THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXAMETHYLENE DIAMINE AND ITS DIHALIDES

THESIS

Presented for the degree of
Doctor of Philosophy
in the
University of Glasgow

by

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PREFACE

The work contained in this thesis is being prepared for publication, in collaboration with Professor J. Monteath Robertson, F.R.S. It will be divided into two parts, one embodying the work on hexamethylene diamine, the other concerned with the work on its dihalides.

I wish to express my sincere thanks to Professor J. Monteath Robertson, F.R.S., for suggesting the problems for research, and for his constant guidance and encouragement. I am grateful to Messrs. I.C.I. Ltd. and to the Department of Scientific and Industrial Research for Scholarships granted during this work, and also to the former for samples of hexamethylene diamine.

September, 1948. W. P. B.

Glasgow University.

SUMMARY

The crystal and molecular structure of hexamethylene diamine and its dihalides have been investigated by X-ray diffraction methods. Atomic parameters have been completely refined by two-dimensional Fourier series, and in the case of the dihalides the structure analysis was immensely aided by two-dimensional Patterson series and also by the fact that they proved to be isomorphous. A technique has been developed for the detailed examination of hygroscopic hexamethylene diamine.

An interesting complex lattice of halogen ions and nitrogen atoms is found in the dihalides, and they also provide bond lengths comparable with those of hexamethylene diamine. These bond lengths are reminiscent of a conjugated molecule. Resolution of the hydrogen atoms of hexamethylene diamine is observed in the Fourier projections, and so their contributions have been included in the calculated structure factors.

CONTENTS

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Introduction

Polyamides of high molecular weight have recently attained considerable practical importance as nylon fibres. These polymers are prepared by condensation of hexamethylene diamine and long-chain aliphatic acids. Structural analyses have been made for several nylons,(1) especially the condensate of hexamethylene diamine and adipic acid, in order to correlate the physical properties with the molecular structure, but no satisfactory structure has yet been released in detail.

The open-chain aliphatic acids were being re-examined in this department,(2) and therefore it was of much interest to make a detailed study of the structure of hexamethylene diamine, the common constituent of most nylon fibres, believing that information gained from this analysis may be useful in dealing with the more complex problems presented by the nylons.

Therefore this inquiry is primarily interested in the crystal and molecular structure of hexamethylene diamine, but due to the experimental difficulties offered by its instability and hygroscopic nature(3) the inquiry will be aided by the application of the heavy atom technique.(4) This choice of approach can be thoroughly appreciated by an explanation of the method.

After the determination of the unit cell and space group of the crystal, the next step in the analysis is the determination of the intensities of the X-ray reflections from a number of planes of the crystal. From these intensities a set of quantities $F^2(hkl)$ can be derived, which are a measure of the actual reflecting power of the various planes, after correction for polarisation and Lorentz factors.

The electron density in a crystal $\rho(xyz)$ is expressed as a three-dimensional Fourier series with coefficients $F(hkl)$ in the form

$$\rho(xyz) = \sum\sum\sum_{hkl=-\infty}^{\infty} F(hkl) \, \mathrm{exp.} \, 2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right).$$

Thus if the quantities $F(hkl)$ are known, crystal analysis would merely mean substituting these values in the above expression. However, $F^2(hkl)$ is only known and the phase of the structure factor F can only be determined by the trial and error process.

However $F^2(hkl)$ is always positive, and Patterson has shown(4) that by making use of these values as coefficients in a Fourier synthesis, the vector inter-atomic distances in a crystal can be determined. This synthesis is a weighted distribution of an electron density function about all points in the crystal.

Therefore, the peaks in this distribution, when drawn out in a contour map, occur in positions such that vectors from the origin of the map to these positions correspond in magnitude and direction to the inter-atomic distances in the crystal.

This method is particularly successful when an atom of high atomic number is included in the molecule such as to swamp vectors due to atoms of low atomic number. Thus the vectors from the origin to the peaks which appear, correspond in magnitude and direction to the inter-atomic distances between the heavy atoms. Having obtained these inter-atomic distances, it remains to fit them in the projection according to the requirements of the space group, and thus the co-ordinates of the heavy atoms can be found.

Therefore with a Patterson series in view, two dihalides of hexamethylene diamine were prepared, the dihydrobromide and dihydrochloride. The Patterson contour map of the dihydrobromide will be examined first because of the greater swamping effect of bromine, and so these ions will be located more readily than those of chlorine, and providing that the two dihalides prove isomorphous, the co-ordinates so found will be utilised for the dihydrochloride, where due to the lighter halogen ion, improved resolution will be obtained in the open carbon-nitrogen chain. The expectation that the two dihalides are isomorphous has been strikingly realised.

The examination of the crystal structure of the dihalides will provide molecular dimensions and bond lengths of the carbon-nitrogen chain, and this information may be useful in interpreting the X-ray diffraction patterns of the diamine itself, providing a satisfactory technique is adopted to preserve its crystals.

Hexamethylene Diamine Dihydrobromide

Crystal Data

Hexamethylene diamine dihydrobromide, $C_6H_{18}N_2Br_2$; mol. wt. 278 ; m.pt. 263°; calculated density 1.656 ; measured density 1.667 ; monoclinic prismatic, with $a = 4.68 \pm .02A.$, $b = 14.53 \pm .04A.$, $c = 16.21 \pm .04A.$, and $\beta = \sim 91^\circ$. Absent spectra, (hol) when l is odd, (oko) when k is odd. Hence space group is $C_{2h}^5(P2_{1/c})$. Four molecules per unit cell ; molecular symmetry, nil. Volume of unit cell, $1103.0A^3$. Total number of electrons per unit cell = F(000) = 552. Absorption coefficient for X-rays ($\lambda = 1.54A.$), $\mu = 91.0cm^{-1}$.

The most suitable solvent found for the dihydrobromide was glacial acetic acid, this solvent giving fine colourless needle crystals. The maximum cross-section of these needles measured 0.05 by 0.05 mm., even after cooling in a vacuum flask. The crystals are elongated along the a axis.

As a result of this extremely fine cross-section only one axis, the a axis, has been measured directly on the rotation camera, the other two axes of the unit cell being obtained from the moving film of this axis. The ß angle of the unit cell cannot be measured in the usual manner, but as parallel work conducted with hexamethylene diamine dihydrochloride showed that the dihalides are isomorphous, an approximate value of 90°- 91° can be given to ß.

Structure Analysis

From moving-film exposures of the (okl) zone for a single crystal of the dihydrobromide, the values of F^2(okl) for a number of planes were obtained and a Patterson series carried out. The Patterson contour map was drawn out with the aid of sections for one quarter of the unit cell projection, and as shown in Fig.1, there are nine distinct peaks, each indicated by a cross. Thus there are nine inter-atomic distances, in magnitude and direction, between the bromine atoms. The co-ordinates (y,z) of these peaks were scaled to the unit cell dimensions, and a vector map, Fig.2, showing inter-atomic distances in the unit cell projection was obtained.

Co-ordinates of these peaks in A. are

(1)	$y = 3.85$	$z = 1.70$
(2)	$y = 3.43$	$z = 2.63$
(3)	$y = 4.60$	$z = 6.35$
(4)	$y = 2.69$	$z = 5.35$
(5)	$y = 0.97$	$z = 3.78$
(6)	$y = 7.27$	$z = 1.08$
(7)	$y = 7.27$	$z = 4.46$
(8)	$y = 6.10$	$z = 8.11$
(9)	$y = 0.66$	$z = 8.11$

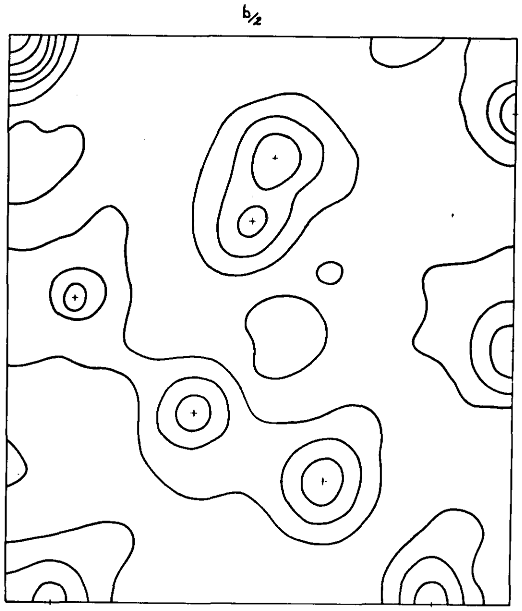


Fig. 1. Patterson contour map for the (okl) projection of hexamethylene diamine dihydrobromide.

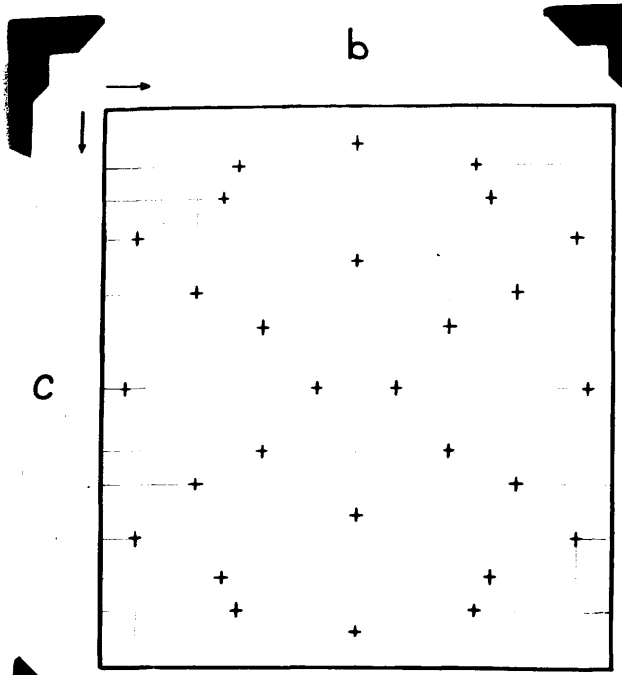


Fig.2. Patterson vector map for the (okl) projection of the dihydrobromide.

It will be observed that peaks (6) and (7) have their y co-ordinates equal to $^b/_2$, while peaks (8) and (9) have their z co-ordinates equal to $^c/_2$

Limitations which will be of help in the examination of the Patterson projection are:-

1. Space group considerations concerned with the packing of the halogen ions.
2. Closest approach of bromine ions is approximately 4.2A.(5)
3. Distance between the two bromine atoms of the same molecule may range from 8 to 16 A.
4. Distance between nitrogen and bromine is approximately 3.6 A.(5)

With these limitations in mind, it now remains to solve the Patterson by finding the positions of the two bromines of each of the four molecules in the unit cell, such that vectors between these bromines correspond in magnitude and direction to those of the vector map.

The space group limitation is important in that from the diagram of symmetry elements, equivalent points can be named, and each quarter of the unit cell shown to be equivalent.(6) It follows therefore that one molecule of the dihydrobromide is the asymmetric unit, and that there is one molecule in each quarter of the unit cell, and thus two bromine atoms.

Equivalent points in the (okl) projection are

(y,z); $(\bar{y},\bar{z})$; $(\frac{1}{2}+y, \frac{1}{2}-z)$; $(\frac{1}{2}-y, \frac{1}{2}+z)$

To solve the Patterson projection, the two bromine atoms of the asymmetric unit must be located, and if they are given the co-ordinates

$Br_1 = (y_1, z_1)$ and $Br_2 = (y_2, z_2)$,

then from symmetry considerations, there must be bromine atoms in the following positions.

(1) y_1, z_1; (2) $\bar{y}_1, \bar{z}_1$; (3) $\frac{1}{2}+y_1, \frac{1}{2}-z_1$; (4) $\frac{1}{2}-y_1, \frac{1}{2}+z_1$;
(5) y_2, z_2; (6) $\bar{y}_2, \bar{z}_2$; (7) $\frac{1}{2}+y_2, \frac{1}{2}-z_2$; (8) $\frac{1}{2}-y_2, \frac{1}{2}+z_2$;

Therefore vectors between these bromine atoms can be expressed mathematically as:-

Vectors between bromine_1 and its equivalents.

(1)(2) $2y_1, 2z_1$. (2)(3) $\frac{1}{2}+2y_1, \frac{1}{2}$.
(1)(3) $\frac{1}{2}, \frac{1}{2}-2z_1$. (2)(4) $\frac{1}{2}, \frac{1}{2}+2z_1$.
(1)(4) $\frac{1}{2}-2y_1, \frac{1}{2}$. (3)(4) $2y_1, -2z_1$.

Vectors between bromine_2 and its equivalents.

(5)(6) $2y_2, 2z_2$. (6)(7) $\frac{1}{2}+2y_2, \frac{1}{2}$.
(5)(7) $\frac{1}{2}, \frac{1}{2}-2z_2$. (6)(8) $\frac{1}{2}, \frac{1}{2}+2z_2$.
(5)(8) $\frac{1}{2}-2y_2, \frac{1}{2}$. (7)(8) $2y_2, -2z_2$.

Vectors between bromine_1 and bromine_2 include:-

(1)(5) $y_1 - y_2, \quad z_1 - z_2.$

(1)(6) $y_1 + y_2, \quad z_1 + z_2.$

(1)(7) $\frac{1}{2} + y_2 - y_1, \quad \frac{1}{2} - z_2 - z_1.$

(1)(8) $\frac{1}{2} - y_2 - y_1, \quad \frac{1}{2} + z_2 - z_1.$

A solution may now be found by considering the following special vectors:-

(1)(3) $\frac{1}{2}, \ \frac{1}{2} - 2z_1.$

(2)(4) $\frac{1}{2}, \ \frac{1}{2} + 2z_1.$

(1)(4) $\frac{1}{2} - 2y_1, \ \frac{1}{2}.$

(2)(3) $\frac{1}{2} + 2y_1, \ \frac{1}{2}.$

(5)(7) $\frac{1}{2}, \ \frac{1}{2} - 2z_2.$

(6)(8) $\frac{1}{2}, \ \frac{1}{2} + 2z_2.$

(5)(8) $\frac{1}{2} - 2y_2, \ \frac{1}{2}.$

(6)(7) $\frac{1}{2} + 2y_2, \ \frac{1}{2}.$

It will be observed from these vector expressions that there are four vectors with y co-ordinate equal to $\frac{1}{2}$, and four vectors with the z co-ordinate equal to $\frac{1}{2}$, and the Patterson projection showed a similar result.

Therefore $\frac{1}{2} - 2z_1 = 1.08$ or 4.46 A.

$\frac{1}{2} - 2z_2 = 1.08$ or 4.46 A.

Solving z_1 or $z_2 = 78.5^\circ$ or 40.5°, as $c/_2 = 8.11$ A. $= 180^\circ$.

Again $\frac{1}{2} - 2y_1 = 6.10$ or 0.66 A.

$\frac{1}{2} - 2y_2 = 6.10$ or 0.66 A.

Solving y_1 or $y_2 = 14^\circ$ or 81°, as $b/_2 = 7.27$ A. $= 180^\circ$

Thus the four co-ordinates for the two bromine atoms have been found, but the correct y co-ordinate cannot yet be grouped with the correct z value, and also ambiguity arises in that the supplement of each angle is also valid.

Therefore valid co-ordinates in degrees are

y_1 y_2	14.	166.	81.	99.
z_1 z_2	78.5	101.5	40.5	139.5

The correct grouping of co-ordinates can be found by an examination of the vectors given by the above values.

These vectors are obtained by drawing each y and z co-ordinates parallel to the z and y axes, and at each intersection a bromine atom may reside, as in Fig.3.

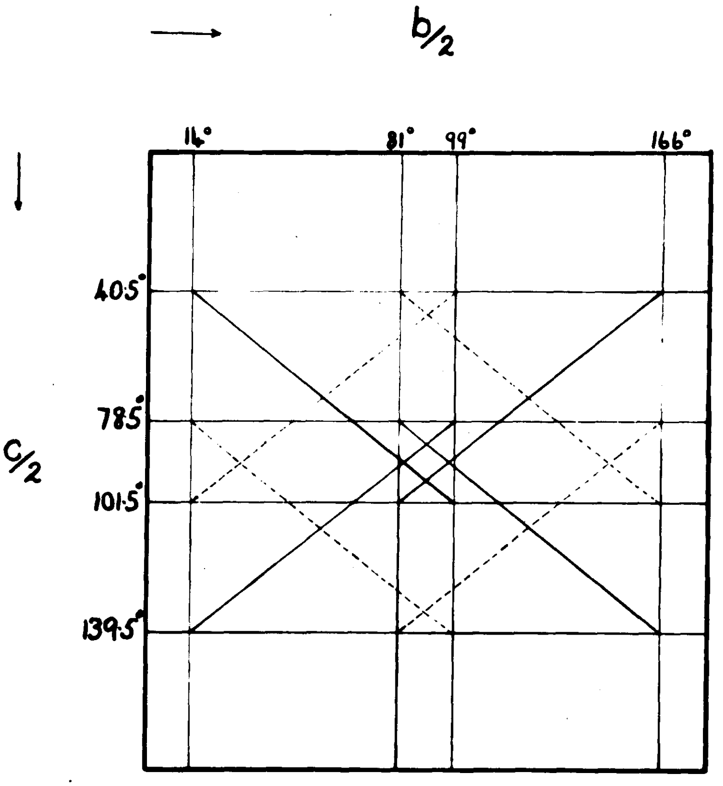


Fig.3 Showing all possible positions occupied by bromine atoms in the quarter unit cell projection, and thus vectors between them. The only valid positions for the bromine atoms are shown by vectors, drawn in full and broken lines, which are similar in magnitude and direction to vectors of the Patterson map.

To find the correct co-ordinates, vectors are measured between these possible bromine positions, in order to find which give values closest to those of the vector map, Fig. 2.

In this respect, the following limitations are of help.

1. Vectors parallel to the y or z axes are invalid.
2. One co-ordinate from each pair of supplements must be in the final choice.
3. No vector less than 3.9A. is valid, as this is the smallest one in the vector map.

Comparison between the vectors of the vector map and those in Fig. 3 gives only one position for each of the two bromine atoms, the vector between which is similar in magnitude and direction to one obtained from the Patterson analysis. Other positions are invalidated by the above limitations.

Now this vector has eight equivalent positions, shown by full and broken lines in Fig.3., and as the vector map can help no further, the correct selection must be made from these eight possible positions by calculating the geometric structure factors A(7) for a number of planes, and comparing them with the corresponding observed structure factors.

Calculation of the geometric structure factors showed that the eight possible positions are grouped into two lots of four, shown by full and broken lines in Fig.3. The numerical values of a number of geometric structure factors of each of the two lots were compared with the corresponding observed structure factor, F obs., as listed.

Plane	A		F obs.
	1st Lot	2nd Lot	
011	0.78	0.32	2.37
021	0.02	0.28	0.49
012	0.17	0.87	0.81
022	1.02	0.96	2.64
013	0.57	0.65	0.97

These values are not on the same scale but undoubtedly the ratio of the values of the 1st Lot is the closer to the ratio of those of F obs.

Therefore the four selections of the 1st Lot give better agreement, and as they are all equivalent, any selection can be taken as the solution of the Patterson projection. The selection chosen is shown overleaf and its choice is justified by plotting its bromine co-ordinates in the unit cell projection (okl), Fig.4, and finding the vectors agree in magnitude and direction with those of the vector map.

	θ_2	θ_3
Br_1	81°	78.5°
Br_2	166°	139.5°

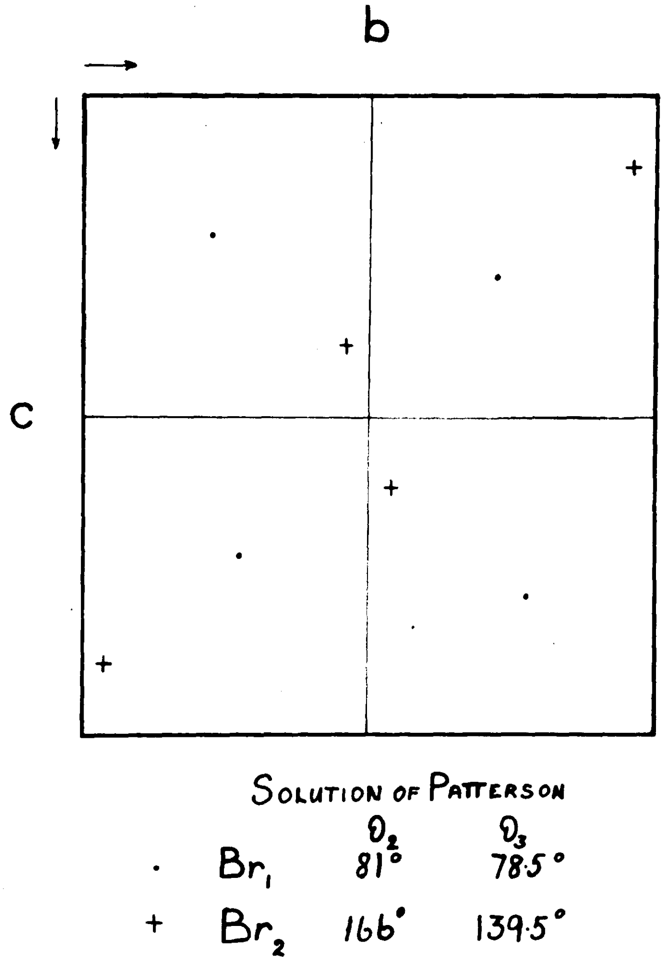


Fig.4. Solution of Patterson projection, showing position of bromine atoms in the (okl) projection.

From the co-ordinates of the bromine atoms, the geometric structure factors for all reflections were calculated, using bromine contributions only, and thus the phase of each reflection was obtained. Associating each phase with the corresponding observed structure factor, these algebraic values were substituted in the two-dimensional Fourier series and in the contour map obtained, all the atoms of the molecule of dihydrobromide in the quarter unit cell were resolved. The angular co-ordinates of these atoms were measured and so their contributions could be included in the calculated F values. These co-ordinates were refined by successive Fourier syntheses, and the final projection obtained is shown in Fig.5

Atomic Co-ordinates

The co-ordinates assigned to the atoms as a result of the final Fourier summations are indicated in Fig.5. and listed in Table 1.

Since the bromine atom is heavy compared with nitrogen and carbon, the co-ordinates of the latter are not accurate, due to the swamping effect, and also to the fact that only 38% of the reflections was used in the synthesis. This small number of recorded reflections was the result of the extremely fine needle crystals used, which required long exposures, and hence the background of the moving film was considerably darkened, so that weak reflections could not be observed.

However, improved resolution should be obtained in the carbon-nitrogen chain when the dihydrochloride, containing a lighter halogen, is examined by Fourier methods. Therefore, the co-ordinates of the atoms of the dihydrobromide will be utilised for the dihydrochloride, this being allowed by isomorphy.

Table 1

Co-ordinates. Centre of symmetry as origin, y and z are referred to the monoclinic crystal axis.

Atom (cf Fig 6)	y, A.	z, A.	$2\pi y/b.$	$2\pi z/c.$
Br_1	3.31	3.50	82.3°	77.7°
Br_2	6.70	6.28	166.4°	139.2°
N_1	5.57	4.03	138.5°	89.3°
C_1	6.54	2.96	162.7°	65.7°
C_2	0.23	5.62	5.8°	124.8°
C_3	1.15	6.45	28.5°	143.0°
C_4	2.22	7.18	55.2°	159.4°
C_5	3.24	7.84	80.3°	174.0°
C_6	3.08	0.18	76.6°	4.0°
N_2	1.60	0.85	39.6°	18.9°

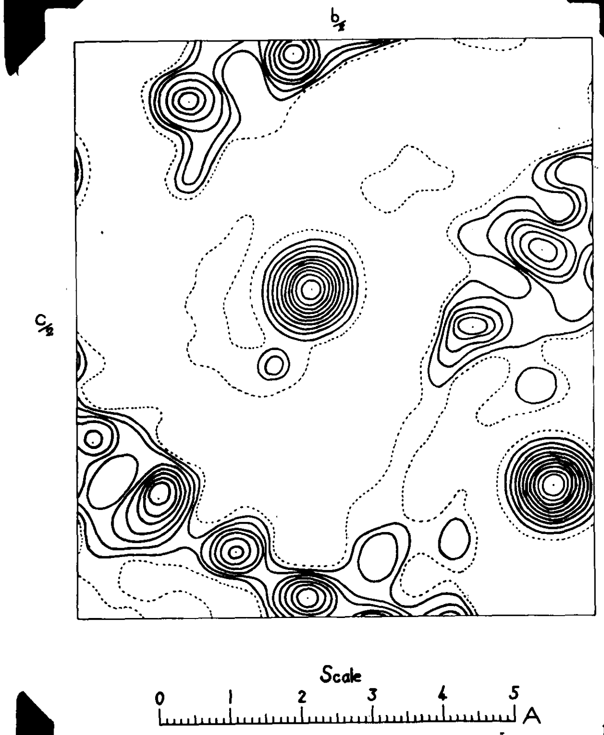


Fig.5 Fourier projection along the a axis on the (okl) plane, showing the asymmetric unit. Contours at intervals of one electron per Å^2, the one electron line being dotted. Density increment of the bromine atoms is five electrons per Å^2.

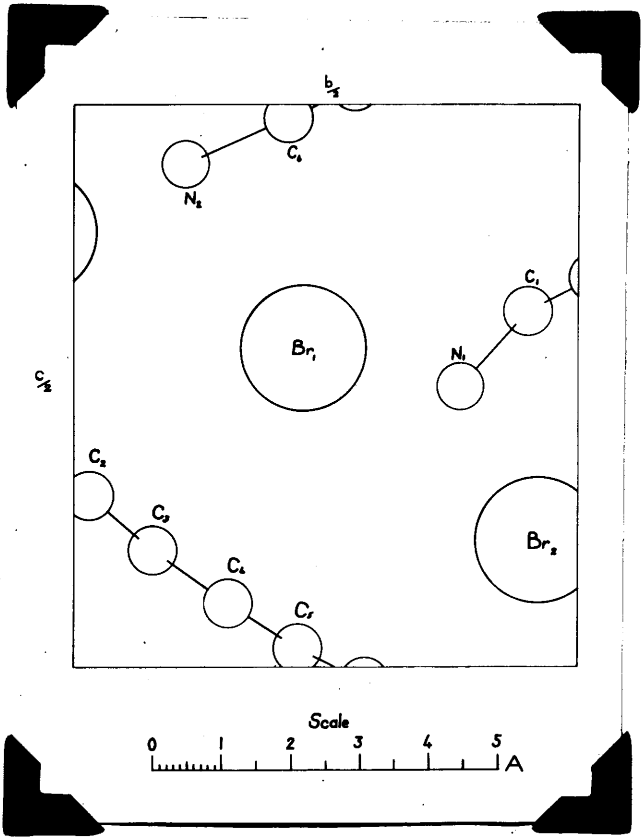


Fig. 6 Explanatory diagram of the (okl) Fourier projection of the dihydrobromide.

Experimental

Preparation and Determination of Data

Hexamethylene diamine dihydrobromide was prepared by slow addition of a concentrated hydrobromic acid solution in acetic acid to a methanolic solution of hexamethylene diamine. Crystals of extremely fine dimensions were obtained from glacial acetic acid, their density being found by the flotation method.

Copper K_α radiation, $\lambda = 1.54$A., was used throughout, and rotation, oscillation, and moving-film photographs of the (okl) zone were taken. The crystal employed for intensity work had a cross-section, normal to the axis of rotation, of 0.05 by 0.05 mm. The specimen was completely immersed in the X-ray beam and the spectra recorded on a series of moving films. The multiple-film technique(8) was used for correlation of intensities, these being estimated visually.

Absorption corrections were not applied, as the dimensions of the crystal render them unnecessary. Structure factor values were finally derived by the usual formulae for mosaic crystals and are listed in Table II. These observed values were brought to the correct scale by correlation with the values finally calculated from the atomic positions found.

Structure Determination

The structure was refined by two successive Fourier synthesis giving a projection on the (100) plane. The Fourier series was summed at 900 points on the asymmetric crystal unit, the axial sub-divisions being $b/_{60}$ = 0.242A., and $c/_{60}$ = 0.270A.

Three-figure methods(9) were employed, and the positions of the contour lines plotted on a scale of 5 cms to 1A. by graphical interpolation from the summation totals. The final map of the asymmetric unit for the projection along a is shown in Fig.5, and in this diagram the final positions assigned to the atoms are indicated by small dots.

The atomic scattering curves for bromine and carbon used in the calculation of the geometric structure factors, the results of which are given in Table II, were taken from the "International Tables",(10) and corrected for temperature according to the Debye-Waller formula.(11) The scattering curve employed for nitrogen was the one obtained for carbon, the error thus introduced being negligible due to the much larger scattering power of bromine.

The discrepancy finally obtained, expressed as

$$\frac{\sum (/F \text{ obs.}/ \;-\; /F \text{ calc.}/)}{\sum /F \text{ obs.}/}$$

is 16.7% for the (okl) reflections.

Table II

Measured and calculated values of the structure factors of Hexamethylene Diamine Dihydrobromide.

(λ = 1.54 A.)

okl	sinθ	F meas	F calc
020	.108	< 9	-8
040	.211	151	+152
060	.319	61	-61
080	.421	< 18	+10
010,0	.529	53	-51
012,0	.635	60	-65
014,0	.739	< 25	-6
002	.095	62	-57
004	.190	< 11	-19
006	.286	99	-83
008	.379	59	+64
00,10	.475	81	+83
00,12	.571	79	-67
00,14	.665	< 25	+1
00,16	.760	< 25	+11
00,18	.855	43	+60
011	.070	60	+72
012	.108	20	-19
013	.151	25	-33
014	.196	112	+105
015	.242	89	-79
016	.289	128	-121
017	.339	< 16	-10
018	.382	60	+65
019	.429	91	+87
01,10	.478	41	-49
01,11	.529	< 22	-2
01,12	.572	40	+47
01,13	.619	48	-44
01,14	.670	< 25	-15
01,15	.717	< 25	-22
01,16	.765	< 25	-11

okl	sinθ	F meas	F calc
021	.115	12	+8
022	.141	66	+80
023	.177	24	+12
024	.217	240	-216
025	.259	54	-53
026	.303	21	-21
027	.348	56	-47
028	.392	61	+61
029	.439	18	+16
02,10	.490	< 21	+8
02,11	.537	< 22	+12
02,12	.583	< 23	+17
02,13	.625	25	+33
02,14	.674	80	-89
02,15	.720	36	-37
02,16	.768	25	+43
031	.166	30	+35
032	.186	141	+120
033	.214	< 12	+7
034	.247	45	-36
035	.285	127	-108
036	.326	< 15	+14
037	.368	47	+36
038	.410	125	-119
039	.454	33	+24
03,10	.501	73	+88
03,11	.550	< 20	+32
03,12	.595	< 26	+8
03,13	.636	43	-48
03,14	.687	< 25	+1
03,15	.731	< 25	-16
03,16	.779	< 24	-25

okl	sinθ	F meas	F calc
041	.216	153	+138
042	.231	70	-60
043	.254	26	+26
044	.285	< 14	+1
045	.319	< 15	+8
046	.354	16	-8
047	.393	56	-48
048	.434	38	+45
049	.477	< 20	-4
04,10	.520	68	+67
04,11	.564	72	+69
04,12	.608	54	-57
04,13	.655	< 25	-7
04,14	.701	< 25	+19
04,15	.747	< 25	-1
04,16	.789	34	-36
051	.268	31	+34
052	.281	69	+57
053	.301	47	-54
054	.326	108	+93
055	.356	17	+27
056	.389	156	-138
057	.425	38	-49
058	.464	< 20	+1
059	.502	67	+74
05,10	.546	< 22	+4
05,11	.589	< 23	-12
05,12	.629	60	+69
05,13	.674	< 25	-9
05,14	.719	< 25	-18
05,15	.760	< 25	-22
05,16	.809	< 23	-32
061	.322	< 15	-13
062	.332	50	+54
063	.349	159	+150
064	.370	48	-53
065	.397	62	-70
066	.427	< 18	+8
067	.459	63	-57
068	.495	< 21	+5
069	.533	< 22	-3
06,10	.572	32	-29
06,11	.611	24	+13
06,12	.655	< 25	+11
06,13	.695	< 25	+33
06,14	.740	< 25	+9
06,15	.782	69	-71
06,16	.825	< 19	+30
071	.374	17	-23
072	.383	119	+103
073	.397	50	+38
074	.418	< 18	+9
075	.440	43	-47
076	.467	28	-21
077	.497	47	+51
078	.529	62	-75
079	.565	46	-55
07,10	.603	42	+55
07,11	.641	35	+45
07,12	.681	< 25	+15
07,13	.721	< 25	-10
07,14	.764	< 25	-18
07,15	.805	< 23	-5
07,16	.847	< 22	+1
081	.426	129	+120
082	.433	33	-31
083	.445	< 19	+10
084	.465	49	+50
085	.485	< 21	+9
086	.509	< 21	-4
087	.538	62	-57
088	.568	23	-11
089	.599	< 24	-16
08,10	.636	< 25	-19
08,11	.674	79	+89
08,12	.709	< 25	-6
08,13	.750	< 25	-9
08,14	.790	< 24	+37
08,15	.831	< 23	+10
091	.478	< 20	-8
092	.486	41	+45
093	.495	< 21	-17
094	.513	30	+27
095	.533	76	+90
096	.555	45	-51

okl	sinθ	F meas	F calc
097	.582	74	-76
098	.607	< 24	-7
099	.638	< 25	+4
09,10	.673	< 25	+17
09,11	.708	25	-36
09,12	.743	< 25	+36
09,13	.781	< 24	+32
09,14	.819	< 23	-11
010,1	.532	31	-32
010,2	.538	< 22	-2
010,3	.549	64	+80
010,4	.562	50	+39
010,5	.580	33	-41
010,6	.597	< 24	+23
010,7	.625	42	-46
010,8	.649	< 25	-16
010,9	.677	< 25	+14
010,10	.711	35	-29
010,11	.741	< 25	-6
010,12	.776	< 24	+15
010,13	.810	< 23	+42
010,14	,849	< 22	+24
010,15	.887	28	-56
010,16	.926	< 18	-3
011,1	.584	53	-57
011,2	.588	< 23	+15
011,3	.599	58	+63
011,4	.610	< 24	-5
011,5	.627	< 24	+9
011,6	.648	25	-28
011,7	.670	36	+42
011,8	.694	< 25	-8
011,9	.721	71	-83
011,10	.750	< 25	+8
011,11	.784	< 24	+31
011,12	.815	< 23	+19

okl	sinθ	F meas	F calc
012,1	.637	49	+56
012,2	.640	< 25	+1
012,3	.651	35	-28
012,4	.662	< 25	+22
012,5	.677	< 25	+30
012,6	.696	25	+25
012,7	.716	25	-17
012,8	.739	37	-32
012,9	.765	< 25	-5
012,10	.793	< 24	-30
012,11	.823	< 23	+36
013,1	.689	35	-46
013,2	.695	< 25	+14
013,3	.703	< 25	-11
013,4	.714	< 25	-11
013,5	.728	71	+82
013,6	.745	< 25	+20
013,7	.764	35	-43
013,8	.785	< 25	-9
013,9	.811	< 23	-3
014,1	.741	35	-53
014,2	.747	< 25	-18
014,3	.755	< 25	+20
014,4	.765	43	+46
014,5	.778	< 24	-16
014,6	.793	< 24	+21
014,7	.812	< 23	+13
014,8	.832	< 23	-23
014,9	.855	< 22	+6
014,10	.880	20	-11
0			
015,1	.795	< 24	-29
015,2	.800	< 24	-18
015,3	.806	33	+46
015,4	.815	< 23	+15

Hexamethylene Diamine Dihydrochloride

Crystal Data

Hexamethylene diamine dihydrochloride, $C_6H_{18}N_2Cl_2$; mol.wt. 189; m.pt. 254.5°C; calculated density 1.212; measured density 1.216; monoclinic prismatic, with $a = 4.60 \pm 0.02$A., $b = 14.19 \pm 0.04$A., $c = 15.68 \pm 0.04$A., and $\beta = 90.8^\circ \pm 0.2^\circ$. Absent spectra, (hol) when l is odd, (oko) when k is odd. Hence space group, $C^5_{2h}(P2_{1/c})$. Four molecules per unit cell; molecular symmetry, nil. Volume of unit cell, 1023A^3. Total number of electrons per unit cell = F(000) = 408. Absorption coefficient for X-rays (λ = 1.54A.), μ = 51.3cm^{-1}.

Well-formed crystals were readily obtained from a mixture of ethyl alcohol and water as slender colourless needles, elongated along the short a axis, the prominent faces formed being 011, $0\bar{1}\bar{1}$, $0\bar{1}1$, $01\bar{1}$. The cross-section of the crystals could be increased by slow cooling in a vacuum flask, the dimensions of these being more suitable for X-ray analysis.

Similarity in the space group and unit cell dimensions of the dihydrochloride and dihydrobromide of hexamethylene diamine point to isomorphy.

Structure Analysis

A set of quantities $F^2(okl)$ was obtained from measured intensities of reflections from the equatorial layer line for a crystal rotated on the a axis. These values were substituted as coefficients in the two-dimensional Fourier series and a Patterson projection drawn, Fig.7, which showed marked similarity to that of the dihydrobromide. This offers conclusive proof of isomorphy.

Nine distinct peaks are shown in the Patterson projection and their co-ordinates (y,z) are comparable with those of the dihydrobromide. Co-ordinates of the peaks in A. are

(1)	$y = 3.71$	$z = 1.64$
(2)	$y = 3.32$	$z = 2.45$
(3)	$y = 4.47$	$z = 6.24$
(4)	$y = 2.63$	$z = 5.20$
(5)	$y = 0.95$	$z = 3.65$
(6)	$y = 7.09$	$z = 1.07$
(7)	$y = 7.09$	$z = 4.31$
(8)	$y = 5.89$	$z = 7.84$
(9)	$y = 0.71$	$z = 7.84$

In view of the analogous nature of the Patterson projections of the dihydrochloride and dihydrobromide, the solution found for the latter is equally correct for the former. Therefore, the co-ordinates of the

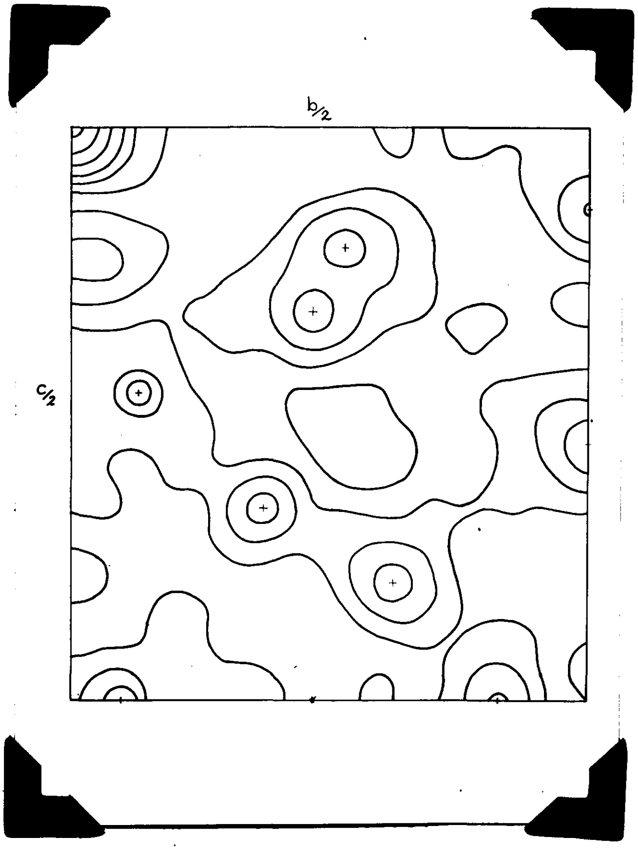


Fig.7 Patterson contour map of the (okl) projection of hexamethylene diamine dihydrochloride.

atoms in the final Fourier map of the dihydrobromide were scaled to the b and c axes of the dihydrochloride unit cell, and these values utilised in the calculation of the structure factors of the latter, the discrepancy between the measured and calculated structure factors then being found as 32.7%. This high discrepancy was considerably reduced by the method of successive approximations, and by extending the number of recorded reflections to 75% of the possible number, by an eight hours exposure of the crystal.

Phases obtained from the geometric structure factors were assigned to the corresponding measured F, and these algebraic values used as coefficients in the double Fourier series, the final electron density map, expressed as electrons per $A.^2$, being shown in Fig.8. Since the swamping effect of chlorine is considerably less than that of bromine, the y and z co-ordinates of the carbons and nitrogens in the normal chain are now more accurately known. The accuracy of each co-ordinate is further increased by the fact that each atom in the projection is separately resolved.

The x co-ordinates of the chlorine atoms were

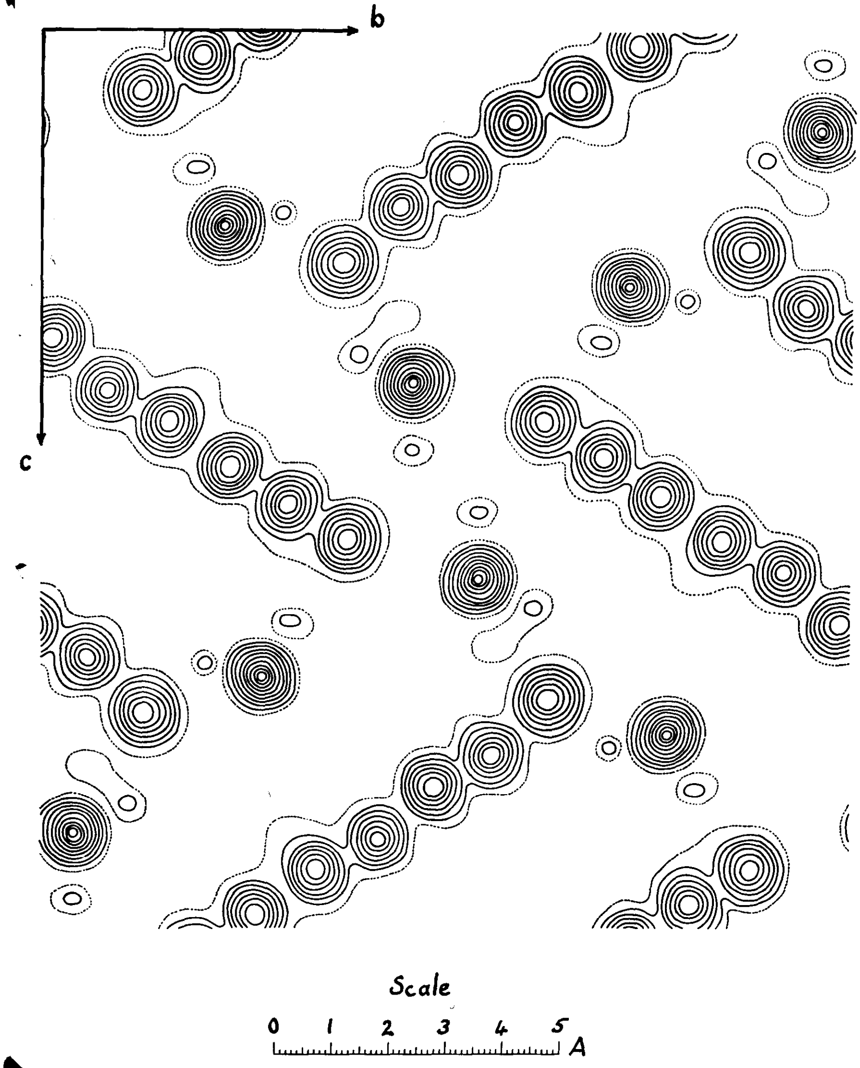


Fig.8 Fourier projection along the a axis on the (okl) plane. Contours at intervals of one electron per A^2. the one electron line being dotted. Density increment of the chlorine atoms is three electrons per A^2.

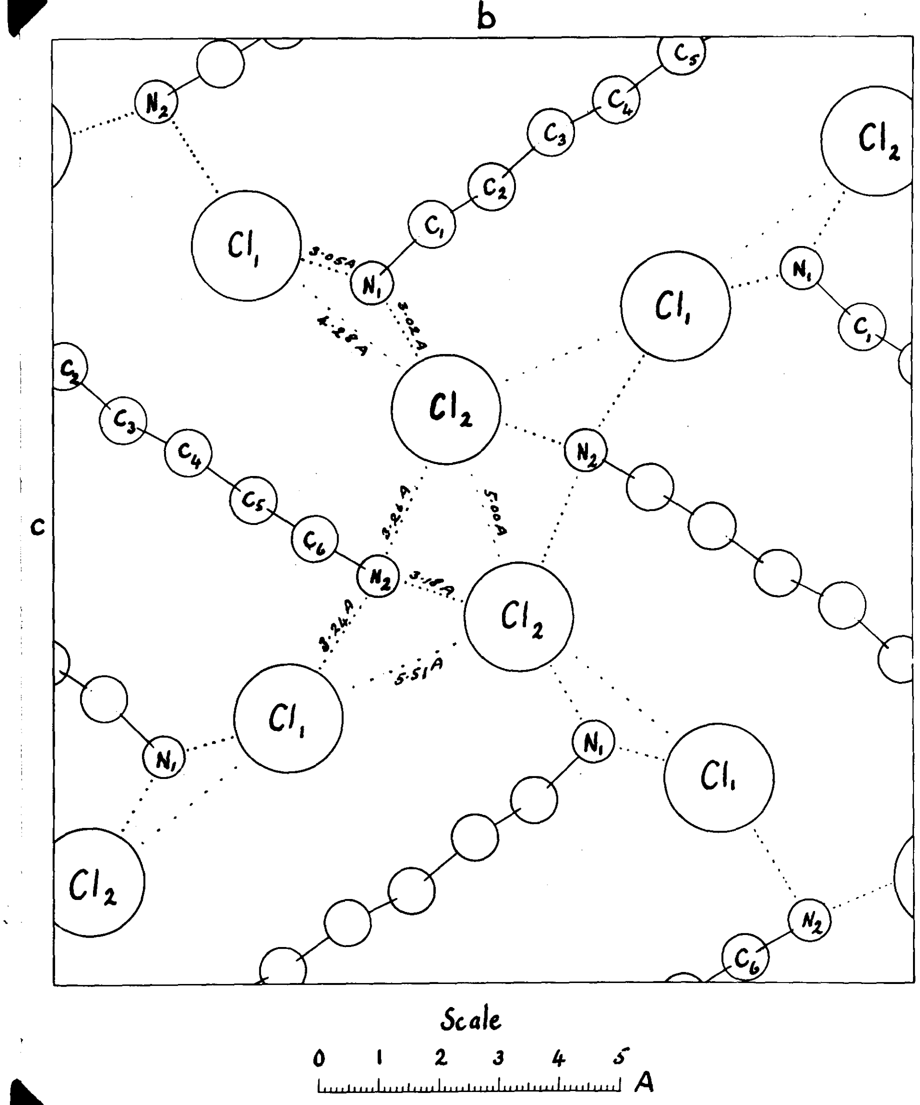


Fig.9 Explanatory diagram of the (okl) Fourier projection of hexamethylene diamine dihydrochloride.

obtained from a Patterson projection normal to the b axis, and those of the open carbon-nitrogen chain obtained by trial.

The Patterson projection (hol), Fig.10, was obtained from the values of F^2(hol), the intensities of which were estimated from the equatorial layer line of a crystal rotated on the b axis. Due to rapid falling-off of reflections with increased angle of diffraction, an eight hours exposure was required to observe 76% of all possible reflections.

This projection does not give such clear indication of inter-atomic distances as the (okl) Patterson, due to the smaller area of projection which results in the gross overlapping of vectors. Nevertheless a solution was readily found, since the z co-ordinates of the chlorines were known, by equating mathematical expressions for the abscissae of vectors and the corresponding angular values obtained from the Patterson projection.

Only two distinct peaks are given by the projection, Fig.10, as indicated by small crosses, and although a number of lesser peaks can be observed, they were not considered as they would probably lead to misinterpretation.

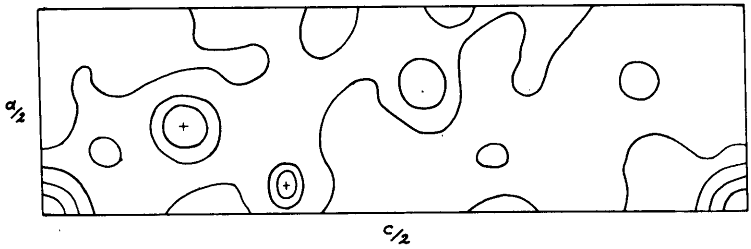
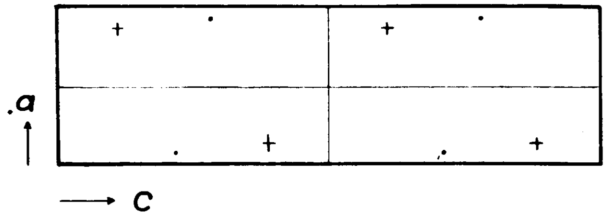


Fig.10 Patterson contour map of the (hol) projection of hexamethylene diamine dihydrochloride.



SOLUTION OF PATTERSON

		θ_1	θ_3
·	Cl_1	26°	78°
+	Cl_2	50°	141°

Fig.11. Solution of Patterson projection, showing positions of chlorine ions in the (hol) projection.

The linear and angular co-ordinates of the peaks are

(1) $x = 0.31$A $\quad$ or $\quad$ $\theta_1 = 24^\circ$
 $z = 2.64$A. $\quad\quad\quad\;\,$ $\theta_3 = 60.5^\circ$

(2) $x = 0.97$A. $\quad$ or $\quad$ $\theta_1 = 75.5^\circ$
 $z = 1.60$A. $\quad\quad\quad\;\,$ $\theta_3 = 36.5^\circ$

Now if the co-ordinates of the two chlorine ions in the asymmetric unit are

$$Cl_1 = (x_1, z_1) \quad \text{and} \quad Cl_2 = (x_2, z_2),$$

then they will be reproduced by symmetry operations in the equivalent positions$^{(6)}$, namely,

(1) x_1, z_1; (2) $\bar{x}_1, \bar{z}_1$; (3) $x_1, \frac{1}{2} + z_1$; (4) $\bar{x}_1, \frac{1}{2} - z_1$;
(5) x_2, z_2; (6) $\bar{x}_2, \bar{z}_2$; (7) $x_2, \frac{1}{2} + z_2$; (8) $\bar{x}_2, \frac{1}{2} - z_2$;

Therefore vectors between chlorine$_1$ and chlorine$_2$ include:-

(1)(5) $x_1 - x_2, \quad z_1 - z_2.$
(1)(6) $x_1 + x_2, \quad z_1 + z_2.$
(1)(7) $x_2 - x_1, \quad \frac{1}{2} + z_2 - z_1.$
(1)(8) $x_1 + x_2, \; -\frac{1}{2} + z_1 + z_2.$

Since the z co-ordinates of the chlorine ions are known from the (okl) Fourier projection, suitable equations can be derived and solved to give the x co-ordinates. Each vector obtained from the Patterson is identified by means of the known z co-ordinates as one of the above mathematical expressions, and the abscissa of this expression is equated with the θ_1 angular co-ordinate of the vector's peak.

The z_1 co-ordinate of $\text{chlorine}_1 = 78^{\circ}$

z_2 co-ordinate of $\text{chlorine}_2 = 141^{\circ}$

Therefore $z_2 - z_1 = 141^{\circ} - 78^{\circ} = 63^{\circ}$ which is comparable with the θ_3 value of peak (1), viz., 60.5°

And $z_2 - z_1$, is the ordinate of the vector expression $(x_2 - x_1, \; z_2 - z_1)$

$\therefore x_2 - x_1 = 24^{\circ}$ .... A

Again $-\frac{1}{2} + z_2 + z_1 = (-180 + 141 + 78)^{\circ} = 39^{\circ}$ which is comparable with the θ_3 value of peak (2), viz. 36.5°.

And $-\frac{1}{2} + z_2 + z_1$ is the ordinate of the vector expression $(x_1 + x_2, \; -\frac{1}{2} + z_1 + z_2)$.

$\therefore x_1 + x_2 = 75.5^{\circ}$.............. B

Solving A and B $x_1 = 26^{\circ}$

$x_2 = 50^{\circ}$

Therefore the solution of the Patterson projection is

x co-ordinate of $\text{chlorine}_1 \theta_1 = 26^{\circ}$

x co-ordinate of $\text{chlorine}_2 \theta_2 = 50^{\circ}$

and is illustrated in Fig. 11.

Since the angular co-ordinates (θ_1, θ_3) of the two chlorine ions and the θ_3 co-ordinates of the carbon-nitrogen chain have been found, it seems probable that trial and error procedure will result in a ready solution of the θ_1 values of the chain. This is aided by the fact that in the (hol) projection of the space group $P2_{1/c}$, the geometric structure factors are expressed as the cosine of a sum or difference of angles(7). The advantage of this is that atoms give a positive maximum contribution to the reflecting power of a plane if they lie exactly on that plane, and as these atoms are moved normally from that plane, their contribution to the reflecting power varies in magnitude and sign as the cosine curve. Therefore a plane with a large measured structure factor means that several atoms are situated on that plane to give a high positive contribution, or else they are placed midway between two parallel planes of the same series to give a high negative contribution.

Another aid to the trial structure is obtained from the alternating long and short bonds of the carbon-nitrogen chain in the (okl) Fourier projection. This ratio of long to short bonds gives a value of 5° for the tilt of the chain to the (okl) projection, and since the c axis is long compared with the a axis (15.68A. to 4.60A.), the molecule is probably directed along c in the (hol) projection. Also the reflecting plane $(10\bar{2})$ has the greatest value of measured F in the whole zone, and since this plane is inclined towards the origin in the unit cell projection, it is probable that the chain is tilted in the same direction, so that the calculated F value of $(10\bar{2})$ can be equally high. The direction of this tilt also determines the shape of the zig-zag which the carbon-nitrogen chain gives in the (hol) projection.

The reflection which is of most importance is $(10,\overline{12})$ because the maximum calculated F is only slightly greater than the measured F, 87 as against 73. Therefore the chain must be tilted towards the origin at 5° to the c axis, and such that pairs of atoms of the zig-zag lie in the maximum positive or maximum negative areas of the $(10,\overline{12})$ series of planes.

Hence a model of the carbon-nitrogen chain was made to scale, and slid up the θ_3 co-ordinates of the atoms drawn on the same scale on the (hol) projection, until planes $(10,\overline{12})$, $(10\bar{2})$, (206), (204), (304), would have large calculated Fs. Such a position was found halfway up the a axis.

The co-ordinates obtained from the Patterson projection and trial method were refined by successive Fourier syntheses, the final projection being shown in Fig.12. In this projection, there is considerable overlapping of atoms, such that only three atoms besides the halogens are separately resolved. However, because the superimposition is almost exact, the remaining atoms can be quite accurately located.

Therefore, co-ordinates of the atoms of the asymmetric unit have been measured, yielding a precise picture of the whole structure.

A further series of the zero layer line of the c axis gave measured values for the structure factors of the reflections of the (hko) zone, the calculated values being obtained from the angular co-ordinates θ_1 and θ_2 of the atoms of the dihydrochloride molecule. However no Fourier series was carried out as gross overlapping of atoms occurs in this projection, and more accurate co-ordinates would not be obtained.

Co-ordinates and Molecular Dimensions

The co-ordinates assigned to the atoms of the asymmetric unit as a result of the final Fourier

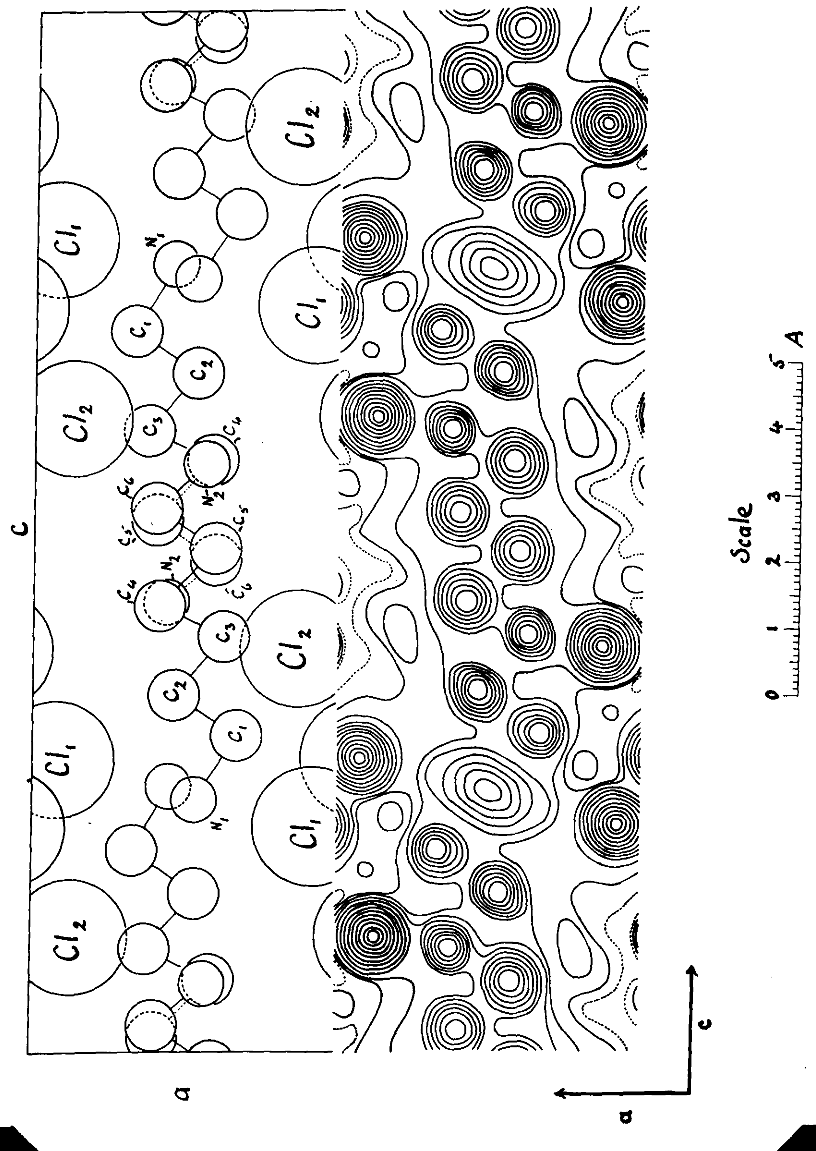


Fig.12 Fourier projection along the b axis on the (hol) plane. Contours at intervals of one electron per A^2, except where overlapping occurs where the interval is two electrons per A^2; the one electron line is dotted. Density increment of the chlorine ions is three electrons per A^2,

summations are indicated in Figs. 14 and 15, and listed in Table III.

These co-ordinates lead to the molecular and intermolecular dimensions shown in Figs. 9, 12, and 13. The orientation of the molecule with respect to the crystal axes is expressed in terms of angles, as in Table IV. λ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M, and χ_N, ψ_N, ω_N, are the angles between the molecular axes L, M, and N, and the crystal axes a, b, and c'; c' being perpendicular to a and b. The molecular axis L is the direction of the carbon chain; M lies in the plane of the molecule and is perpendicular to L; N is the normal to the molecular plane. The co-ordinates of the atoms with respect to these molecular axes are given in Table V, where the chain of carbon atoms is shown to be coplanar, with the nitrogens displaced from this plane.

Table III

Co-ordinates. Centre of symmetry as origin, x,y,z are referred to the monoclinic crystal axes. x′,y,z are rectangular co-ordinates referred to the a and b crystal axes, and their perpendicular, c′.

Atom (cf.Fig.9)	x,A.	y,A.	z,A.	x′,A.
Cl$_1$	0.360	3.204	3.404	0.326
Cl$_2$	0.590	6.520	6.116	0.529
N$_1$	2.150	12.380	3.810	2.112
C$_1$	1.520	13.370	4.770	1.473
C$_2$	2.480	0.164	5.390	2.426
C$_3$	1.720	1.148	6.270	1.657
C$_4$	2.600	2.220	6.836	2.532
C$_5$	1.840	3.300	7.630	1.764
C$_6$	2.780	4.294	8.240	2.698
N$_2$	1.940	5.392	8.856	1.852

	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
Cl$_1$	28.0°	81.3°	78.0°
Cl$_2$	46.0°	165.5°	141.1°
N$_1$	168.5°	313.5°	87.5°
C$_1$	119.0°	340.0°	110.5°
C$_2$	194.0°	4.2°	124.0°
C$_3$	135.1°	29.2°	144.1°
C$_4$	204.1°	56.4°	157.0°
C$_5$	144.5°	84.0°	175.1°
C$_6$	217.0°	109.0°	189.2°
N$_2$	152.1°	136.8°	203.3°

Table IV

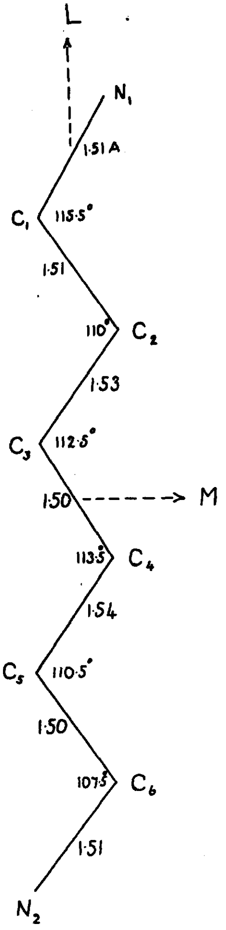
Orientation of the molecule in the crystal.

$\chi_L = 87.6^\circ$	$\psi_L = 35.2^\circ$	$\omega_L = 54.9^\circ$
$\cos \chi_L = 0.0421$	$\cos \psi_L = 0.8172$	$\cos \omega_L = 0.5746$
$\chi_M = 10.8^\circ$	$\psi_M = 85.9^\circ$	$\omega_M = 100.0^\circ$
$\cos \chi_M = 0.9822$	$\cos \psi_M = 0.0715$	$\cos \omega_M = -0.1737$
$\chi_N = 79.5^\circ$	$\psi_N = 124.9^\circ$	$\omega_N = 36.9^\circ$
$\cos \chi_N = 0.1831$	$\cos \psi_N = -0.5718$	$\cos \omega_N = 0.7998$

Table V

Co-ordinates of atoms with respect to molecular axes.

Atom.	L,A.	M,A.	N,A.
N_1	-4.429	0.244	-0.187
C_1	-3.100	-0.480	-0.107
C_2	-1.893	0.419	0.000
C_3	-0.619	-0.419	-0.001
C_4	0.619	0.419	0.001
C_5	1.924	-0.396	-0.100
C_6	3.123	0.486	-0.029
N_2	4.340	-0.373	-0.282



$C_6H_{18}N_2Cl_2$

Fig.13 Dimensions of the hexamethylene diamine dihydrochloride molecule.

Experimental

Preparation and Determination of Data

Hexamethylene diamine dihydrochloride was prepared by saturation of a methanolic solution of the hexamethylene diamine with dry hydrochloric acid gas.(12) Slender needle crystals which were thickened by slow cooling in a Dewar flask, were obtained from a mixture of ethyl alcohol and water in the proportion 20 to 1. Density measurements were made by the flotation method, carbon tetrachloride and benzene being used as the suspension mediums, and the highest value obtained was 1.216, in good agreement with the calculated value of 1.211 for four molecules in the unit cell.

Copper K_α radiation, λ = 1.54A., was employed in all the measurements. Rotation, oscillation and moving-film photographs were used, the latter chiefly for intensity records. The axial and zonal halvings found were in accordance with the space group $P_{2_{1/c}}$. The (okl), (hol) and (hko) zones were explored in detail by moving-film exposures of the equatorial layer lines for crystals rotated about the unit cell edges. The multiple-film technique(8) was used to correlate the strong and weak reflections, the intensities of which were estimated visually and ranged from 1500 to 1. The absolute scale of the measured F values was determined by correlation with the calculated F values, and the former listed in Table VI.

Small crystals were used for the Weissenberg series and were completely bathed in a uniform X-ray beam. The cross-sections of the crystals normal to the rotation axes for the zones (okl), (hol), (hko) were 0.18 by 0.18 mm., 0.26 by 0.28 mm., and 0.53 by 0.56 mm. respectively. Absorption corrections were not employed, as the uniform cross-sections of the crystal specimens render them unnecessary.

Fourier Analysis and Structure Determination

After preliminary determination of atomic positions by trial and Patterson's methods, the structure was refined by successive two-dimensional Fourier syntheses giving projections on (100) and (010). The electron densities on these planes were computed at 900 and 450 points respectively on the asymmetric unit from the usual formulae for $\rho(y,z)$ and $\rho(x,z)$. Axial sub-divisions were $a/_{30}$ = 0.153A., $b/_{60}$ = 0.236A., and $c/_{60}$ = 0.261A. The early summations were carried out by Beever-Lipson Strips(13) and the final syntheses summed to three-figure accuracy by using the stencils recently introduced by Robertson.(14)

The positions of the contour lines were obtained by graphical interpolation from the summation totals, by making sections of the rows and columns. The resulting contour maps are shown in Figs. 14 and 15, from which the centres of the atoms were taken. The co-ordinates of these centres are found to be consistent with the molecular model, Fig.13, and the orientation listed in Table IV.

From these co-ordinates, all the structure factors were recalculated and the results listed in Table VI. The atomic scattering curves for the chlorine ion and carbon were taken from the "International Tables,"(10) and corrected for temperature according to the Debye-Waller formula.(11) Nitrogen was given the same weight as carbon. This will not appreciably affect the accuracy because of the presence of the heavy chlorine ions.

The discrepancy finally obtained, expressed as the sum of all the discrepancies divided by the total of the measured structure factors, is 15.9% for (okl) reflections, 16.3% for (hol) reflections, 18.2% for (hko) reflections, and 16.6% for all reflections.

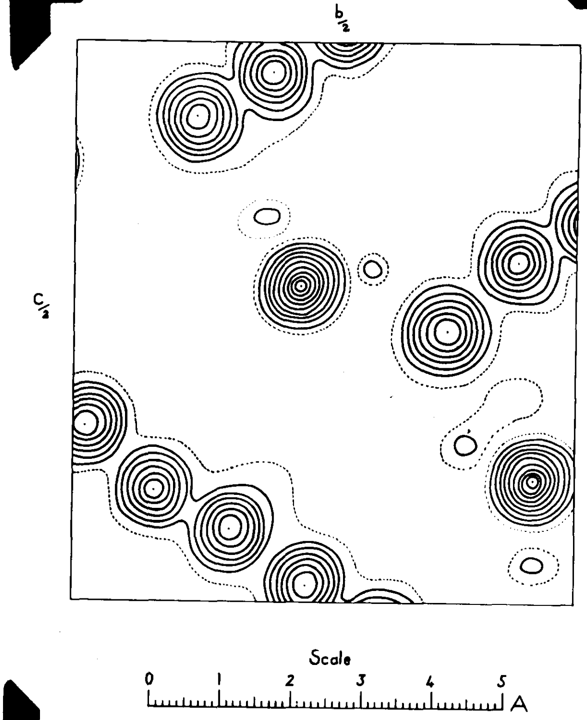


Fig.14 Co-ordinates assigned to the atoms in the asymmetric crystal unit projection (okl)

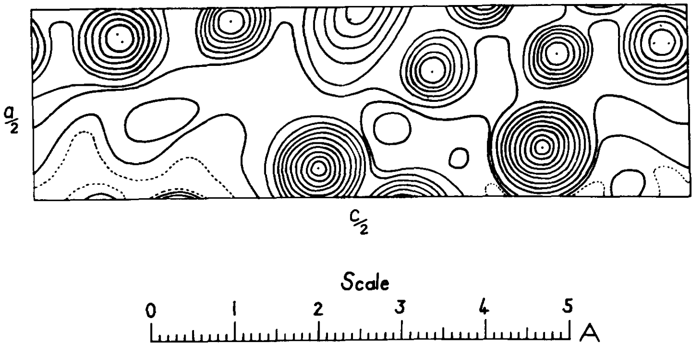


Fig 15. Co-ordinates assigned to the atoms in the asymmetric crystal unit projection (hol)

The discrepancy is of the order usually encountered in such investigations, and it substantiates the employment of the temperature corrected scattering curves of the "International Tables", especially where there is a heavy ion in the asymmetric unit, as this will compensate for any error in the temperature correction applied to the lighter atoms.

Table VI

Measured and calculated values of the structure factors of Hexamethylene Diamine Dihydrochloride.

(λ = 1.54 A.)

hkl	sinΘ	F meas	F calc	hkl	sinΘ	F meas	F calc
100	.168	39.	-33	110,0	.567	20.5	-16
200	.335	45.5	+49.5	111,0	.620	7.5	-7
300	.503	13.5	-15.5	112,0	.674	19.5	-17.5
400	.670	41.5	-38.5	113,0	.726	< 5.5	+0.5
500	.838	11.	-12.	114,0	.779	7.5	-8.
020	.109	< 2.	-2.5	115,0	.833	< 5.	-0.5
040	.218	47.5	+56.5	116,0	.886	18.	-20.
060	.327	23.5	-24.	117,0	.939	12.5	+12.
080	.435	6.5	+4.	118,0	.993	3.	+8
010,0	.544	26.	-24.5	210	.338	48.	-44.
012,0	.653	29.	-28.	220	.350	29	-25.
014,0	.761	< 6.	-1	230	.370	< 4.	+3.5
016,0	.870	10.	-12.5	240	.399	11.5	+9.
018,0	.979	8.5	+9.	250	.430	37.5	-43.
002	.098	11	-12	260	.466	6.5	+1.5
004	.197	13	+8	270	.504	42.	-39.
006	.295	48	-43.5	280	.547	20.	+20.
008	.393	20.5	+15.5	290	.591	26.	-23.5
00,10	.491	34.	+36.5	210,0	.637	5.5	+3.
00,12	.590	19.5	-17.5	211,0	.684	8.	-10.
00,14	.690	< 6.	-2.5	212,0	.733	< 5.5	-3.
00,16	.785	8.	-12.5	213,0	.782	13.5	+13.
00,18	.885	15.	+20.5	214,0	.830	7.	+7.
00,20	.985	< 2.5	+4.	215,0	.881	< 4.5	+2.
				216,0	.931	< 3.5	-3.
110	.176	30.5	-34.5	217,0	.983	12.5	+18.
120	.199	10.5	-12.	310	.504	32.5	-32.
130	.235	< 3.	-1.	320	.512	23.5	-21.
140	.276	56.	+59.	330	.526	17.	+10.
150	.320	43.5	-45.	340	.546	8.5	-5.
160	.365	26.	-23.	350	.570	41.5	-45.5
170	.414	5.5	+2.5	360	.597	18.5	-14.5
180	.466	15.5	-11.	370	.628	8.	+11.5
190	.516	19.	-18.	380	.663	5.5	-7.

hkl	sinθ	F meas	F calc	hkl	sinθ	F meas	F calc
390	.699	14.	-14.	10,$\overline{10}$	.526	29.5	+29.5
310,0	.738	9.5	+8.5	10,$\overline{12}$	.619	73.5	-70.
311,0	.779	< 5.5	-3.5	10,$\overline{14}$	.716	< 6.	+6.5
312,0	.822	10.5	+12.	10,$\overline{16}$	.816	< 5.5	-7.5
313,0	.866	8.	+6.5	10,$\overline{18}$	.910	16.5	+19.5
314,0	.911	10.	+9.	20,18	.945	7.5	+11.
315,0	.957	< 3.5	+1.	20,16	.854	22.	-27.
410	.671	22.5	-20.5	20,14	.765	< 6.	+1.5
420	.676	8.5	-5.5	20,12	.676	< 6.	+4.
430	.689	16.	+19.5	20,10	.594	17.	-24.5
440	.703	11.5	-17.5	208	.513	< 5.	+2.
450	.720	< 5.5	-3.	206	.443	68.5	-65.5
460	.743	16.	+11.5	204	.385	66.5	+61.5
470	.768	< 5.5	+2.5	202	.347	11.	+7.
480	.797	9.	+13.	20$\overline{2}$	.350	46.	-35.5
490	.827	< 5.	-3.5	20$\overline{4}$	.393	24.	-20.5
410,0	.860	13.5	+11.5	20$\overline{6}$	.451	37.5	+42.
411,0	.896	< 4.5	-2.1	20$\overline{8}$	.524	< 5.5	-0.5
412,0	.935	13.	+12.	20,$\overline{10}$	.603	< 6.	+12.
413,0	.973	< 3.	+1.	20,$\overline{12}$	.688	< 6.	-5.
510	.838	7.	-3.5	20,$\overline{14}$	.776	23.5	+24.
520	.841	< 5.	-5.	20,$\overline{16}$	.869	12.5	+14.
530	.850	14.	+17.5	20,$\overline{18}$	.958	3.5	+2.5
540	.863	15.	-14.	30,16	.931	7.	-9.
550	.878	< 4.5	-0.5	30,14	.850	9.	-9.5
560	.895	< 4.5	+3.	30,12	.774	33.5	+38.
570	.916	11.5	+14.	30,10	.701	10.5	+9.
580	.940	6.	-2.	308	.636	< 6.	-2.
590	.966	4.5	+7.5	306	.580	31.5	-24.5
510,0	.995	< 2.	+8.5	304	.539	56.	+46.5
				302	.513	< 5.	-0.5
10,18	.901	18.	+18.5	30$\overline{2}$	.515	< 5.	-3.
10,16	.805	22.5	-25.5	30$\overline{4}$	.545	5.5	-7.5
10,14	.710	6.	+3.	30$\overline{6}$	.589	50.5	+52.5
10,12	.615	6.	+9	30$\overline{8}$	.647	29.	-28
10,10	.521	46.	+43.5	30,$\overline{10}$	.714	< 6.	-0.5
108	.427	11.	+10	30,$\overline{12}$	.784	35.	-44.
106	.339	53.	-56.	30,$\overline{14}$	.865	< 5.	+5.
104	.258	9.	+7.5	30,$\overline{16}$	.949	6.5	+6.5
102	.193	24.5	-19.5	40,14	.956	< 3.5	+1.5
10$\overline{2}$	.195	105.	-96.	40,12	.890	4.5	+6.5
10$\overline{4}$	.262	45.	-38.5	40,10	.828	38.	-46.5
10$\overline{6}$	.344	22.	+16.	408	.774	6.	+4.5
10$\overline{8}$	.434	14.5	+16.5	406	.729	6.	+0.5

hkl	sinθ	F meas	F calc	hkl	sinθ	F meas	F calc
404	.696	19.	+23.5	025	.271	29.5	-28.5
402	.677	8.5	-7.5	026	.317	9.	-8.
$40\bar{2}$	.679	10.5	-11.5	027	.364	23.5	-15.5
$40\bar{4}$	.702	< 6.	-1.	028	.410	12.	+8.
$40\bar{6}$	.738	24.	+21.5	029	.457	11.5	+7.5
$40\bar{8}$	.785	20.	-22.5	02,10	.508	5.	+3.
$40,\overline{10}$	.841	<5.5	-2.5	02,11	.555	9.5	+8.5
$40,\overline{12}$	.903	8.	+13.5	02,12	.604	8.	+11.5
$40,\overline{14}$	.973	9.5	+15.5	02,13	.653	13.	+14.
50,10	.969	9.5	-15.	02,14	.699	34.	-33.5
508	.921	7.5	+12.	02,15	.751	14.5	-18.
506	.885	< 5.	+4.	02,16	.797	16.	+16.
504	.858	5.	+5.	02,17	.849	< 5.	+1.
502	.842	< 5.5	-3.5	02,18	.897	< 4.5	+3.5
$50\bar{2}$	.845	42.5	+47.	02,19	.945	< 3.5	-8.
$50\bar{4}$	.863	5.	+2.5	031	.172	7.	+10.
$50\bar{6}$	.893	< 4.5	+10.4	032	.192	68.	+60.5
$50\bar{8}$	.932	12.	-19.	033	.222	14.	+12.5
$50,\overline{10}$	.980	< 3.	-1.5	034	.258	15.5	+12.
				035	.297	65.5	-60.5
011	.074	32.	+28.	036	.339	5.5	-4.5
012	.112	2.	-3.5	037	.383	16.5	+12.
013	.159	14.	+ 7.5	038	.428	47.	-50.
014	.206	53.	+49.	039	.473	11.5	+11.5
015	.253	43.5	-38.5	03,10	.520	32.5	+38.
016	.301	56.	-55.5	03,11	.568	16.	+15.5
017	.353	4.	-5.	03,12	.615	< 5.5	+1.5
018	.399	20.5	+21.5	03,13	.663	20.5	-18.5
019	.448	34.	+37.	03,14	.709	< 6.	+8.5
01,10	.500	18.5	-20.	03,15	.759	< 6.	-1.5
01,11	.548	5.5	-4.	03,16	.807	16.	-16.5
01,12	.595	18.	+17.	03,17	.857	12.	+14.
01,13	.646	16.5	-15.	03,18	.905	9.	-14.5
01,14	.694	< 6.	-0.5	03,19	.952	< 3.5	+6.
01,15	.745	8.5	-10.5	041	.223	74.	+63.
01,16	.795	10.	-9.5	042	.239	27.	-27
01,17	.842	12.	+13.	043	.264	11.	+11.5
01,18	.892	6.5	+10.5	044	.295	3.5	-1.
01,19	.942	< 4.	+5.	045	.330	8.5	+15.5
01,20	.990	< 2.5	-4.	046	.368	24.	+19.5
021	.121	8.5	+3.	047	.409	10.5	-7.5
022	.148	10.5	+13.	048	.451	17.	+18.5
023	.186	67.	-53.5	049	.495	5.	-6.
024	.227	118.	-111.	04,10	.540	30.	+30.5

hkl	sinΘ	F meas	F calc	hkl	sinΘ	F meas	F calc
04,11	.584	35.4	+36.	06,17	.902	< 4.5	+1.
04,12	.630	20.	-22.	06,18	.949	< 3.5	-4.
04,13	.679	< 6.	-4.5	071	.386	9.5	-10.5
04,14	.724	< 6.	+7.5	072	.394	47.5	+43.
04,15	.772	< 6.	-2.5	073	.410	17.	+17.5
04,16	.820	17.5	-22.5	074	.430	11.	+7.
04,17	.870	7.	-6.5	075	.455	18.5	-17.5
04,18	.916	11.	+13.5	076	.484	18.	-16
04,19	.964	8.	+11.5	077	.516	17.5	+16.
051	.278	9.2	+13.	078	.549	30.5	-30.5
052	.290	27.5	+28.	079	.585	11.	-12.5
053	.311	16.	-16	07,10	.624	5.5	+9.
054	.338	52.	+49.5	07,11	.664	20.5	+20.5
055	.369	9.	+8.5	07,12	.705	< 6.	-4.
056	.403	68.	-62.	07,13	.747	< 6.	-7.
057	.441	17.	-20.	07,14	.789	10.	-8.
058	.479	8.5	+8.5	07,15	.834	< 5.5	+2.
059	.520	35.5	+38.	07,16	.877	12.	-13.5
05,10	.564	< 5.5	-0.5	07,17	.925	< 4.	+6.5
05,11	.608	< 5.5	-8.5	07,18	.969	< 3.	-5.
05,12	.651	33.	+33	081	.440	53.5	+50.5
05,13	.698	13.5	-13.	082	.448	18.	-14.5
05,14	.744	< 6.	+3.	083	.462	< 5.	+1.
05,15	.789	8.	-10.	084	.479	25.5	+23.
05,16	.837	15.	-14.5	085	.502	11.	+10.
05,17	.885	6.5	-7.	086	.528	< 5.	-1.5
05,18	.932	< 4.	+1.	087	.556	30.5	-28.
05,19	.978	< 3.	+6	088	.589	5.5	-3.
061	.331	10.5	-8	089	.622	< 5.5	-6.5
062	.341	18.5	+19.5	08,10	.659	23.5	-19.5
063	.360	70.	+67.5	08,11	.696	41.5	+42.
064	.381	18.	-18.5	08,12	.735	8.5	+8.5
065	.410	24.5	-26.5	08,13	.776	< 6.	+2.5
066	.441	8.	+6.5	08,14	.817	15.5	+18.5
067	.476	23.5	-22.5	08,15	.860	< 5.	+4.5
068	.514	5.	-3.	08,16	.905	< 4.5	+0.5
069	.550	21.5	-18.	08,17	.946	10.5	-16.5
06,10	.592	25.	-23.5	08,18	.992	< 2.5	+3.
06,11	.634	10.	+5.5	091	.494	< 5.	-2.
06,12	.676	10.5	+10.5	092	.500	22.	+20.5
06,13	.720	< 6.	+7.5	093	.513	9.	-9.
06,14	.764	< 6.	-6.5	094	.530	10.5	+10.5
06,15	.809	31.5	-30.5	095	.549	33.5	+36.
06,16	.856	7.	+8.	096	.574	9.5	-12.

hkl	$\sin\theta$	F meas	F calc
097	.601	45.5	-44.
098	.630	8.	+6.
099	.660	< 6.	+0.5
09,10	.697	13.5	+12.
09,11	.732	17.	-17
09,12	.769	11.5	+12.5
09,13	.807	12.4	+12.
09,14	.848	< 5.	+3.
09,15	.890	9.5	+12.
09,16	.931	5.5	-6.5
09,17	.975	4.	-4.
010,1	.548	12.	-14.
010,2	.555	< 5.5	+1.5
010,3	.565	31.	+30.
010,4	.580	12.5	+13.
010,5	.599	11.	-11.
010,6	.620	13.	+13.5
010,7	.646	29.	-24.
010,8	.674	6.	-6.5
010,9	.704	6.	+5.5
010,10	.735	17.	-16.5
010,11	.770	< 6.	-1.5
010,12	.805	8.	+5.5
010,13	.844	13.5	+22.
010,14	.881	6.5	+9.
010,15	.921	14.5	-23.
010,16	.961	5.5	-9.5
011,1	.601	19.5	-20.5
011,2	.608	< 5.5	+1.
011,3	.617	36.5	+31.5
011,4	.631	20.	-16.
011,5	.648	16.5	+12.5
011,6	.669	14.5	-15
011,7	.692	22.	+20.5
011,8	.719	< 6.	-3.
011,9	.745	29.	-32.
011,10	.778	< 6.	+1.5
011,11	.810	8.	+11.
011,12	.844	7.5	+5.
011,13	.880	< 5.	+0.5
011,14	.915	< 4.	-1.5
011,15	.953	8.	+12.5
012,1	.656	14.5	+14.
012,2	.663	< 6.	+5.5
012,3	.673	10.	-10.
012,4	.685	6.	+4.5
012,5	.701	10.5	+12.
012,6	.720	15.5	+9.
012,7	.742	8.5	-7.5
012,8	.766	13.	-11.
012,9	.792	< 5.5	-5.5
012,10	.821	9.5	-10.5
012,11	.851	10.5	+11.5
012,12	.885	10.5	+9.5
012,13	.919	9.5	-11.
012,14	.954	8.	+11.
012,15	.990	< 2.5	+10.5
013,1	.712	34.	-30.5
013,2	.717	8.5	+10.
013,3	.726	6.	-8.
013,4	.738	6.	-7.
013,5	.752	29.	+32.
013,6	.770	11.5	+12.
013,7	.790	14.	-15.
013,8	.813	< 5.5	-1.
013,9	.838	< 5.5	-0.5
013,10	.865	< 5.	+0.5
013,11	.895	10.	-13.5
013,12	.925	< 4.	-1.
013,13	.958	6.	+10.
013,14	.991	< 2.5	+0.5
014,1	.765	28.5	-30.5
014,2	.771	11.5	-14.
014,3	.779	8.	+8.5
014,4	.789	16.	+17.5
014,5	.803	< 5.5	-3.5
014,6	.820	5.5	+4.
014,7	.839	7.5	+9.5
014,8	.861	10.	-10.5
014,9	.884	8.	+5.
014,10	.910	< 4.5	-6.5
014,11	.939	5.5	-9.5
014,12	.966	< 3.	+1.
015,1	.821	< 5.5	-4.
015,2	.825	< 5.5	-0.5
015,3	.833	15.	+22.5
015,4	.844	7.5	+7.
015,5	.860	5.	+5.

hkl	sinθ	F meas	F calc
015,6	.872	< 5.	+2.
015,7	.890	6.5	+9.5
015,8	.910	10.5	+13.
015,9	.931	12.5	-16.5
015,10	.958	10.5	-16.5
015,11	.985	< 2.5	+2.
016,1	.875	< 5.	-2.5
016,2	.880	< 5.	+3.5
016,3	.888	15.	-19.
016,4	.897	< 4.5	+5.5
016,5	.910	8.5	+12.5
016,6	.924	6.	+9.
016,7	.942	6.5	+7.
016,8	.962	< 3.5	-3.5
016,9	.982	< 2.5	+0.5
017,1	.931	< 4.	-3.
017,2	.935	< 4.	-4.
017,3	.943	< 4.	-2.
017,4	.952	11.	-18.5
017,5	.964	< 3.	-0.5
017,6	.978	< 3.	+13.
017,7	.995	< 2.	-13.
018,1	.983	< 2.5	-11.
018,2	.988	< 2.5	-11.5

Hexamethylene Diamine

Crystal Data

Hexamethylene diamine, $C_6H_{16}N_2$; mol.wt. 116 ; m.pt. 42°C ; calculated density 0.9888, measured density 0.8941 - 1.026 ; orthorhombic bipyramidal, with $a = 6.94 \pm 0.02$A., $b = 5.77 \pm 0.02$A., $c = 19.22 \pm 0.05$A. Absent spectra, (hol) when l is odd, (okl) when k is odd, (hko) when h is odd. Hence space group, D_{2h}^{15} (P_{bca}). Four molecules per unit cell; molecular symmetry, centre. Volume of unit cell, 769.6A^3. Total number of electrons per unit cell = F(000) = 264. Absorption coefficient for X-rays (λ = 1.54A.), μ = 5.4cm^{-1}.

Extremely fine needle crystals were obtained from dioxan,but owing to the diamine's hygroscopic nature it was found impossible to work with them. Sublimation gave leaflets, also too fine, but distillation in bulk provided large irregular transparent plates which could be cut to suitable dimensions.

The space group of the diamine is different from that of the dihalides. Therefore the structure of the latter will give no information to aid the analysis of the diamine, except for the dimensions of the carbon-nitrogen chain. However, a centre of symmetry within the molecule will simplify the examination, as it reduces the asymmetric unit to half of the molecule.

The unit cell dimensions were checked by measurements of the face diagonals, their values being found as:-

diagonal of the ab plane = 9.02A.
diagonal of the ac plane = 20.44A.

Structure Analysis

From the dimensions of the unit cell, it is highly probable that the molecule is directed along the c axis, and by using scale models of the molecule and unit cell, it can be shown from packing considerations that the tilt of the molecule to the c axis in the (hol) projection is not greater than 5°, and the tilt to c in the (okl) projection is approximately 47°.

The (hol) projection was examined first and it was observed that the F value of plane (0016) was very large. Therefore the atoms of the asymmetric unit must lie either in the positive or negative maximum areas of these planes. Also the spacing of (0016) planes is 1.20A. which is a reasonable value for the carbon-

carbon bond length in projection. These observations suggest that the atoms of the normal chain diamine lie along the c axis at spacings of 1.20A. Thus if this is the case, the phase of (0016) must be negative, since the molecule has a centre of symmetry at the origin. This was later found to be correct.

Therefore approximate positions for the atoms along the c axis could be found and a line Fourier projected on to this axis was carried out. This was refined by a second line Fourier series to give the projection shown in Fig.16, in which the three carbons and one nitrogen of the asymmetric unit are separately resolved. The z co-ordinates of these atoms obtained in this manner will be sufficiently accurate to utilise in a two-dimensional Fourier series. The x co-ordinates cannot be found similarly as the a axis is small and its planes (hoo) lack contrast in their amplitudes. Trial methods were adopted, and these gave a ready solution for the x co-ordinates, since the z co-ordinates have been fixed.

These co-ordinates were refined by successive Fourier syntheses, giving projections on the (010) plane. The final projection is shown in Fig.17 from which

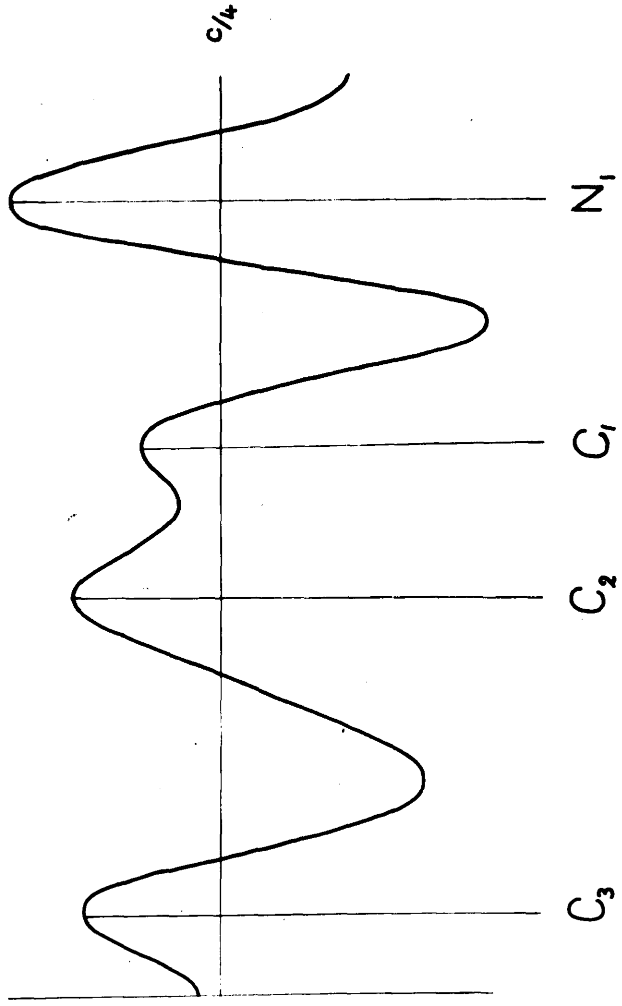


Fig.16 One-dimensional Fourier projection on the c axis, showing each atom of the asymmetric unit resolved.

accurate values of the x and z co-ordinates of all the atoms can be obtained.

The y co-ordinates were readily obtained by trial since the molecule has a centre of symmetry at the origin and thus its position is fixed. The molecular dimensions in the (hol) projection gave the required tilt in the (okl) projection, so that the co-ordinates could be calculated mathematically. Fourier syntheses were used to refine the y co-ordinates, and this also served as a check on the z co-ordinates. The final projection is shown in Fig.18, where each atom is again separately resolved.

Therefore Figs. 17 and 18 considered together are sufficient to yield a precise picture of the whole structure.

Co-ordinates, Orientation and Dimensions.

The co-ordinates of the atoms can be measured directly from the contour maps in Figs. 17 and 18, where all the atoms of the asymmetric unit are separately resolved, and thus accurate values can be assigned to them. These results, referred to the crystal axes, are collected in Table VII. As the molecule has a centre of symmetry, only half of the

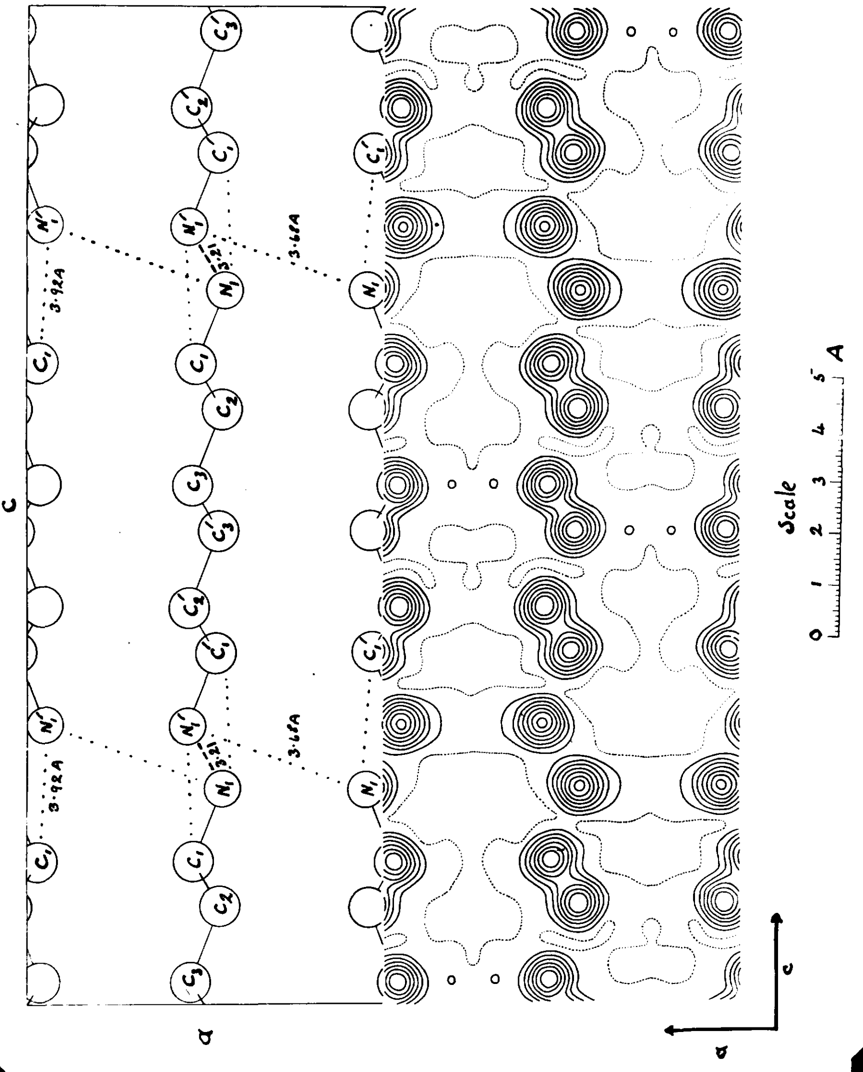


Fig.17. Fourier projection along the b axis on the (hol) plane. Contours at intervals of one electron per A^2., the one electron line being dotted.

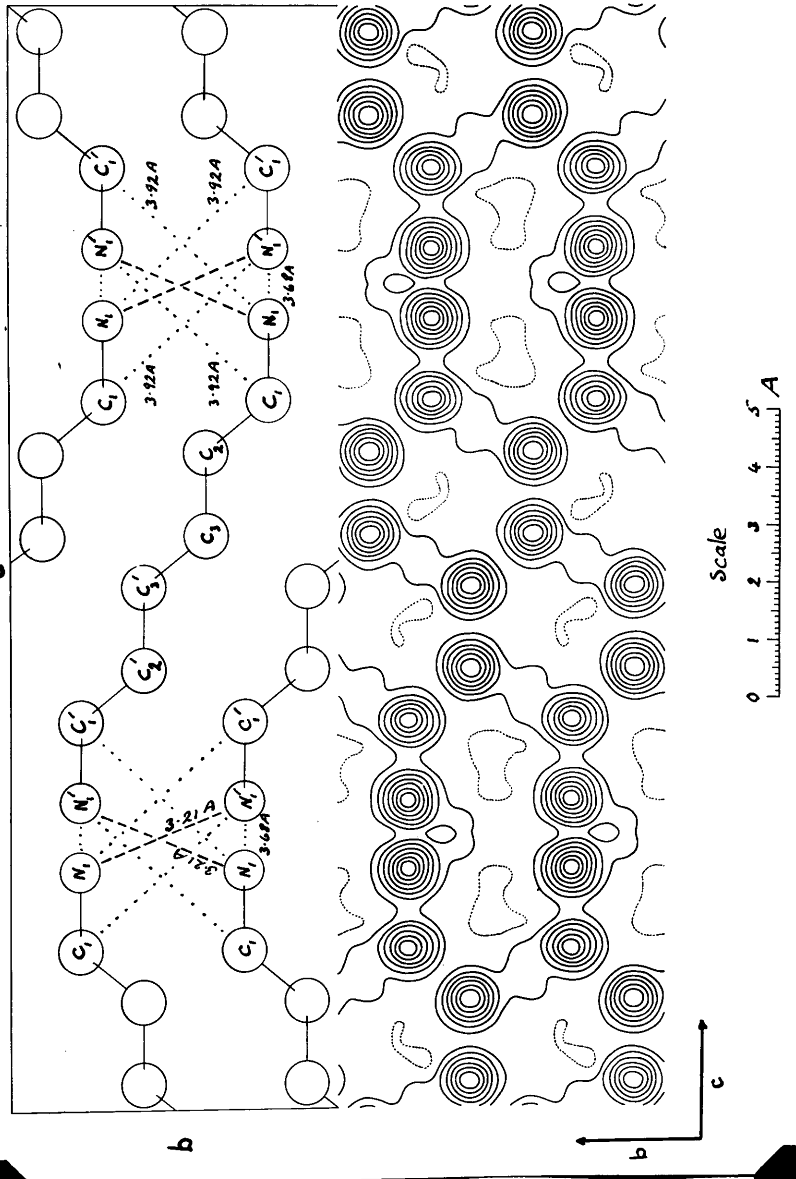


Fig.18. Fourier projection along the a axis on the (okl) plane. Contours at intervals of one electron per A^2, the one electron line being dotted.

Table VII

Co-ordinates. Centre of symmetry as origin, x, y, z, are referred to the orthorhombic crystal axes.

Atom (cf.Fig.17)	x,A.	y,A.	z,A.	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
N_1	0.337	1.650	4.187	17.5°	102.9°	78.4°
C_1	-0.211	1.650	2.778	-10.9°	102.9°	52.0°
C_2	0.297	0.550	1.893	15.2°	34.3°	35.5°
C_3	-0.258	0.550	0.442	-13.4°	34.3°	8.3°

Table VIII

Orientation of the molecule in the crystal.

$\chi_L = 89.1^\circ$ $\psi_L = 64.6^\circ$ $\omega_L = 25.2^\circ$

$\cos\chi_L = 0.0167$ $\cos\psi_L = 0.4259$ $\cos\omega_L = 0.9044$

$\chi_M = 49.1^\circ$ $\psi_M = 133.5^\circ$ $\omega_M = 71.8^\circ$

$\cos\chi_M = 0.6451$ $\cos\psi_M = -0.6887$ $\cos\omega_M = 0.3123$

$\chi_N = 139.2^\circ$ $\psi_N = 125.9^\circ$ $\omega_N = 73.2^\circ$

$\cos\chi_N = -0.7563$ $\cos\psi_N = -0.5870$ $\cos\omega_N = 0.2892$

atoms of the molecule are listed, and all the other atoms in the unit cell may be derived from these by the symmetry operations and translations applicable to the space group P_{bca}.

The orientation of this molecule with respect to the crystal axes is given in Table VIII, where χ_L, ψ_L, ω_L ; χ_M, ψ_M, ω_M and χ_N, ψ_N, ω_N, are the angles between the molecular axes L, M, and N and the crystal axes a, b and c. The molecular axis L is in the direction of the carbon chain; M lies in the plane of the molecule and is perpendicular to L ; N is the normal to the molecular plane.

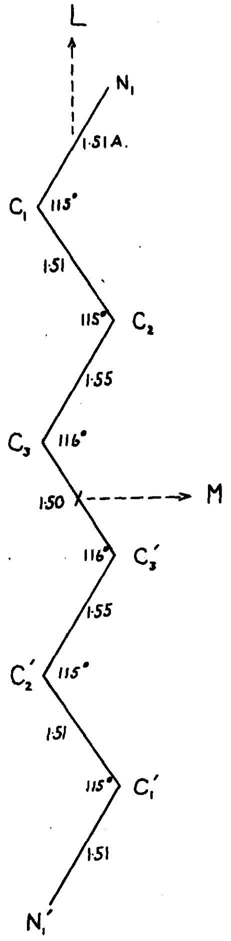
To illustrate the coplanar nature and symmetry of the molecule, the co-ordinates of the atoms of the asymmetric unit are given with reference to the molecular axes L, M and N in Table IX.

Table IX

Co-ordinates of atoms with respect to the molecular axes.

Atom	L,A.	M,A.	N,A.
N_1	4.498	0.393	-0.013
C_1	3.216	-0.405	-0.004
C_2	1.951	0.408	0.001
C_3	0.630	-0.409	0.001

The results of this analysis are expressed in terms of bond distances and bond angles in Fig.19. Intermolecular distances are illustrated in Figs. 17 and 18.



$C_6H_{16}N_2$

Fig. 19. Dimensions of hexamethylene diamine molecule.

Experimental

Crystal Preparation and Preservation.

Crystals of hexamethylene diamine obtained from the solvents dioxan and amyl alcohol were extremely fine. Their hygroscopy severely limited their life in the atmosphere so that they could not be preserved. However large crystal plates could be obtained by distillation of a 50% solution in methanol from a little caustic soda, in vacuo with a stream of nitrogen. The diamine distilled at 100°C under a pressure of 20 mms. These plates, the thickness of which proved to be the long c axis, were too large for accurate X-ray work, but specimens of suitable dimensions could be cut with a razor blade.

To preserve a crystal of the diamine, the specimen was mounted within a gelatine capsule, the atmosphere of which was kept dry by the presence of a small quantity of phosphorus pentoxide. Rubber solution was used to adhere the crystal to the glass fibre, and the capsule was sealed to a plasticine mount by durofix. In this manner the crystal can be preserved for two or three days, after which time a slow diffusion of water vapour completely hydrolyses the phosphorus pentoxide, and attacks the crystal itself.

The crystal when within the capsule, Fig.20, is opaque and is orientated about the desired axis by trial. Photographs obtained show distinct powder lines, due to the random arrangement of molecules on the surface of the crystal. A sample of the photographs taken is shown in Fig. 21.

Determination of Data

An accurate measurement of the density of the diamine could not be obtained by the flotation method, owing to its extreme hygroscopy. However it was possible to place limits on it by using different suspension mediums and observing whether the crystal floated or sank in them. In this way, it was found that the value of the density lay between those of benzene and aniline, i.e. between 0.8941 - 1.026. Within this range there can only be four molecules in the unit cell.

Copper K_α radiation, λ = 1.54A., was used throughout and rotation, oscillation and moving-film photographs of the principal zones were taken. For the (hol) zone, the crystal employed had a cross-section normal to the b axis of 0.53 by 0.50 mm. Crystals smaller than this rapidly gave complete powder photographs.

Fig.20. Crystal of hexamethylene diamine within the gelatine capsule.

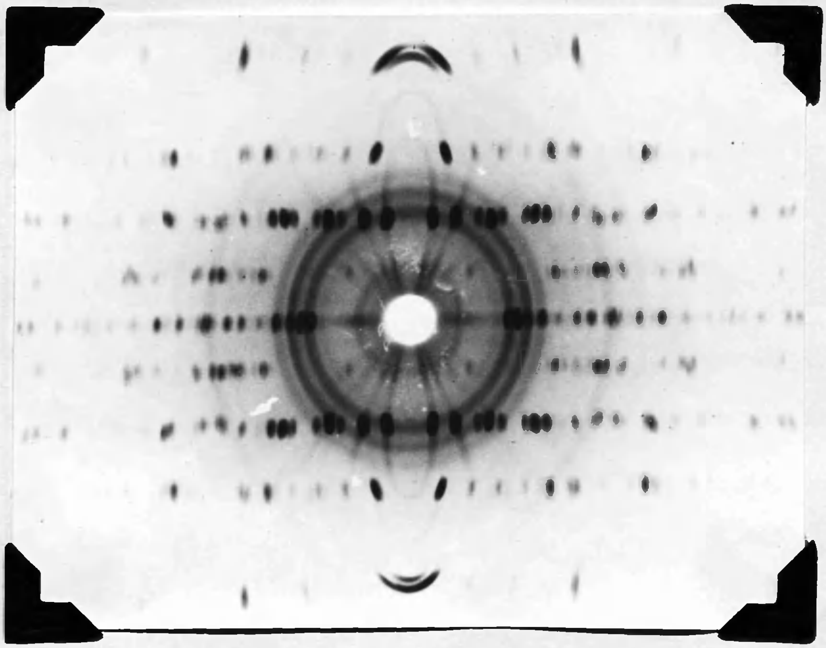


Fig.21. Sample photograph of hexamethylene diamine showing layer lines and powder rings.

The use of a large crystal need not result in loss of accuracy, as it ensures the true mosaic character of the specimen. For the (okl) zone, a crystal of cross-section 0.58 by 0.61 mm. normal to the a axis was used. These crystals were completely immersed in a uniform X-ray beam, and the spectra recorded up to the limit for λ = 1.54A. on a series of moving-films. The multiple-film technique(8) was used to correlate the reflections, the intensities of which were estimated visually. Absorption corrections were not employed because of the uniform cross-section of the crystals. Observed values of F were finally derived from the usual formulae for mosaic-type crystals and are listed in Table XI. Absolute measurements were not carried out, and the scale of the F values was obtained by correlation with the values finally calculated from the atomic positions found.

Fourier Analysis and Structure Determination.

Using the phase constants determined from the trial structures and the measured values of F, two-dimensional Fourier series were carried out giving projections on the (010) and (100) planes. For the projection along the b axis, the electron density was computed at 900 points on the asymmetric unit, the axial sub-divisions being $a/_{60}$ = 0.116A., $c/_{120}$ = 0.160A. The summations were carried out to three-figure accuracy by means of Robertson's stencils.(14) The positions of the contour lines were obtained by the method of graphical interpolation from the summation totals. The final plot of the asymmetric unit for the b projection is shown in Fig.22. The projection along the a axis was computed in a similar manner and the resulting contour map shown in Fig.23. In this case the summations were over 450 points on the asymmetric unit, the axial sub-divisions being $b/_{30}$ = 0.192A., $c/_{120}$ = 0,160A.

The co-ordinates measured from the final Fourier projections are consistent with the molecular model shown in Fig.19, and the orientation listed in Table VIII. All the structure factors were recalculated using these final co-ordinates. For these calculations, a composite experimentally derived atomic scattering curve was employed, with the carbon and nitrogen coefficients weighted in the ratio of 6 to 7. There is no theoretical justification for the use of a single f-curve for all the atoms. It is employed merely because it is found to give a sufficiently good approximation for the purpose on hand.

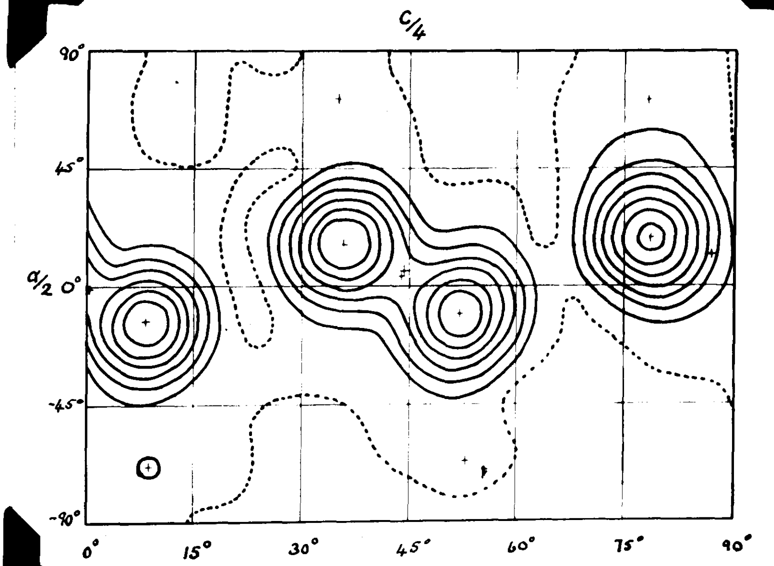


Fig.22. Co-ordinates assigned to the atoms in the asymmetric crystal unit,(hol) projection.

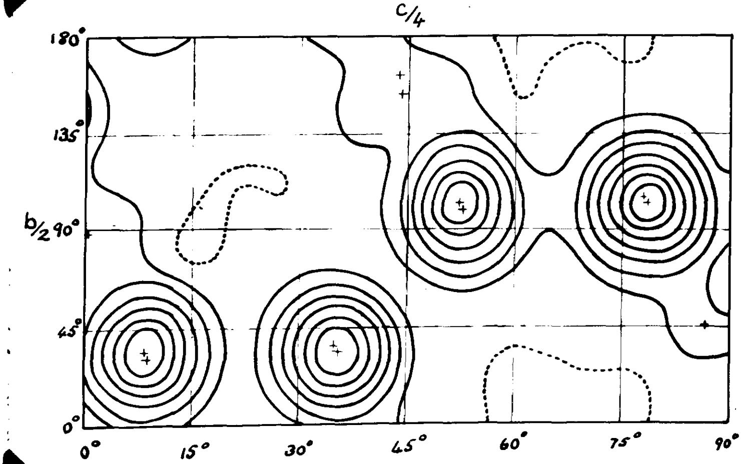


Fig.23. Co-ordinates assigned to the atoms in the asymmetric crystal unit,(okl) projection.

The discrepancy obtained from these calculations, expressed as in the former cases, was however surprisingly high, approximately 25% for both the (hol) and (okl) projections. This discrepancy was not the result of a uniform disagreement for all the reflections, as planes with 2 sinθ greater than 1.1 - 1.3 gave good comparison between the measured and calculated structure factors, whereas the majority of planes with 2 sinθ less than these values gave poor agreement, this sometimes being as much as 50%.

In spite of these high discrepancies, the electron density maps show clear resolution and well-shaped atoms. Therefore the phases associated with the measured structure factors used in the final Fourier summations are correct, and the large discrepancy is not due to the wrong structure. The reason for these discrepancies must be sought from the Fourier projections, and there it is found that the two electron line surrounds two carbon atoms, belonging to different molecules, 2A. apart in projection, but no such line encircles pairs of carbon atoms of the same molecule and these are necessarily less than 1.54A. apart in projection. This is illustrated in Fig 18. The linkage of carbon atoms 2A. apart can only be explained by partial resolution of the remaining atoms of the molecule, namely, hydrogens. The hydrogen atoms therefore play a part in diffraction and so their contributions must be included in the calculated structure factors. These atoms contribute 24% of the scattering power of the molecule, this being equivalent to 8/6 carbon atoms. This represents the maximum contribution hydrogens could make to this type of compound.

A similar effect to this, but to a smaller extent, was observed in sebacic acid,(2) prior to the start of this investigation.

The partial resolution of the hydrogen atoms does not allow accurate co-ordinates to be measured for them, but taking the length of the carbon-hydrogen bond as that found in methane, 1.09A.,(15) and the nitrogen-hydrogen bond as 1.02A.(15) and the bond angles as given by Pauling,(16) theoretical positions can be given to the hydrogen atoms, Table X, which agree remarkably well with those which might have been measured, as illustrated in Figs. 30 and 31.

Table X

Co-ordinates. Centre of symmetry as origin, x, y, z are referred to the orthorhombic crystal axes.

Atom (cf.Fig.31)		x,A.	y,A.	z,A.	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
N_1	H_1	1.356	1.690	4.168	70.2°	105.5°	78.1°
	H_2	0.224	0.738	4.630	11.6°	46.1°	87.0°
C_1	H_1	-1.300	1.610	2.814	-67.3°	100.5°	52.8°
	H_2	0.077	2.600	2.332	4.0°	162.5°	43.7°
C_2	H_1	1.386	0.590	1.874	71.9°	36.8°	35.1°
	H_2	0.110	-0.420	2.352	5.7°	-26.2°	44.0°
C_3	H_1	-1.347	0.510	0.460	-69.9°	31.8°	8.6°
	H_2	0.003	1.500	-0.020	0.2°	93.6°	-0.4°

Therefore from these co-ordinates, the contributions of the hydrogen atoms were included in the calculated structure factors for reflections with $2 \sin\theta \leq 1.2$ and listed in Table XI. Above $2 \sin\theta = 1.2$, the atomic scattering factor approaches zero very rapidly, so that hydrogen contributions are exceedingly small and can be neglected. The atomic scattering curve for hydrogen was obtained by taking 1/6 of the values of the experimentally derived curve of carbon and nitrogen. The scattering curve so obtained is remarkably similar to the one given by Hartree,(10) for hydrogen.

The inclusion of the hydrogen atoms did not alter the phase of any reflection, but it considerably reduced the percentage discrepancy of each projection. They are now 14.9% for the (hol) reflections, 15.3% for the (okl) reflections and 15.0% for all reflections.

Therefore, despite the fact that reflections with small values of $2 \sin\theta$ are masked by powder lines, so that their intensities are difficult to estimate accurately, good agreement has been obtained. The clear resolution in both projections, allowing accurate co-ordinates to be measured, is no doubt responsible for this.

Table XI

Measured and calculated values of the structure factors of Hexamethylene Diamine.

(λ = 1.54A.)

hkl	sinθ	F meas	F calc	hkl	sinθ	F meas	F calc
200	.222	105.5	+107.3	206	.324	3.3	+3.1
400	.444	35.9	+39.4	208	.387	21.0	+25.7
600	.666	2.0	+2.3	20,10	.453	5.2	+6.5
800	.888	7.2	-5.9	20,12	.523	6.5	-5.4
020	.267	29.1	-29.2	20,14	.592	5.8	+5.0
040	.534	4.0	-2.7	20,16	.666	16.1	-11.8
060	.801	13.0	-11.2	20,18	.740	3.1	-4.0
002	.080	< 0.2	+5.8	20,20	.815	< 0.8	+0.9
004	.160	< 0.4	-5.2	20,22	.890	< 0.7	+0.6
006	.241	< 0.4	+3.6	20,24	.966	4.6	-5.7
008	.321	36.7	+40.6	302	.345	7.4	-6.2
00,10	.401	13.1	+12.9	304	.370	5.8	+3.8
00,12	.481	11.3	-9.1	306	.409	5.5	-3.2
00,14	.561	10.3	+9.1	308	.461	29.0	+30.3
00,16	.641	24.2	-23.6	30,10	.516	< 0.7	-0.1
00,18	.721	3.9	-4.1	30,12	.579	< 0.8	+0.2
00,20	.801	1.6	+0.8	30,14	.642	< 0.9	-0.7
00,22	.881	< 0.7	+0.7	30,16	.711	8.7	+8.2
00,24	.961	7.3	-7.5	30,18	.781	6.9	+5.8
				30,20	.853	3.5	-3.0
102	.138	8.1	-6.6	30,22	.925	2.0	+2.0
104	.193	5.9	+3.9	402	.453	3.9	+4.3
106	.261	4.0	-3.4	404	.474	3.7	-3.9
108	.334	28.4	+29.6	406	.505	3.2	+1.6
10,10	.409	< 0.6	+1.2	408	.547	11.9	+14.6
10,12	.485	< 0.7	-0.4	40,10	.596	1.4	+2.0
10,14	.559	< 0.8	-0.1	40,12	.650	< 0.9	-1.6
10,16	.637	4.5	+6.0	40,14	.708	2.5	+2.8
10,18	.715	3.3	+1.8	40,16	.770	7.7	-7.9
10,20	.792	1.4	-1.3	40,18	.834	3.2	-3.2
10,22	.869	< 0.7	+0.9	40,20	.903	< 0.7	+0.8
10,24	.948	2.7	-1.6	40,22	.921	0.4	+0.1
202	.238	4.1	+4.8	502	.562	4.0	-4.5
204	.273	6.8	-4.6	504	.579	2.7	+2.4

hkl	$\sin\theta$	F meas	F calc
506	.604	1.4	-1.7
508	.640	24.0	+25.1
50,10	.682	2.5	+1.1
50,12	.731	< 0.9	-0.8
50,14	.783	< 0.9	-0.1
50,16	.839	7.4	+8.1
50,18	.899	5.0	+5.2
50,20	.962	2.0	-2.4
602	.675	1.9	+2.9
604	.687	2.5	-3.3
606	.709	4.8	+4.3
608	.739	1.7	+1.9
60,10	.776	3.7	-1.8
60,12	.819	< 0.8	+0.5
60,14	.865	< 0.7	+0.4
60,16	.916	1.0	+0.3
60,18	.970	0.8	-1.9
702	.786	< 0.9	-0.1
704	.796	< 0.9	+0.5
706	.815	< 0.8	-0.9
708	.842	15.4	+15.4
70,10	.875	3.7	+2.6
70,12	.913	1.0	-1.0
70,14	.954	0.7	+0.4
802	.895	< 0.7	+0.9
804	.904	< 0.7	-1.4
806	.920	2.0	+1.9
808	.944	< 0.5	-0.5
80,10	.973	2.3	-2.5
021	.275	3.8	+2.9
022	.283	38.8	+37.1
023	.296	28.1	-30.3
024	.314	5.3	-3.7
025	.335	22.5	-25.1
026	.360	12.8	-11.3
027	.387	< 0.9	+0.2
028,	.416	< 1.0	-2.8
029	.446	< 1.0	-0.3
02,10	.478	9.0	+11.1
02,11	.511	13.1	-14.7
02,12	.545	6.1	+6.5
02,13	.580	27.9	-30.1
02,14	.614	25.6	-24.3
02,15	.649	2.6	-1.3
02,16	.687	6.9	+6.0
02,17	.722	< 1.3	-0.3
02,18	.759	4.1	-2.5
02,19	.796	1.8	+1.1
02,20	.834	< 1.2	-0.6
02,21	.870	< 1.1	-2.4
02,22	.908	1.7	-2.9
02,23	.945	< 0.8	-0.9
02,24	.983	< 0.6	+0.5
041	.541	17.5	-21.6
042	.545	19.2	-18.8
043	.553	5.8	-4.8
044	.562	< 1.2	-1.9
045	.575	5.2	-3.5
046	.588	6.1	+6.9
047	.606	< 1.3	-0.9
048	.625	< 1.3	-1.4
049	.645	3.2	-5.6
04,10	.668	6.9	-8.4
04,11	.692	8.0	-8.0
04,12	.717	3.5	-4.6
04,13	.744	3.9	-1.6
04,14	.770	12.3	+11.4
04,15	.799	9.0	-10.5
04,16	.829	1.7	+1.3
04,17	.859	3.4	+3.0
04,18	.890	3.1	+2.1
04,19	.921	2.1	+1.4
04,20	.954	< 0.8	+0.3
04,21	.987	< 0.6	-0.5
061	.809	8.8	+9.8
062	.811	3.9	-4.3
063	.815	< 1.2	+1.0
064	.822	< 1.2	-0.1
065	.831	< 1.2	-0.6
066	.840	< 1.2	+0.5
067	.853	< 1.1	-0.5
068	.866	3.5	-2.9
069	.881	3.0	+3.3
06,10	.897	2.9	-3.3
06,11	.916	2.3	+2.5
06,12	.934	< 0.9	-0.1
06,13	.956	< 0.8	-1.9
06,14	.977	< 0.6	+1.6

Discussion

To make reliable assessments of the limits of accuracy obtainable by the Fourier series method is difficult, because they depend on many factors, such as the size and perfection of the crystal specimens, the range and accuracy of the intensities and the methods of computation and interpolation employed. However an estimate of the accuracy has recently been made(17) by investigating a hypothetical structure. Structure factors were calculated from given co-ordinates and substituted in the two-dimensional Fourier series, and it was found that the original atomic positions were reproduced to within 0.01 - 0.02A. In terms of bond lengths, the maximum discrepancy obtained was 0.024A. This accuracy of atomic co-ordinates derived from Fourier series was confirmed by mathematical treatment by Booth.(18) (19)

However such accurate measurements cannot be made in the case of hexamethylene diamine dihydrochloride, since the presence of the comparatively heavy chlorine ions results in considerable swamping effect which distorts the contours of the lighter atoms. It is fortunate, however, that separate resolution of each atom of the molecule is obtained in the (okl) projection, so that two co-ordinates of each atom can be measured with reasonable accuracy. The (hol) projection provides a check on the z co-ordinates, but the x co-ordinates cannot be obtained precisely, owing to considerable overlapping. Thus the limits of accuracy which should be attached to the internal dimensions and valency angles of the open carbon-nitrogen chain, as indicated in Fig.13, are ± 0.04A. and ± 5°.

The carbon-carbon bond lengths are of the usual covalent length, whilst the carbon-nitrogen bonds are greater than the more recently published values of 1.47A.,(20) 1.48A.,(21) and 1.49A.,(22) but the difference is within experimental error. The alternating long and short bonds of the chain can equally be due to experimental error. The molecular co-ordinates, given in Table V, are in favour of a centro-symmetrical coplanar structure of the carbon chain with both extreme nitrogens removed from this plane in the same direction, such that the bonds $N_1 - C_1$ and $N_2 - C_6$ make angles of 7°and 10° respectively with it. Although these values cannot be relied upon as accurate measurements, they are sufficiently appreciable to suggest that the nitrogens are deflected from the plane, in order to fit into the ionic lattice. The centre of symmetry of the carbon chain is not utilised in the construction of the lattice.

This is illustrated by the (okl) projection, Fig.24, where the carbon-nitrogen chains of the dihydrochloride molecules are grouped in pairs about centres of symmetry. Also it can be observed that a different arrangement of chlorine ions exists at either end of the open chain. The projection along the b axis, Fig.25, shows that the chains lie parallel in layers at a small tilt to the c axis. These layers are interleaved by layers of chlorine ions such that the nitrogens of the molecule are associated with different numbers of chlorine ions. N_1 is associated with two chlorine ions, and N_2 with three. Similarly the two chlorine ions of the molecule, Cl_1 and Cl_2, are associated with two and three nitrogen atoms respectively. This allows two different measurements of the nitrogen-chlorine distance to be made.

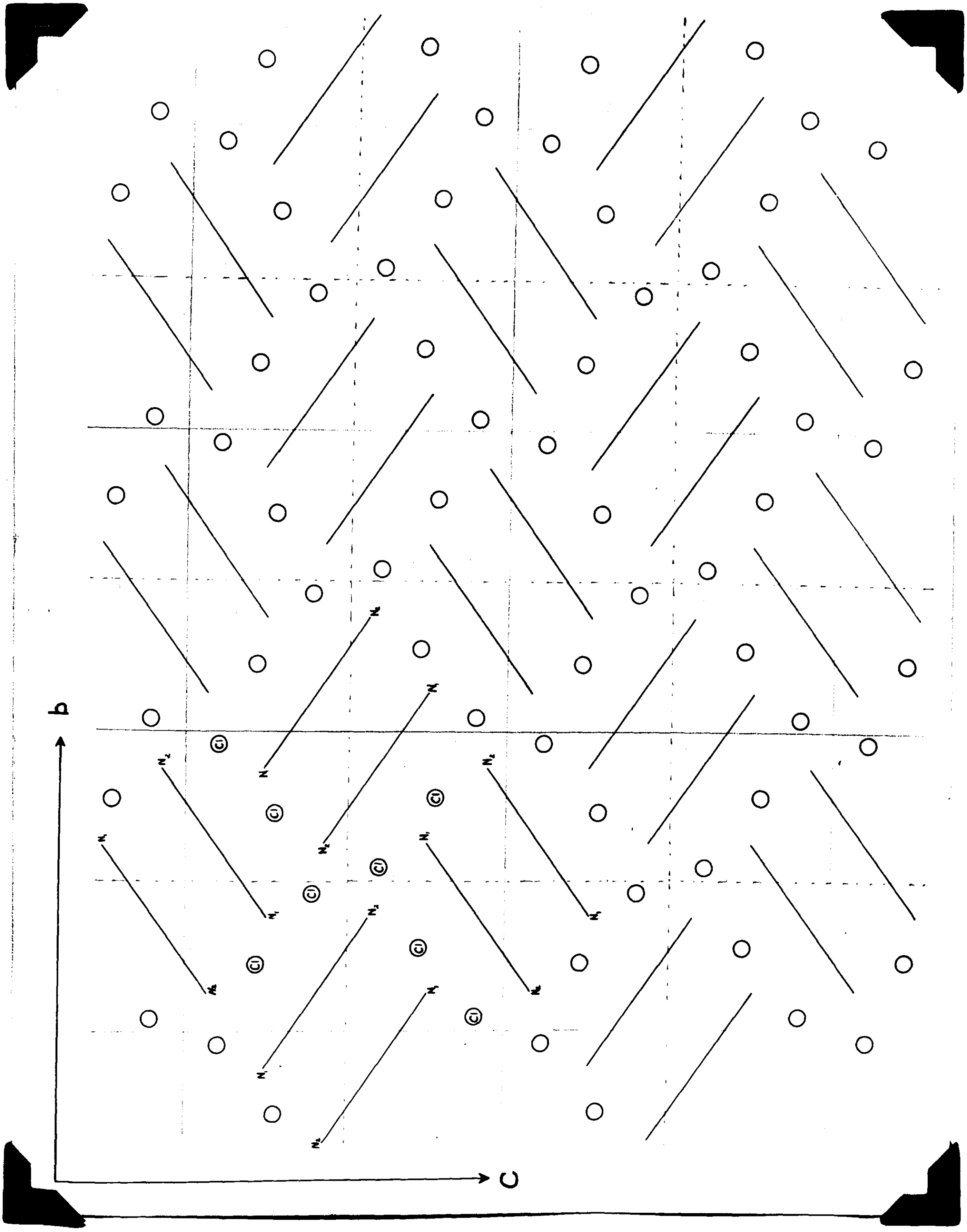


Fig.24. Showing pairing of molecules in (okl) projection. Full lines are unit cell projection's sides; projection is quartered by broken lines.

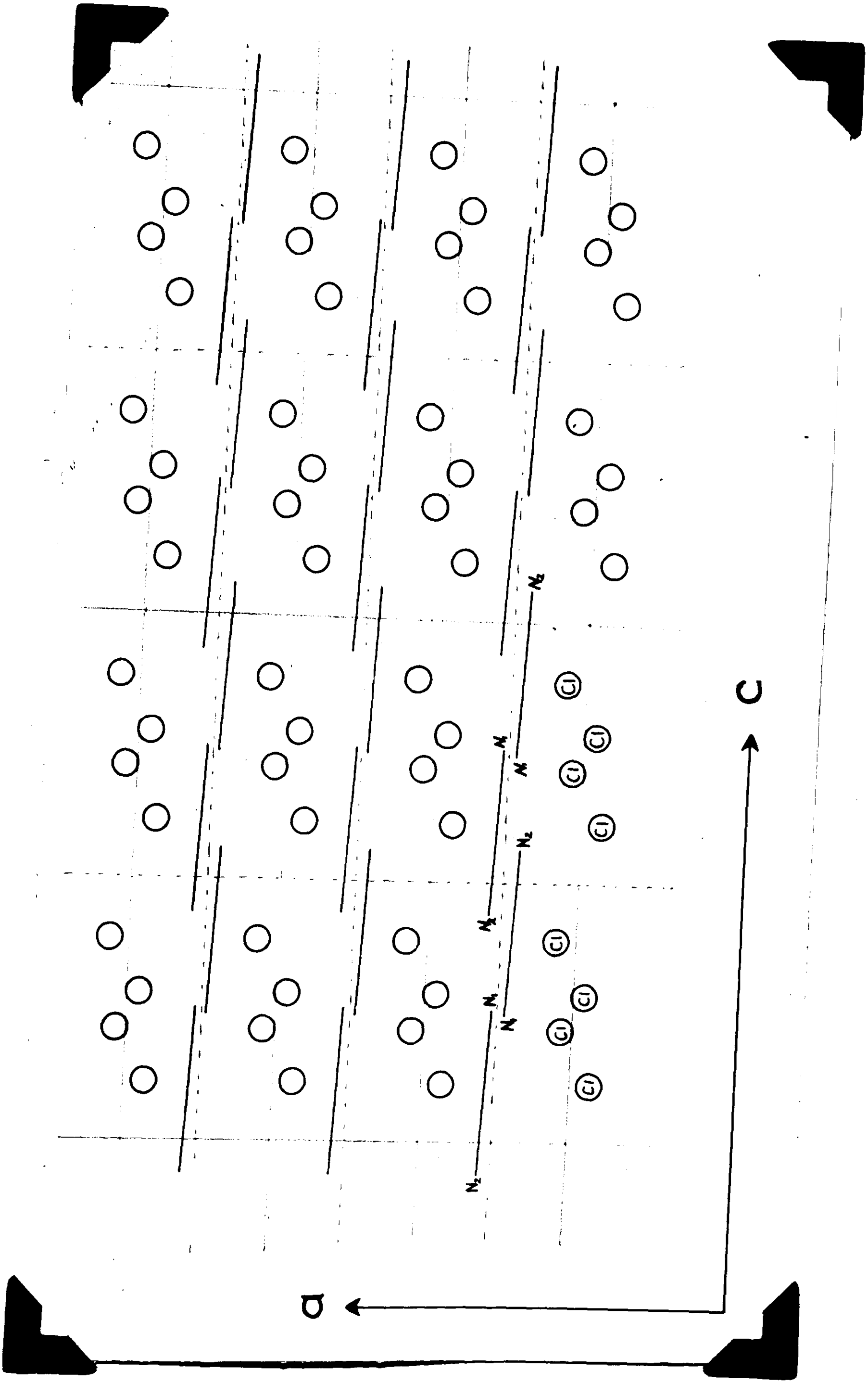


Fig.25. Showing interlacing of halogen ions and the carbon-nitrogen chains in the (hol) projection. Full lines are unit cell projection's sides; projection quartered by broken lines.

Distances of N_1 from two chlorine ions measured 3.05A. and 3.02A., the average being 3.04A.

Distances of N_2 from three chlorine ions measured 3.18A., 3.26A., and 3.24A., the average being 3.23A.

Therefore N_1 is equidistant from two chlorine ions, and N_2 equidistant from three. This may be the reason that N_2 is removed by the greater angle from the plane containing the carbon atoms.

If the ionic radius for the chlorine ion is taken as 1.81A.(23), and that for the ammonium ion as 1.40A.(20), the non-bonded distance $N......Cl^-$ is calculated as 3.21A. which is in good agreement with the observed average value for N_2, 3.23A. This value is also comparable with the values of 3.24A. and 3.17A., obtained for geranylamine hydrochloride(22), 3.18A., for methyl ammonium chloride(20), and 3.26A. and 3.21A. for hydroxyl ammonium chloride.(26) The bonds of N_1 to the chlorine ions are shorter than the sum of the ionic radii, and Donohue and Lipscomb(24) have suggested that this may be due to the formation of hydrogen bonds leading to $N - H ......Cl^-$, which will be smaller than the sum of the ionic radii. The values of 3.02A., and 3.05A., are smaller than that quoted for this kind of bond, 3.10A.,(24) but this may be due to the more compact ionic lattice leading to stronger and consequently shorter N - H .....Cl^- bonds. However, this suggestion may be invalid as it is usually accepted that chlorine does not form hydrogen bonds.(25)

This compactness is well illustrated in Fig.27, where the lattice is shown to consist of an infinite array of monoclinic octahedrons with common vertices, and the centre of each octahedron coincides with a centre of symmetry. These octahedrons lie along the diagonals of the (okl) projection such that each octahedron shares vertices with four neighbours.

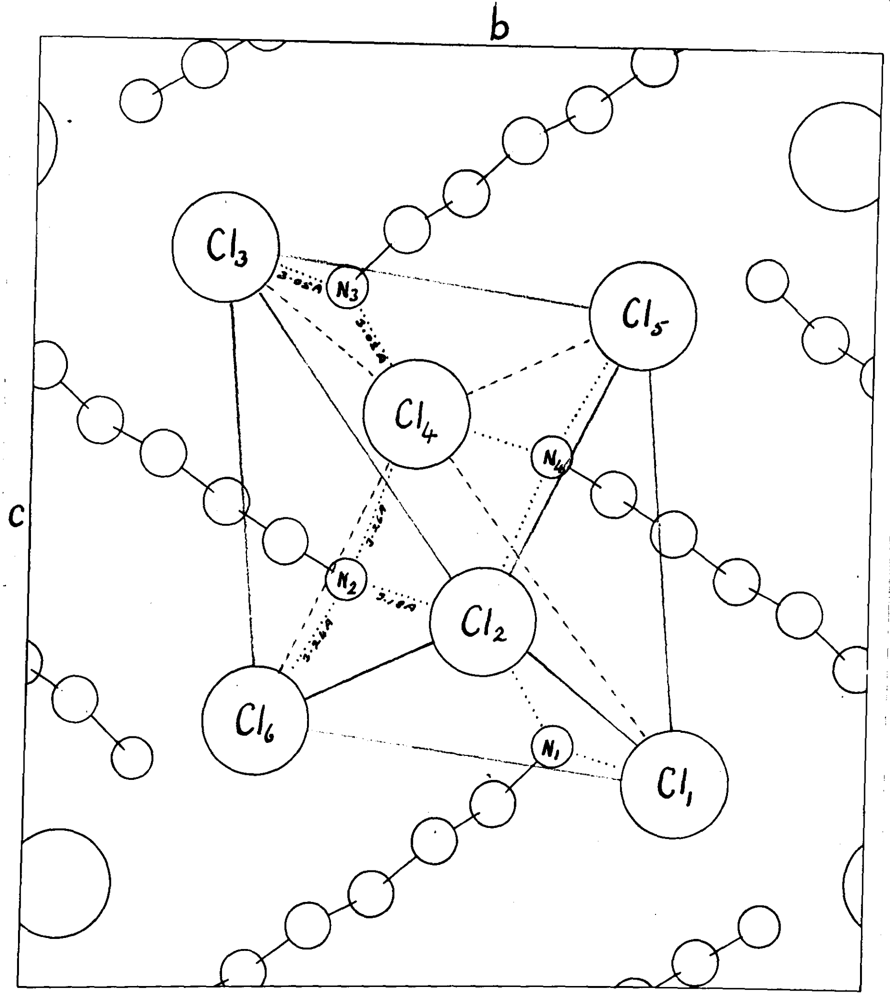
An example of the octahedron is the grouping of the six chlorine ions around the centre of symmetry within the unit cell projection,(okl), Fig.26. If the ions are named as shown, then the dimensions of the monoclinic octahedron can be given as follows.

Axial lengths $Cl_1 - Cl_3 = 12.42$A.

$Cl_2 - Cl_4 = 5.00$A.

$Cl_5 - Cl_6 = 10.14$A.

The axes are at right angles to one another except $Cl_1 - Cl_3$ and $Cl_2 - Cl_4$ where the angle is 147°.



<u>Fig.26</u>. Unit cell projection (okl), showing monoclinic octahedron of halogen ions.

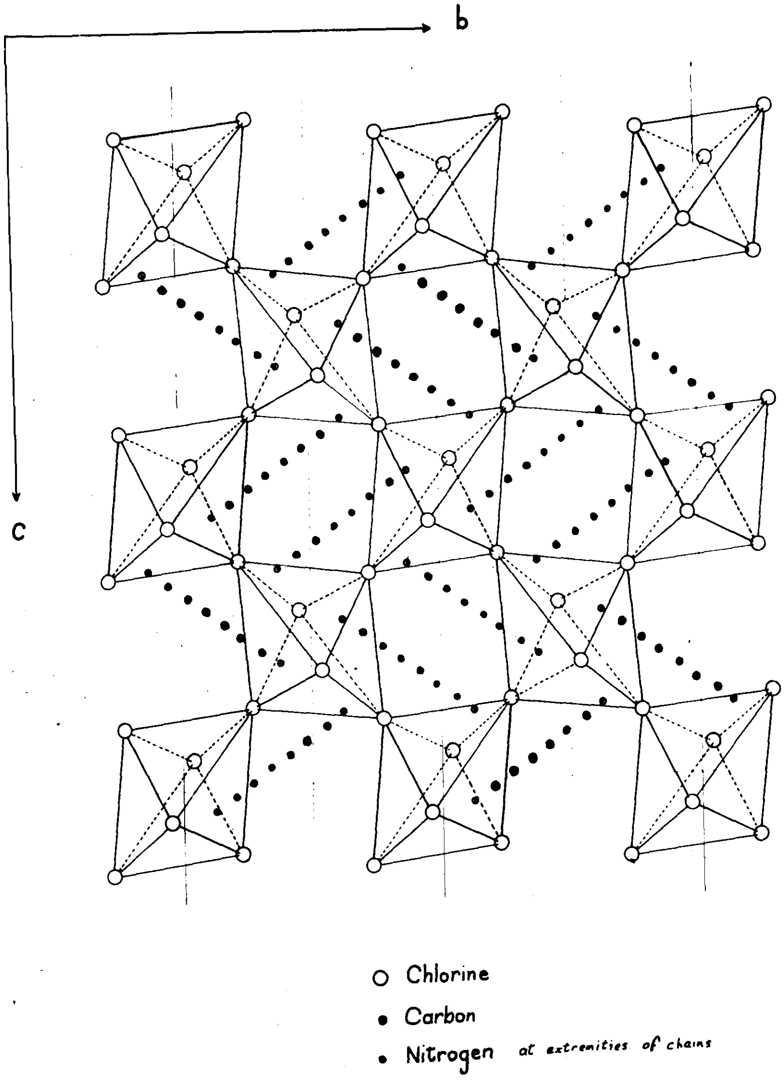


Fig.27. Illustration of the octahedrons of halogen ions along the diagonals of the (okl) projection, and the arrangement of the nitrogen atoms within them.

The octahedrons lying along the diagonals of the (okl) projection, Fig.27, are identical in dimensions, but only alternate ones have the same orientation. The orientation of neighbouring octahedrons along the diagonals differ by a rotation about the centre of symmetry, so that the axis Cl_1 - Cl_2 moves through 84° in clockwise and anti-clockwise directions alternately.

Also within each octahedron of chlorine ions, there is a planar arrangement of four nitrogen atoms, which together with Cl_2 and Cl_4 form another monoclinic octahedron, with its centre coinciding with a centre of symmetry, Fig. 26. The dimensions of this octahedron are as follows.

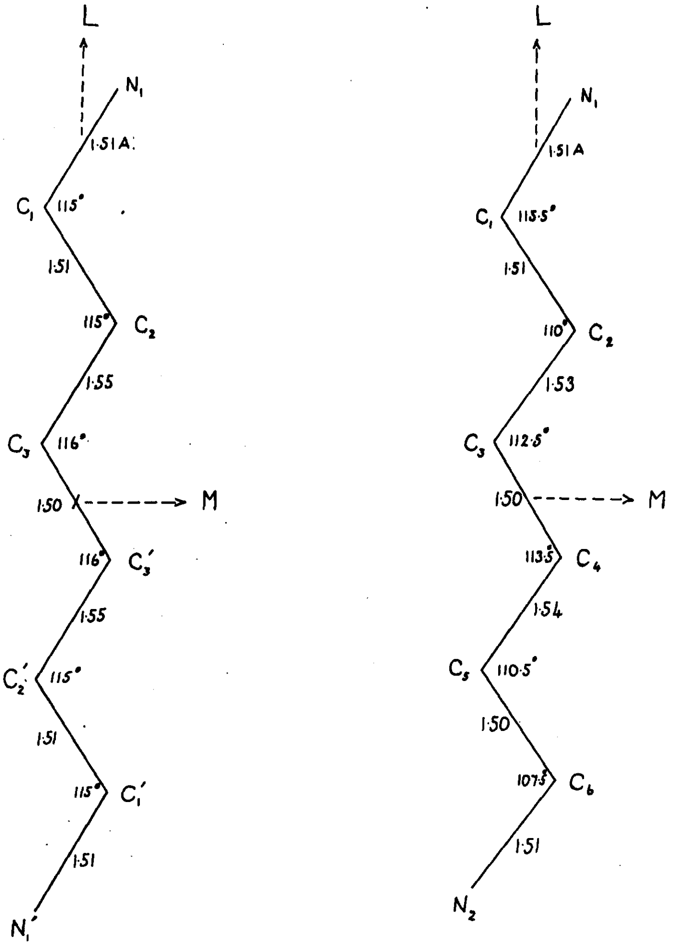
Axial lengths Cl_2 - Cl_4 = 5.00A.
N_2 - N_4 = 4.59A.
N_1 - N_3 = 8.42A.

These axes are at right angles except N_1 - N_3 and Cl_2 - Cl_4 where the angle is 134°.

This is illustrated in Fig.26, where N_2 and N_4 are equidistant, within experimental error, from Cl_2, Cl_4, Cl_6 and Cl_2, Cl_4, Cl_5 respectively, the average distance being 3.23A. Likewise N_1 and N_3 are equidistant from Cl_1, Cl_2 and Cl_3, Cl_4 respectively, the average distance being 3.04A.

Therefore this compact arrangement of nitrogen atoms within octahedrons of chlorine ions will give an extremely strong lattice, and hence, if Donohue and Lipscomb's suggestion is true, shorter $N - H \ldots\ldots Cl^-$ bonds will be formed, which would account for the distances measured between N_1 and the nearest halogen ions.

The accuracy with which the molecular dimensions of hexamethylene diamine can be measured is greater than that given for the dihydrochloride, due to the clear and separate resolution of the atoms of the asymmetric unit and to the absence of heavy atoms. The bond lengths and valency angles are shown in Fig.19, where the discrepancy can be quoted as $\pm$ (0.02 - 0.03)A. and $\pm 4^\circ$. It is a striking feature that the corresponding bonds measured in the diamine and the hydrochloride are almost identical, Fig.28, which probably means that the formation of the dihalide does not appreciably alter the bond lengths within the chain. In both cases the carbon-nitrogen bond is measured as 1.51A., and the accuracy of this value must be placed within $\pm$ 0.02A., as three separate estimations have been made for it.



$C_6H_{16}N_2$ $C_6H_{18}N_2Cl_2$

<u>Fig.28.</u> The bond lengths of hexamethylene diamine and hexamethylene diamine dihydrochloride.

The value of the carbon-nitrogen single bond distance is of special interest because of its occurrence in amino acids, proteins and related substances. An accurate measurement of its length was made the subject of a recent investigation.(20) This gave a value of 1.465 ± 0.01A., which is consistent with the usual table of covalent radii.(27)

However, values of this bond obtained by electron diffraction studies of gas molecules are usually higher than those given by X-ray investigations, Table XII. This is probably partly due to the different methods employed, but it suggests that the error given for this bond has been quoted too narrowly. Accurate estimates of this bond are required to be made by triple Fourier analysis of compounds containing no heavy atoms.

Table XII

Values of the carbon-nitrogen single bond in various compounds.

X-ray Investigations	
Methyl ammonium chloride	1.465A.(20)
Hexamethylene tetramine	1.45A. (28)
Geranylamine hydrochloride	1.49A. (22)
Electron Diffraction Investigations	
Trimethylamine oxide	1.49A. (29)
Hexamethylene tetramine	1.48A. (28)
Borinetrimethylamine	1.53A. (30)

The open chain of the diamine is reminiscent of a conjugated molecule, with the middle bond considerably shorter than the neighbouring $C_2 - C_3$ and $C_4 - C_5$ bonds. A similar shortening of the middle bond is shown in the chain of the dihydrochloride. Therefore in the latter molecule it does not appear that the amine hydrochloride group is directly responsible for this effect. Bateman and Jeffrey(31) reported a similar finding in the central bond of the group $C = C - C - C - C = C$, such as in geranylamine hydrochloride(22) and dibenzyl,(32),(33) and suggested that the hybrid character may result from a hyperconjugation process in which methylenic C - H electrons become partially localised in the central bond.

Walsh finds this in agreement with his theory(34) that when two of the hydrogen atoms of ethane are changed to give the compound $CH_2X.CH_2X$, where X is a group of higher electronegativity than H, then the strength of the central bond increases. Since an unsaturated carbon atom has a high electronegativity, X can be the group $C = C-$.

However, even though nitrogen is more electronegative than hydrogen, the apparent hyperconjugation of the diamine chain cannot be reasoned from the electronegativities of bonded groups, as this effect would not be transmitted through so many atoms. Discussion of other factors influencing the strength of bonds is probably not justified, until this hyperconjugation be proved real by further refinement of the atomic co-ordinates by triple Fourier analysis, and also by a study of the upper homologues of hexamethylene diamine. This is emphasised by the fact that in tetraphenyl cyclo-butane, a central bond measured as 1.48A. by the two-dimensional Fourier method was corrected to 1.55A. on further refinement by triple Fourier sections.(35)

Since hexamethylene diamine is the first solid in its series, the minimum intermolecular bonds to form a crystal should be present. This is illustrated by Figs. 17 and 18, where the nearest approach is by the nitrogen atoms of neighbouring molecules, through a hydrogen bond. This measures 3.21A., which is in good agreement with Pauling's value of 3.38A., in ammonia.(36) This hydrogen bond is strikingly shown in the Fourier projections of the diamine, where a hydrogen of each amino group, being partially resolved, is seen to be directed towards the nitrogen of a neighbouring amino group. All other forces within the crystal are van der Waals forces and they measure 3.68A. for a second nitrogen-nitrogen distance, and 3.92A. for the distance between an α methylene group and an amino group of a neighbouring molecule, this latter group forming the hydrogen bond with the amino group adjacent to the methylene group. These values are substantiated by the van der Waals radii of the methylene group, 2.0A.,(37) and amino group, 1.8A.(20) The closest approach of two molecules up the a axis, related by a plane of symmetry in projection, is 4.02A. between the two nitrogen atoms at one end and this increases to 5.04A. at the other, Fig.29. The molecular co-ordinates of the diamine, Table IX, show that the molecule is coplanar.

The principles of packing of hydrocarbon molecules are not entirely clear, but it may be that the methylene group should not be regarded as an unresolved packing unit, and that the positions of the hydrogen nuclei are important. Partial resolution of the hydrogen atoms have been obtained in the Fourier projections of the diamine, Figs. 17 and 18, where it can be seen that each atom is directed towards a carbon or nitrogen atom of a neighbouring molecule. Mark(38) has suggested that in several hydrocarbons the packing is determined by this kind of interlocking of hydrogen atoms. Examination of a model of the present diamine structure suggests that here the arrangement of hydrogen nuclei may play a part in determining the orientation of the chain.

An attempt was made to obtain the phases of the Fourier coefficients of the diamine directly from the crystal data by Harker and Kasper's method.(39)(40) This method makes the reasonable assumption that the electron density ρ (xyz) is non-negative and it requires the structure factors to be expressed in the "unitary" form, namely,

$$U_{hkl} = \frac{F_{hkl}}{Z.\hat{f}}$$

where Z = total number of electrons in the unit cell = 264

$\hat{f}$ is a function of $\sin\theta/\lambda$ such that $f_j = z_j.\hat{f}$

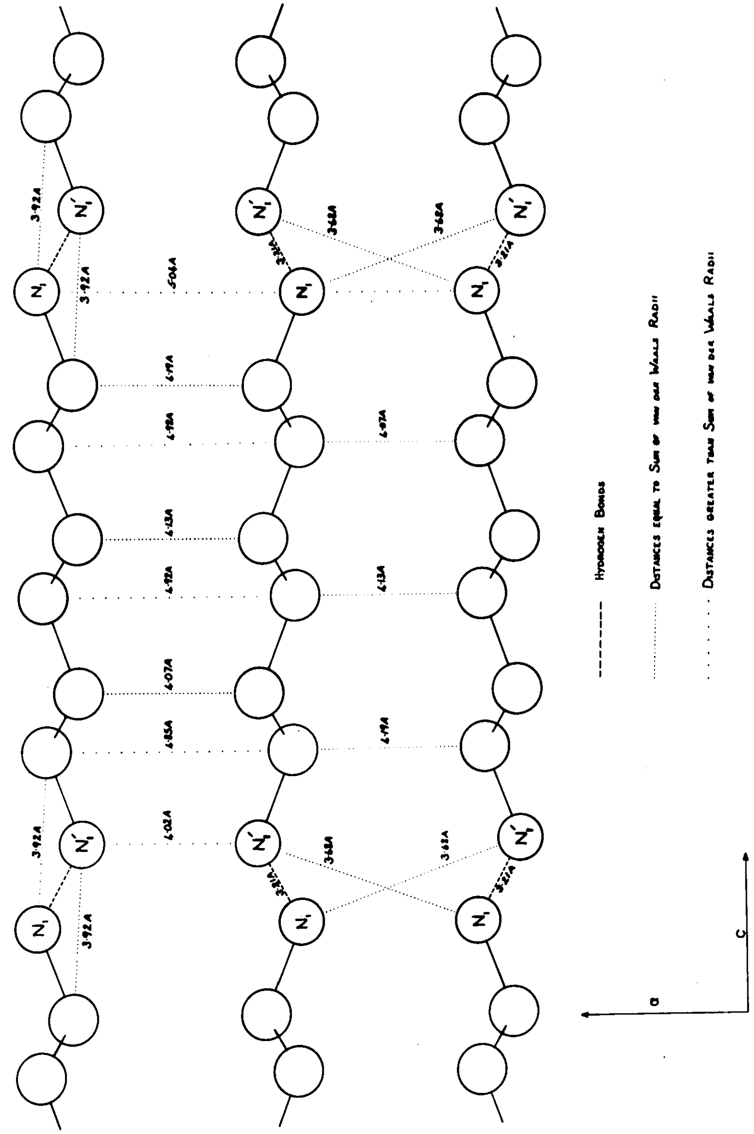


Fig.29. Intermolecular distances between molecules of hexamethylene diamine up the a axis.

$$\therefore \hat{f} = \frac{f_j}{z_j} = \frac{\text{atomic scattering value for the jth.atom}}{\text{atomic number of jth. atom}}$$

$$\therefore U_{hkl} = \frac{F_{hkl} + z_j}{Z.\ f_{jhkl}}$$

$$= \frac{F_{hkl}}{n.\ f_{jhkl}}$$

where n = number of atoms in the unit cell = 32.

Therefore, this expression requires that the atoms of the asymmetric unit should have approximately the same scattering power, and as this condition is satisfied by hexamethylene diamine, when the hydrogen atoms are excluded, it would be expected that this compound would lend itself to this method. However, it was found that some of the phases thus found were different from those given by trial.

For example, using the inequality

$$U_{hkl}^{2} \leq \tfrac{1}{2} + \tfrac{1}{2} U_{2h2k21}$$

and substituting the unitary structure factors for the planes (008) and (00,16), the final expression obtained is

$$0.21 \leq \tfrac{1}{2} \pm \tfrac{1}{2} (0.68)$$

$$\therefore 0.21 \leq 0.84 \text{ or } 0.16$$

Therefore the phase of plane (0016) is positive, and yet by trial it is persistently negative.

An error has thus been incorporated in the inequality, and it probably arose from the assumption that all the atoms of the diamine scattered equally. This is a pointer that the hydrogen atoms play an appreciable part in diffracting the X-rays, and that their contributions should be included in the structure factor calculations.

This is confirmed by analysis of the Fourier projections, Figs. 30 and 31, where it can be observed that the hydrogens are responsible for the shaping of the two-electron contour line. Significant improvement resulted between the measured and calculated structure factors for planes of large spacing by the introduction of their contributions. The discrepancy for planes with $2 \sin\theta \leq 1$ fell from 23.2% to 13.6% and from 25.8% to 15.0% for the (hol) and (okl) zones respectively. Hydrogen atoms were first considered as appreciable scattering units by Hughes and Lipscomb in their study of methyl ammonium chloride,(20) and it was also found necessary to include them in the recent analysis of normal dicarboxylic aliphatic acids.(2) In both cases, however, such striking resolution of the hydrogen atoms was not obtained.

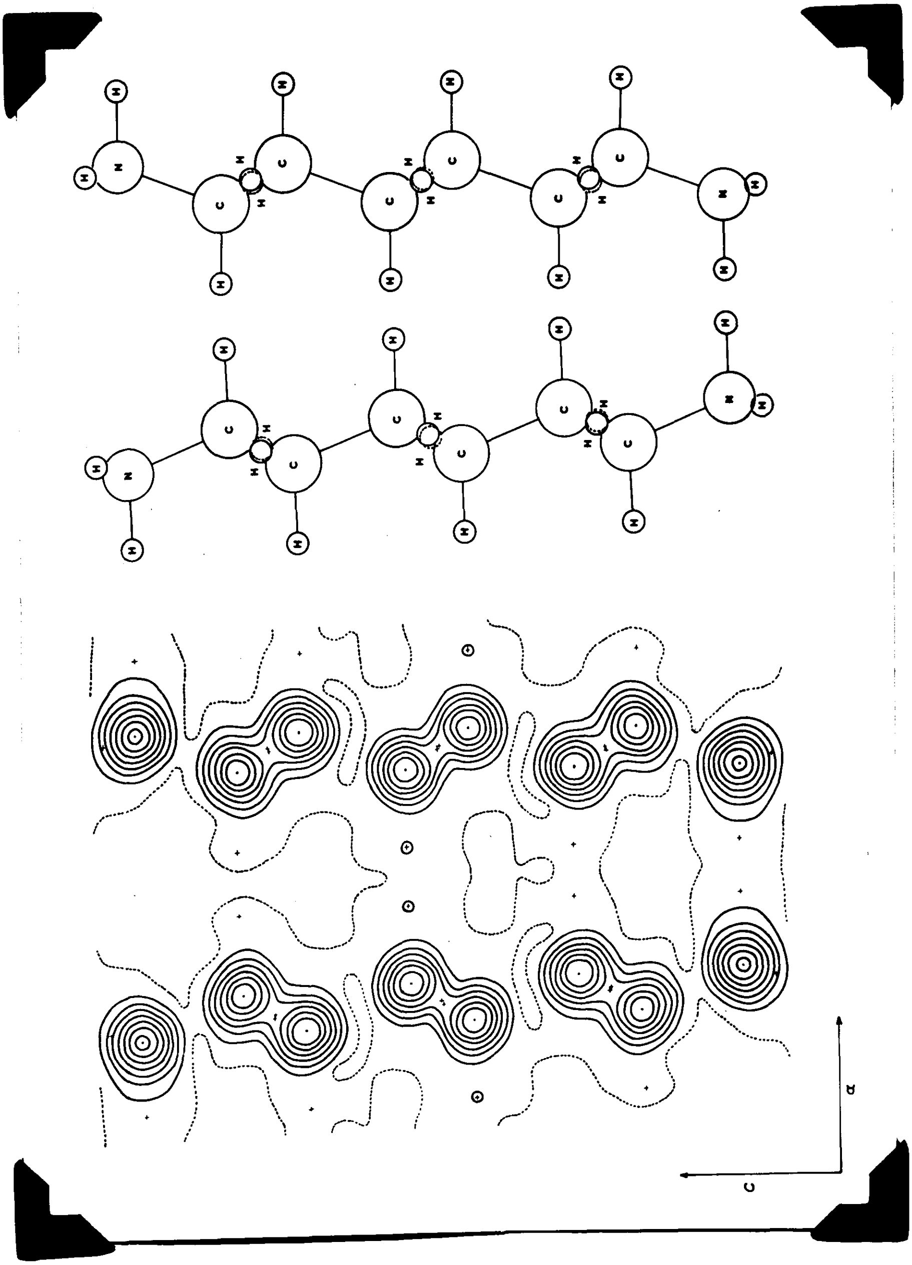


Fig.30 (hol) Fourier projection of hexamethylene diamine, showing partial resolution of hydrogen atoms

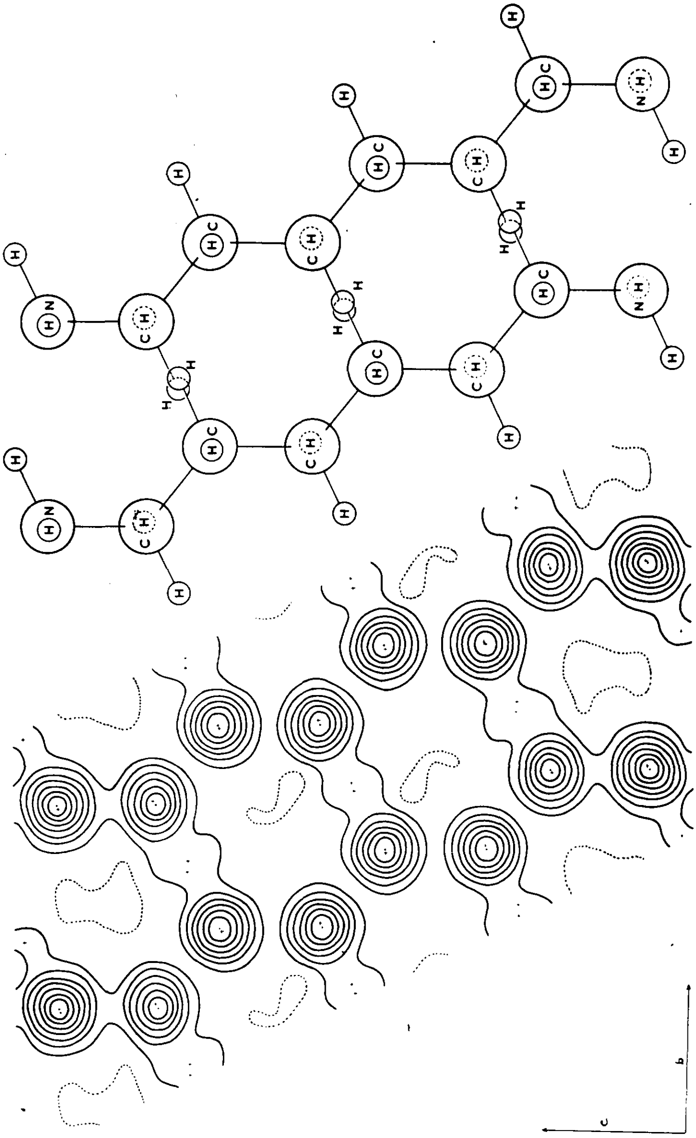


Fig.31 (okl) projection of hexamethylene diamine, showing partial resolution of hydrogen atoms.

The most recent and detailed interpretation of the X-ray diffraction patterns of polyamides has been made by Bunn and Garner.(1) The amount of information obtained from polymer photographs is essentially limited and cannot provide an independent determination of all the atomic positions, such as is possible in single crystal photography. Nevertheless, Bunn and Garner have succeeded in defining the structures of polyhexamethylene adipamide and sebacamide. The parameters given for the former imply small distortions of the carbon-nitrogen chain from the planar form, but in view of the strictly coplanar nature of hexamethylene diamine, it is highly probable that they are meaningless.

By varying the carbon-carbon bonds of the adipamide in the trial structure by ± 0.03A. from the accepted value, Bunn and Garner have ensured that they do not overlook the possibility of a conjugated molecule, which is more possible in the polyamide than in the diamine. Both molecules belong to different crystal systems, yet there is remarkable similarity between the unit cell dimensions.

Hexamethylene diamine.

a = 6.94A. b = 5.77A. c = 19.22A.

Polyhexamethylene adipamide.

a = 4.9A. b = 5.4A. c = 17.2A.

The adipamide is monoclinic, whereas the diamine is orthorhombic, which is the system of high molecular weight normal hydrocarbons such as $C_{29}H_{60}$(41), $C_{60}H_{122}$(42), $C_{30}H_{62}$(43).

The relative positions of any two neighbouring molecules in the polyamide have the effect of placing the methylene groups in the very same manner as found in the (hol) projection of the diamine, Fig.29. Therefore it is possible that the hydrogen nuclei may play identical rôles in both compounds in determining the orientation of the chains, as suggested by Mark.(38)

Bunn and Garner state that entirely satisfactory agreement between observed and calculated intensities could not be attained, and that no adjustments of atomic co-ordinates could possibly remove all the discrepancies. They found that the best agreement was obtained by placing the oxygen atom appreciably out of the plane of the chain, and with this non-planar structure, they offered two explanations of these discrepancies, namely thermal vibrations of the molecules, and crystal distortions. Although these explanations are reasonable, it is still doubtful if the position favoured for the oxygen atom is genuine, in view of the uncertainties of interpretation of powder photographs.

This is emphasised by the fact that the planes quoted with the poor agreement are those of large spacing, and here an analogy is found with hexamethylene diamine. In the latter, planes of large spacing also gave poor agreement between calculated and observed intensities, and this was only corrected by including the contributions of the hydrogen atoms in the geometric structure factors. Therefore, it is equally possible that the hydrogen atoms of polyhexamethylene adipamide, which are responsible for 13.4% of the scattering power of the asymmetric unit, should be taken into consideration, when comparing the calculated and observed intensities.

Similar discrepancies have been encountered in polyethylene(44) and again agreement may be improved by the inclusion of the hydrogen atoms in the structure factor calculations.

It follows therefore that in the case of the polyamides, the exact definition of the asymmetric unit, and particularly that of the oxygen atom, must await the results of a trial method analysis which considers the hydrogen atoms as scattering units. Powder photography will not yield accurate atomic co-ordinates, but triple

Fourier analysis of hexamethylene adipamide would not only decide if the structure was coplanar and if the conjugation within the chain was real, but would also provide more striking correspondences between itself and the polyamide. In this manner the more complex problems of the polyamides could be tackled and probably solved.

Atomic Scattering Curves.

The atomic scattering factors for the chlorine ion and carbon atom were taken from Hartree's Tables(10), and those for bromine from Thomas-Fermi Tables(10). A suitable temperature correction was applied in each case, according to the Debye-Waller formula(11). No separate scattering curve was used for the nitrogen atom, its contribution to the structure factor being added to that of carbon. The scattering factors for these atoms are given in Table XIII, expressed in terms of 2 $\sin\theta$.

For hexamethylene diamine, a composite experimentally derived atomic scattering curve was employed with the carbon and nitrogen coefficients weighted in the ratio of 6 to 7. The scattering factors for the hydrogen atom were obtained from the curve used for carbon and nitrogen, and these figures agree remarkably well with those given by Hartree, Table XIV.

Table XIII.

Atomic scattering factors employed in the dihalides.

$2\sin\theta$	Bromine	Chlorine	Carbon
0.	35.00	18.00	6.00
0.1	34.25	17.51	5.75
0.2	32.83	16.22	5.35
0.3	31.15	14.93	4.78
0.4	29.10	13.45	4.10
0.5	26.90	12.02	3.33
0.6	24.75	10.70	2.80
0.7	22.70	9.66	2.34
0.8	20.75	8.68	2.00
0.9	18.85	7.86	1.79
1.0	17.10	7.17	1.59
1.1	15.45	6.53	1.43
1.2	14.00	5.96	1.31
1.3	12.75	5.44	1.21
1.4	11.60	4.95	1.12
1.5	10.50	4.48	1.03
1.6	9.43	4.05	0.95
1.7	8.40	3.65	0.88
1.8	7.50	3.30	0.81
1.9	6.70	3.00	0.74

Table XIV.

Atomic scattering factors employed in hexamethylene diamine.

2 sinθ	Carbon-nitrogen composite values.	Hydrogen.	Hartree's values for hydrogen.	2sinθ
0.	6.25	1.00	1.00	0.
0.1	5.99	0.96		
0.2	5.40	0.87		
0.3	4.78	0.77	0.79	0.31
0.4	4.05	0.65		
0.5	3.37	0.54		
0.6	2.78	0.45	0.44	0.62
0.7	2.30	0.37		
0.8	1.98	0.32		
0.9	1.71	0.27	0.23	0.93
1.0	1.47	0.23		
1.1	1.30			
1.2	1.13			
1.3	0.98			
1.4	0.85			
1.5	0.74			
1.6	0.62			
1.7	0.54			
1.8	0.45			
1.9	0.36			

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