83	56	61	-56	63	65	682	0	85	6	529	668	-668
70	23	-15	83	108	105	84	57	61	-56	64	66	693	0	86	6	536	681	-681
71	-3	0	84	5	2	85	58	61	-56	65	67	704	0	87	6	543	694	-694
72	128	141	85	92	94	86	59	61	-56	66	68	715	0	88	6	550	707	-707
73	24	21	86	-2	1	87	60	61	-56	67	69	726	0	89	6	557	720	-720
74	45	-54	87	150	126	88	61	61	-56	68	70	737	0	90	6	564		

### Intramolecular features

The bond distances and angles in the molecule are shown in Fig. 4 and listed in Table 3.

The three C-C bond distances in the asymmetric half of the molecule are 1.37, 1.39 and 1.40 Å. The average value of these three distances is 1.387 Å which is in good agreement with the accepted value of 1.395 Å for the C-C distances in a benzene ring.

Table 3. Bond lengths and bond angles in the molecule\*

Bond	Length	Atoms	Angle
C(1)-C(2)	1.37 Å	C(2)-C(1)-C(3')	116.7°
C(1)-C(3')	1.40	C(3')-C(1)-H(4)	123.4
C(1)-H(4)	0.92	C(2)-C(1)-H(4)	119.8
C(2)-C(3)	1.39	C(1)-C(2)-N	116.8
C(2)-N	1.49	C(1)-C(2)-C(3)	123.9
C(3)-H(5)	1.07	C(3)-C(2)-N	119.2
N-H(1)	0.90	C(2)-C(3)-C(1')	119.3
N-H(2)	1.15	C(2)-C(3)-H(5)	124.8
N-H(3)	0.94	C(1')-C(3)-H(5)	115.7
		C(2)-N-H(1)	109.1
		C(2)-N-H(2)	111.2
		C(2)-N-H(3)	112.7

\* The standard deviations are: bonds and angles not involving hydrogen, 0.013 Å and 1.0°; bonds and angles involving hydrogen ~0.14 Å and 9°.

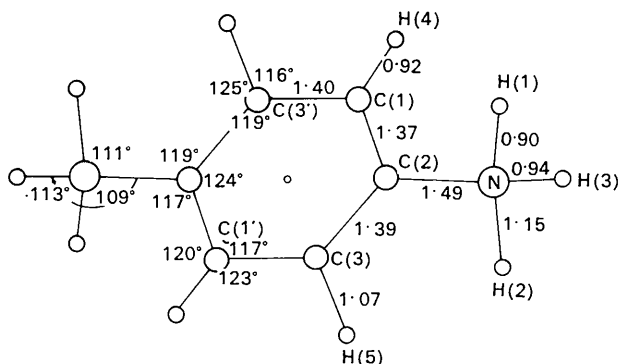


Fig. 4. Bond lengths and angles in the molecule.

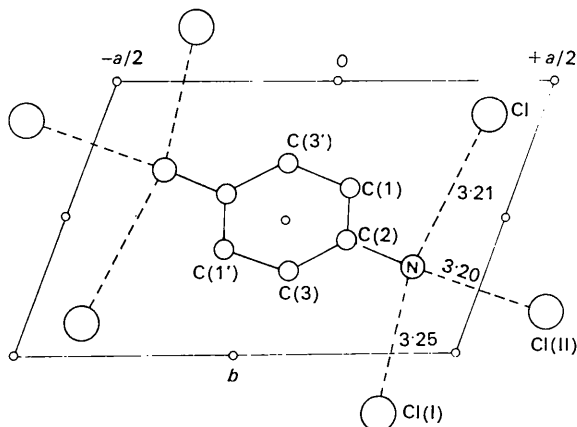


Fig. 5. The structure in projection viewed down the *c* axis.

The structures of very few aromatic compounds with an attached amino group have been solved so far. If the amino group is not protonated, the expected C-N distance would be 1.37 Å. For example, the experimental values of such distances are 1.37 Å in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), 1.39 Å in *p*-aminophenol (Brown, 1951), 1.39 Å in 4-aminosalicylic acid (Bertinotti, Giacomello & Liquori, 1954), 1.41 Å in 2,5-dichloroaniline (Sakurai, Sundaralingam & Jeffrey, 1963). In all these cases, there is a significant degree of double bond character in the C-NH<sub>2</sub> bond, and the -NH<sub>2</sub> group is coplanar with the aromatic ring (Trueblood *et al.*, 1961), as one would expect from the resonance consideration.

In the compound under investigation, in the form of the hydrochloride, the -NH<sub>2</sub> group becomes -NH<sub>3</sub><sup>+</sup>, and in fact all three protons have been located. The C-NH<sub>3</sub><sup>+</sup> distance is found to be 1.49 Å and the C-N distance for a single bond is 1.47 Å (Pauling, 1958). There are only a few examples of aromatic compounds for comparison with the present case. The reported values of C-NH<sub>3</sub><sup>+</sup> distances are 1.455 Å in *m*-tolidine hydrochloride (Fowweather & Hargreaves, 1950), 1.45 Å in *p*-tolidine hydrochloride (von Eller, 1955), 1.474 Å in *o*-aminophenol hydrochloride (Cesur & Richards, 1965) and 1.35 Å in aniline hydrochloride (Brown, 1949). The distances in the first three examples are compatible with the present observation. The short length of 1.35 Å in aniline hydrochloride is significantly different, but the coordinates may not have been accurately determined since only projection data were used for refining the structure. The observed C-N distance of 1.49 Å in the present investigation supports the idea that the -NH<sub>3</sub><sup>+</sup> is not conjugated with the benzene ring (Sakurai, *et al.* 1963).

It may, however, be mentioned that in amino acids, when the amino group gets protonated, the C-NH<sub>3</sub><sup>+</sup> distance has a value slightly larger than single bond value of C-N = 1.47 Å (Pauling, 1958). The weighted mean value for the C-NH<sub>3</sub><sup>+</sup> distance in accurately solved crystal structures of amino acids is 1.487 Å (Marsh & Donohue, 1967). However, the carbon atom is *sp*<sup>3</sup> hybridized in these cases. It would therefore be expected that in the aromatic molecule under investigation in which the carbon atom is *sp*<sup>2</sup> hybridized, the C-NH<sub>3</sub><sup>+</sup> distance would be somewhat shorter than the value observed in amino acids.

The average values of the two C-H bond distances and the three N-H bond distances are 1.0 Å and 1.0 Å respectively and the individual values are not significantly different from these values.

As expected, the phenylenediamine molecule is planar, except for the amino hydrogens. The equation of the least-squares plane passing through the eight heavier atoms is given by

$$0.0184X + 0.4255Y + 0.9047Z = 2.844 \text{ \AA},$$

where *X*, *Y*, *Z* are coordinates in Å referred to an orthogonal system in which the *X* axis is along the *a* axis,

the *Y* axis is in the *ab* plane normal to the *X* axis and the *Z* axis is normal to the *XY* plane. The deviations of the atoms from this plane are C(1), -0.002 Å; C(2), 0.022 Å; C(3), -0.002 Å; N, -0.010 Å

### Intermolecular hydrogen bonding

A view of the structure projected down the *c* axis is shown in Fig. 5. The molecules in the lattice are held together by a three-dimensional network of hydrogen bonds. There are three protons available with the  $-\text{NH}_3^+$  group. The nitrogen atom has three close neighbours and all of them are chloride ions. The distances from the nitrogen atom to Cl, Cl(I) and Cl(II) are 3.21, 3.25 and 3.20 Å respectively. The protons are oriented almost tetrahedrally towards these ions, with respect to the C(2)-N bond. The angles N-H...Cl indicate that these hydrogen bonds are fairly linear. The values of the hydrogen bond lengths and angles are given in Table 4.

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Table 4. *Hydrogen bonding distances and angles*

X-H...Y	X...Y	X-H	H...Y
N-H...Cl	3.21 Å	0.90 Å	2.32 Å
N-H...Cl(I)	3.25	1.15	2.11
N-H...Cl(II)	3.20	0.94	2.99
C(2)-N...Cl	102.8°	N-H(1)...Cl	170.6°
C(2)-N...Cl(I)	107.4	N-H(2)...Cl(I)	169.5
C(2)-N...Cl(II)	116.2	N-H(3)...Cl(II)	166.3
Standard molecule at	<i>x</i>	<i>y</i>	<i>z</i>
Molecule I	at <i>x</i>	1 + <i>y</i>	<i>z</i>
Molecule II	at 1 - <i>x</i>	1 - <i>y</i>	1 - <i>z</i>

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## Least-Squares Weighting Schemes for Diffractometer-Collected Data.

### II. The Effect of Random Setting Errors

BY D. F. GRANT AND R. C. G. KILLEAN

*Department of Physics, University of St. Andrews, St. Andrews, Scotland*

AND J. L. LAWRENCE

*Department of Physics, University of Stirling, Stirling, Scotland*

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An analysis is made of the weighting function derived on the basis of counting statistics and random setting errors for a constant-time diffractometer experiment. It is shown that these two random errors must make a major contribution to the weighting function and a practical application of this function is discussed in detail.

#### Introduction

It has been shown (Killean, 1967*a*) that, on consideration of counting statistics alone, the weighting schemes

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#### References

- BERTINOTTI, F., GIACOMELLO, G. & LIQUORI, A. M. (1954). *Acta Cryst.* **7**, 808.  
 BROWN, C. J. (1949). *Acta Cryst.* **2**, 228.  
 BROWN, C. J. (1951). *Acta Cryst.* **4**, 100.  
 BUERGER, M. J. (1951). *Acta Cryst.* **4**, 531.  
 CESUR, A. F. & RICHARDS, J. P. G. (1965). *Z. Kristallogr.* **122**, 283.  
 CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Vol. 4, p. 32. Oxford: Pergamon Press.  
 ELLER, G. VON (1955). *Bull. Soc. franç. Min. Crist.* p. 257.  
 FOWWEATHER, F. & HARGREAVES, A. (1950). *Acta Cryst.* **3**, 81.  
 GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). University of California Program UCLALS 1.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 MARSH, R. E. & DONOHUE, J. (1967). *Advances in Protein Chemistry*. Vol. 22, p. 235. New York: Academic Press.  
 PAULING, L. (1958). *The Nature of the Chemical Bond*, p. 229. Ithaca: Cornell Univ. Press.  
 PHILLIPS, D. C. (1962). *International Tables for X-ray Crystallography*, Vol. III, p. 140. Birmingham: Kynoch Press.  
 SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354.  
 STANLEY, E. (1955). *Acta Cryst.* **8**, 58.  
 TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

for constant-count and constant-time experiments are very different, and that the weights obtained for the constant-time experiment are not suitable for a satisfactory least-squares refinement. These weighting