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The Crystal Structure of Hexamethylenediamine

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The crystal structure of hexamethylenediamine, $C_6H_{16}N_2$, has been determined, and all the carbon and nitrogen atoms are clearly resolved on the electron-density projections. There is also evidence of resolution of many of the hydrogen atoms. The bond lengths found within the chain molecule are probably accurate to within ± 0·02 or ± 0·03 A., and there is evidence of small variations in bond length within the saturated chain. The carbon–nitrogen bond length (1·51 A.) appears to be slightly longer than normal. A hydrogen bridge of length 3·21 A. occurs between the nitrogen atoms at the ends of successive molecules, but the other intermolecular contacts are all of the weak van der Waals type.

Introduction

In previous papers (Binnie & Robertson, 1949 *a*, *b*) the crystal structures of the dihalides of hexamethylenediamine have been examined. The heavy atoms in these molecules lead to a very direct determination of the structures, but the accuracy is necessarily reduced, for two reasons. First a large part of the structure amplitude is on the average due to the halogen contributions, and so a much higher accuracy in intensity measurements would be necessary in order to fix the positions of the light atoms with the same precision as might be obtained if the whole structure amplitude were due to the light atoms alone. In the second place, the accuracy realizable in making the intensity measurements is actually less when heavy atoms are present, owing to the high absorption coefficient for X-rays and consequent errors due to the details of shape and size of the crystal specimens. In spite of these limitations, some interesting bond-length observations were made on the hexamethylenediamine chain, but it is clearly important to confirm these measurements by a study of the chain molecule itself.

Hexamethylenediamine has a low melting-point (42° C.) and is extremely hygroscopic, but by means of a special technique (see Experimental section) we have now been able to carry out a fully quantitative X-ray investigation of this structure. All the carbon and nitrogen atoms are separately resolved in each of the electron-density maps (Figs. 1, 2). Consequently, the double Fourier series method of refinement leads to a very direct determination of the structure of this molecule. The dimensions are indicated in Fig. 3, and these appear to confirm the bond-length variations in the saturated chain which were observed in the case of the dihydrochloride. Another interesting result of the present study is the very striking resolution obtained for most of the hydrogen atoms. This is shown on the electron-density map in Fig. 1, and especially in Fig. 2, where the overlapping of certain hydrogen atoms lying at different depths in the crystal increases the effect.

Crystal data

Hexamethylenediamine, $C_6H_{16}N_2$; M, 116·1; m.p. 42° C.; d calc. 0·989, found 0·90–1·02. Orthorhombic bipyramidal,

$$a = 6{\cdot}94 \pm 0{\cdot}02,\ b = 5{\cdot}77 \pm 0{\cdot}02,\ c = 19{\cdot}22 \pm 0{\cdot}05\ \text{A.}$$

Absent spectra, $(0kl)$ when k is odd, $(h0l)$ when l is odd, $(hk0)$ when h is odd. Space group, D_{2h}^{15}–*Pbca*. Four molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 769·6 A.^{3} Absorption coefficient for X-rays ($\lambda = 1{\cdot}542$ A.), $\mu = 5{\cdot}4$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 264$.

Extremely fine needle crystals may be obtained by crystallization from dioxan and other solvents, and thin leaflets are formed by sublimation. The hygroscopic nature of the compound makes it difficult to carry out any measurements on such specimens, but distillation in bulk provides large irregular transparent plates from which suitable specimens may be cut.

Structure analysis

There is no resemblance in cell dimensions or space groups between hexamethylenediamine and its dihalides. The latter structures therefore do not provide any direct aid to the present analysis except as regards the dimensions and geometry of the chain molecule. It is necessary to proceed by means of a trial model for the molecule, which can be based on the dimensions previously found, and by considerations of the most probable packing and arrangement in the present orthorhombic unit cell.

The long c axis provides an obvious clue to the general direction of the chains, although their inclination to this axis may be considerable (up to 40°). The $(h0l)$ reflexions are the most useful in narrowing down the possibilities, and the great strength of the (200) reflexion indicates clearly that the chain directions must be almost perpendicular to the a axis. A very prominent (0.0.16) reflexion, of spacing 1·20 A., serves to place the atoms more accurately. If an origin is taken

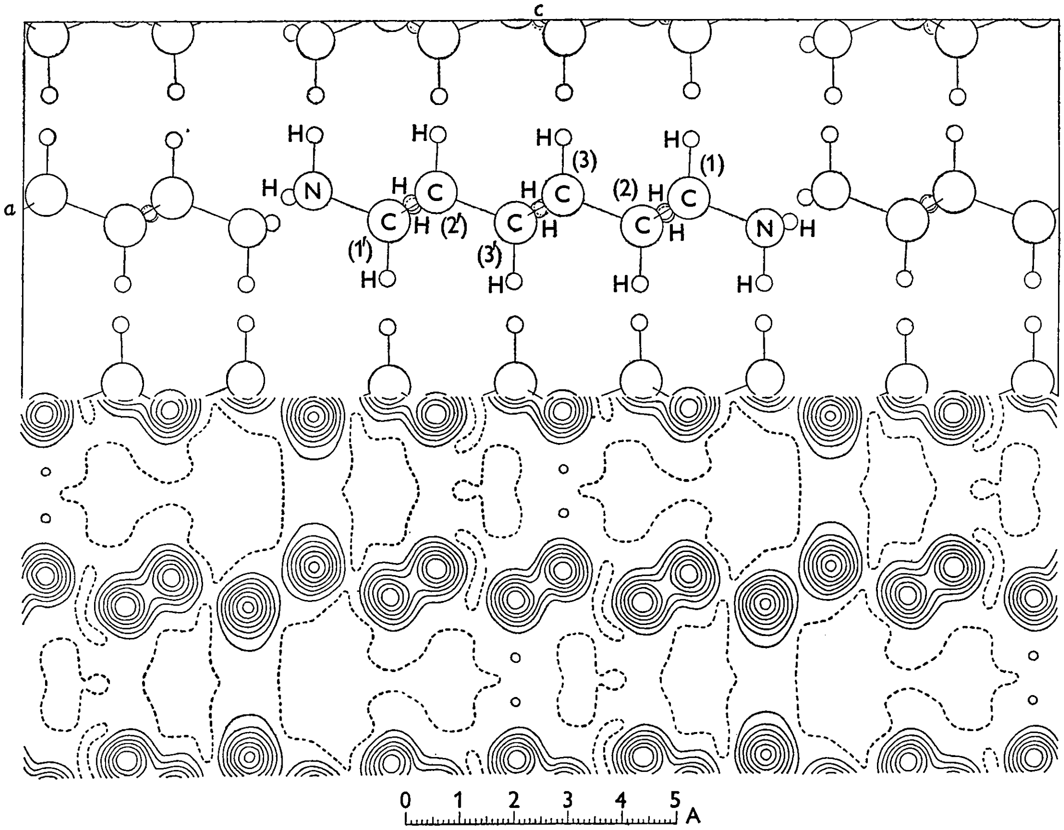

Fig. 1. Electron-density projection along *b* axis on (010). Contours at intervals of 1 e.A.$^{-2}$, the one-electron line being dotted.

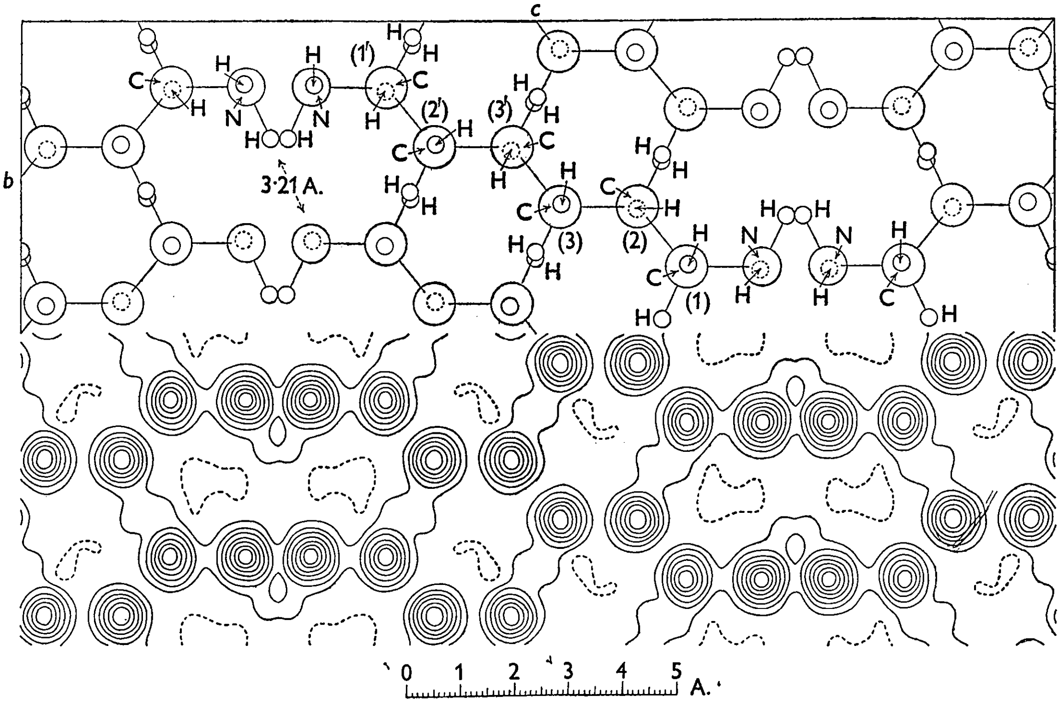

Fig. 2. Electron-density projection along *c* axis on (100). Contour scale as in Fig. 1.

at the centre of symmetry, which must lie between the two central carbon atoms of the chain, it follows that the sign of the (0.0.16) structure factor must be negative. A one-dimensional Fourier synthesis evaluated along the c axis was found to give resolution of all the carbon and nitrogen atoms and enabled their z co-ordinates to be fixed with some accuracy.

From this point it was easy to calculate probable orientations for the molecule, and the results were refined by carrying out successive double Fourier syntheses giving projections of the structure on the (010) and (100) planes. The maps finally obtained are shown in Figs. 1 and 2.

Co-ordinates and dimensions

The co-ordinates obtained from the final projection are listed in Table 1. The origin is chosen at a centre of symmetry, and the co-ordinates x, y and z are expressed as fractions of the orthorhombic axial lengths, a, b and c. Absolute co-ordinates expressed in Ångström units are also given under X, Y and Z. Only the atoms of the asymmetric crystal unit (half the chemical molecule) are listed, the co-ordinates of the other atoms in the unit cell being obtained from the relations applicable to the space group *Pbca*, viz.

$$x, y, z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z;\ \tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z;$$
$$\bar{x}, \bar{y}, \bar{z};\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, z;\ x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\ \tfrac{1}{2}+x, y, \tfrac{1}{2}-z.$$

The orientation of the molecule in the crystal is given in Table 2, with reference to the molecular axes indicated in Fig. 3 (N is perpendicular to L and M). The co-ordinates of the atoms with reference to these molecular axes are given in Table 3, and finally the dimensions of the chain molecule obtained from these figures are shown in Fig. 3.

Table 1. *Co-ordinates*

Atom (cf. Fig. 1)	x	y	z	X	Y	Z
N (1)	0·049	0·286	0·218	0·337	1·650	4·187
C (1)	−0·030	0·286	0·145	−0·211	1·650	2·778
C (2)	0·043	0·095	0·098	0·297	0·550	1·893
C (3)	−0·047	0·095	0·023	−0·258	0·550	0·442

Table 2. *Orientation*

$Loa = 89{\cdot}1°$ $Moa = 49{\cdot}1°$ $Noa = 139{\cdot}2°$
$Lob = 64{\cdot}6°$ $Mob = 133{\cdot}5°$ $Nob = 125{\cdot}9°$
$Loc = 25{\cdot}2°$ $Moc = 71{\cdot}8°$ $Noc = 73{\cdot}2°$

Table 3. *Co-ordinates referred to 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

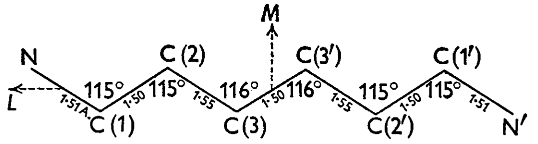

Fig. 3. Dimensions of the hexamethylenediamine molecule.

Effect of hydrogen atoms

When the co-ordinates finally obtained for the carbon and nitrogen atoms (Table 1) were employed in a recalculation of the structure factors, the average discrepancies, expressed in the usual way, remained relatively high, at about 25% for both the ($h0l$) and ($0kl$) zones. This figure was surprising, in view of the good resolution of the atoms, and it was not found possible to reduce it appreciably by any adjustment of the empirical scattering curve employed for the carbon and nitrogen atoms.

The discrepancies were particularly noticeable in the case of large-spacing reflexions, and it seemed likely that they might be due to the effect of the hydrogen atoms. Direct evidence of the presence of these atoms is found on the contour maps (Figs. 1, 2), particularly between widely separated carbon atoms on neighbouring chains where the hydrogen positions as viewed in the projections may be expected to overlap to some extent. The hydrogen contribution to the low-angle reflexions must be considerable, as 24% of the total atomic number of the molecule $C_6H_{16}N_2$ is due to hydrogen.

The partial resolution of the hydrogen atoms on the electron-density maps does not allow accurate co-ordinates to be assigned to them, but assuming the carbon–hydrogen bond length to be 1·09 A. as in methane (Pauling, 1939) and the nitrogen–hydrogen bond length to be 1·02 A., with appropriate bond angles, the most probable co-ordinates can easily be deduced, and these are given in Table 4. The hydrogen positions marked on the explanatory diagrams accompanying Figs. 1 and 2 are taken from these co-ordinates, and it will be seen that they explain the outstanding features of the contour maps extremely well.

Table 4. *Co-ordinates assigned to hydrogen atoms*

Atom		x	y	z	X	Y	Z
N (1)	H (1)	0·195	0·293	0·217	1·36	1·69	4·17
	H (2)	0·032	0·128	0·241	0·22	0·74	4·63
C (1)	H (1)	−0·187	0·279	0·146	−1·30	1·61	2·81
	H (2)	0·011	0·451	0·121	0·08	2·60	2·33
C (2)	H (1)	0·200	0·102	0·098	1·39	0·59	1·87
	H (2)	0·016	−0·073	0·122	0·11	−0·42	2·35
C (3)	H (1)	−0·194	0·088	0·024	−1·35	0·51	0·46
	H (2)	0·000	0·260	−0·001	0·00	1·50	−0·02

From these co-ordinates the contributions of the hydrogen atoms to the structure factors were calculated for all reflexions with $\sin\theta$ less than 0·6. For larger-angle reflexions the contribution will be so near to zero that it may be neglected. In these calculations an f_H curve was assumed of similar shape to the empirical scattering curve deduced for carbon and nitrogen but of one-sixth the height.

The effect of including the hydrogen contributions in this manner did not change the phase of any of the structure factors, but it led to a very marked reduction in the discrepancies between the calculated and observed values. The final calculations are listed in

Table 5, where the average discrepancy expressed in the usual way now amounts to 14·9 % for the (*h*0*l*) structure factors, 15·3 % for the (0*kl*) and 15·0 % overall. found are almost identical with those obtained for hexamethylenediamine dihydrochloride (Binnie & Robertson, 1949*b*).

Table 5. *Measured and calculated values of the structure factor*

hkl	sin θ ($\lambda = 1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$
200	0·222	105·5	+107·3
400	0·444	35·9	+39·4
600	0·666	2·0	+2·3
800	0·888	7·2	−5·9
020	0·267	29·1	−29·2
040	0·534	4·0	−2·7
060	0·801	13·0	−11·2
002	0·080	<0·2	+5·8
004	0·160	<0·4	−5·2
006	0·241	<0·4	+3·6
008	0·321	36·7	+40·6
0,0,10	0·401	13·1	+12·9
0,0,12	0·481	11·3	−9·1
0,0,14	0·561	10·3	+9·1
0,0,16	0·641	24·2	−23·6
0,0,18	0·721	3·9	−4·1
0,0,20	0·801	1·6	+0·8
0,0,22	0·881	<0·7	+0·7
0,0,24	0·961	7·3	−7·5
102	0·138	8·1	−6·6
104	0·193	5·9	+3·9
106	0·261	4·0	−3·4
108	0·334	28·4	+29·6
1,0,10	0·409	<0·6	+1·2
1,0,12	0·485	<0·7	−0·4
1,0,14	0·559	<0·8	−0·1
1,0,16	0·637	4·5	+6·0
1,0,18	0·715	3·3	+1·8
1,0,20	0·792	1·4	−1·3
1,0,22	0·869	<0·7	+0·9
1,0,24	0·948	2·7	−1·6
202	0·238	4·1	+4·8
204	0·273	6·8	−4·6
206	0·324	3·3	+3·1
208	0·387	21·0	+25·7
2,0,10	0·453	5·2	+6·5
2,0,12	0·523	6·5	−5·4
2,0,14	0·592	5·8	+5·0
2,0,16	0·666	16·1	−11·8
2,0,18	0·740	3·1	−4·0
2,0,20	0·815	<0·8	+0·9
2,0,22	0·890	<0·7	+0·6
2,0,24	0·966	4·6	−5·7
302	0·345	7·4	−6·2
304	0·370	5·8	+3·8
306	0·409	5·5	−3·2
308	0·461	29·0	+30·3
3,0,10	0·516	<0·7	−0·1
3,0,12	0·579	<0·8	+0·2
3,0,14	0·642	<0·9	−0·7
3,0,16	0·711	8·7	+8·2
3,0,18	0·781	6·9	+5·8
3,0,20	0·853	3·5	−3·0
3,0,22	0·925	2·0	+2·0
402	0·453	3·9	+4·3
404	0·474	3·7	−3·9
406	0·505	3·2	+1·6
408	0·547	11·9	+14·6
4,0,10	0·596	1·4	+2·0
4,0,12	0·650	<0·9	−1·6
4,0,14	0·708	2·5	+2·8
4,0,16	0·770	7·7	−7·9
4,0,18	0·834	3·2	−3·2
4,0,20	0·903	<0·7	+0·8
4,0,22	0·921	0·4	+0·1
502	0·562	4·0	−4·5
504	0·579	2·7	+2·4
506	0·604	1·4	−1·7
508	0·640	24·0	+25·1
5,0,10	0·682	2·5	+1·1
5,0,12	0·731	<0·9	−0·8
5,0,14	0·783	<0·9	−0·1
5,0,16	0·839	7·4	+8·1
5,0,18	0·899	5·0	+5·2
5,0,20	0·962	2·0	−2·4
602	0·675	1·9	+2·9
604	0·687	2·5	−3·3
606	0·709	4·8	+4·3
608	0·739	1·7	+1·9
6,0,10	0·776	3·7	−1·8
6,0,12	0·819	<0·8	+0·5
6,0,14	0·865	<0·7	+0·4
6,0,16	0·916	1·0	+0·3
6,0,18	0·970	0·8	−1·9
702	0·786	<0·9	−0·1
704	0·796	<0·9	+0·5
706	0·815	<0·8	−0·9
708	0·842	15·4	+15·4
7,0,10	0·875	3·7	+2·6
7,0,12	0·913	1·0	−1·0
7,0,14	0·954	0·7	+0·4
802	0·895	<0·7	+0·9
804	0·904	<0·7	−1·4
806	0·920	2·0	+1·9
808	0·944	<0·5	−0·5
8,0,10	0·973	2·3	−2·5
021	0·275	3·8	+2·9
022	0·283	38·8	+37·1
023	0·296	28·1	−30·3
024	0·314	5·3	−3·7
025	0·335	22·5	−25·1
026	0·360	12·8	−11·3
027	0·387	<0·9	+0·2
028	0·416	<1·0	−2·8
029	0·446	<1·0	−0·3
0,2,10	0·478	9·0	+11·1
0,2,11	0·511	13·1	−14·7
0,2,12	0·545	6·1	+6·5
0,2,13	0·580	27·9	−30·1
0,2,14	0·614	25·6	−24·3
0,2,15	0·649	2·6	−1·3
0,2,16	0·687	6·9	+6·0
0,2,17	0·722	<1·3	−0·3
0,2,18	0·759	4·1	−2·5
0,2,19	0·796	1·8	+1·1
0,2,20	0·834	<1·2	−0·6
0,2,21	0,870	<1·1	−2·4
0,2,22	0·908	1·7	−2·9
0,2,23	0·945	<0·8	−0·9
0,2,24	0·983	<0·6	+0·5
041	0·541	+17·5	−21·6
042	0·545	19·2	−18·8
043	0·553	5·8	−4·8
044	0·562	<1·2	−1·9
045	0·575	5·2	−3·5
046	0·588	6·1	+6·9
047	0·606	<1·3	−0·9
048	0·625	<1·3	−1·4
049	0·645	3·2	−5·6
0,4,10	0·668	6·9	−8·4
0,4,11	0·692	8·0	−8·0
0,4,12	0·717	3·5	−4·6
0,4,13	0·744	3·9	−1·6
0,4,14	0·770	12·3	+11·4
0,4,15	0·799	9·0	−10·5
0,4,16	0·829	1·7	+1·3
0,4,17	0·859	3·4	+3·0
0,4,18	0·890	3·1	+2·1
0,4,19	0·921	2·1	+1·4
0,4,20	0·954	<0·8	+0·3
0,4,21	0·987	<0·6	−0·5
061	0·809	8·8	+9·8
062	0·811	3·9	−4·3
063	0·815	<1·2	+1·0
064	0·822	<1·2	−0·1
065	0·831	<1·2	−0·6
066	0·840	<1·2	+0·5
067	0·853	<1·1	−0·5
068	0·866	3·5	−2·9
069	0·881	3·0	+3·3
0,6,10	0·897	2·9	−3·3
0,6,11	0·916	2·3	+2·5
0,6,12	0·934	<0·9	−0·1
0,6,13	0·956	<0·8	−1·9
0,6,14	0·977	<0·6	+1·6

Discussion

The high resolution achieved in the electron-density maps, and the good agreements obtained in the structure-factor calculations indicate that the accuracy of the bond-length determinations should at least be as high as ±0·02 or ±0·03 A., and the valency angles should be accurate to within 3° or 4°. The variations in bond length found in the hexamethylenediamine chain (Fig. 3) are therefore probably significant. It is also a striking feature of this work that the bond lengths now

It seems clear that the carbon–nitrogen bond (1·51 A.) is slightly longer than normal, and also that there is a slight alternating effect of long and short bonds extending over the whole length of the saturated chain. This latter effect must, however, be accepted with reserve until it can be confirmed or disproved by more accurate three-dimensional analysis, or by the study of other homologues in this series.

The molecular co-ordinates (Table 3) show that the molecule is quite accurately co-planar. In conjunction with the apparent conjugation effect extending along the chain, this is probably a significant result, and might support an explanation of the bond-length alternations on the basis of hyperconjugation theory.

Since hexamethylenediamine is the first solid in this series, only weak intermolecular bonds would be expected. One distinct hydrogen bridge, of length 3·21 A., occurs between the terminal nitrogen atoms of successive chains in the crystal. From Fig. 2 there is some evidence that a hydrogen atom lies in the direction of this bond between the molecules, and in fact there is some evidence of partial resolution.

The other intermolecular approach distances are all of the weak van der Waals type, being 3·68 A. for a second nitrogen–nitrogen distance, and 3·92 A. for the distance between an α-methylene group and the amino-group of a neighbouring molecule. In the direction of the a axis, the closest intermolecular approach is just over 4·0 A.

Experimental

Crystals of hexamethylenediamine obtained from solvents such as dioxan and amyl alcohol are extremely fine and so hygroscopic that they cannot be preserved for any time in the open atmosphere. However, it was found that 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 mm. These plates, the thickness of which proved to be the crystal 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 inside a gelatine capsule and kept dry by the presence of a small quantity of phosphorous pentoxide. The crystal was mounted on a fine glass fibre inside the capsule, which was then sealed by plasticine. In this manner it was found that crystals could be preserved for several days, enabling a full X-ray examination to be made. Photographs show distinct powder lines due to decomposition on the surface of the crystal, but this did not seriously affect the estimations of the intensities of the single-crystal reflexions.

It was not possible to make an accurate determination of the density, but by observation in different suspension mediums a value of between 0·95 and 1·0 was indicated. This is sufficient to determine the number of molecules in the unit cell as 4.

Copper $K\alpha$ radiation, $\lambda = 1{\cdot}54$ A., was used in all the X-ray work, and rotation, oscillation and moving-film photographs of a number of zones were taken. For the ($h0l$) 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. For the ($0kl$) 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 were recorded up to the limit for the radiation used on a series of moving films. The multiple-film technique (Robertson, 1943) was used to correlate the strong and weak reflexions, and the intensities were estimated visually. Absorption corrections were not employed because of the uniform cross-section of the crystals. The F values were finally derived by the usual formulae for mosaic-type crystals, and are listed in Table 5 under '$F_{\text{meas.}}$'. Absolute measurements were not carried out, the scale being obtained by correlation with the values finally calculated from the atomic positions found.

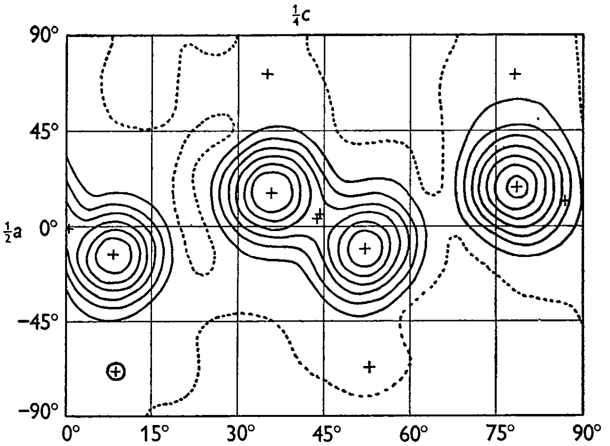

Fig. 4. Co-ordinates assigned to the atoms in the asymmetric crystal unit, b-axis projection.

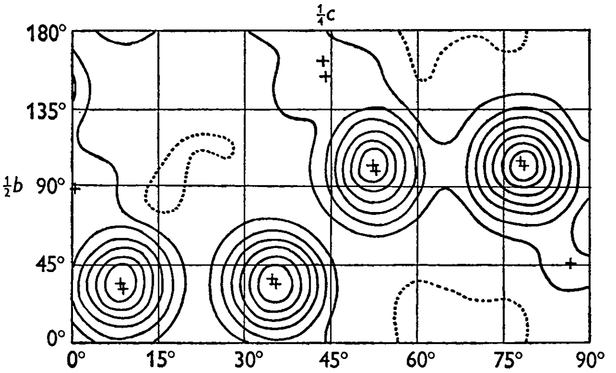

Fig. 5. Co-ordinates assigned to the atoms in the asymmetric crystal unit, a-axis projection.

The Fourier syntheses were carried out by three-figure numerical methods (Robertson, 1948). For the projection along the b axis the electron density was computed at 900 points on the asymmetric unit, the axial subdivisions being $a/60 = 0{\cdot}116$ A. and $c/120 = 0{\cdot}160$ A. For the projection along the a axis summations were taken at 450 points on the asymmetric unit, the axial subdivisions being $b/30 = 0{\cdot}192$ A. and $c/120 = 0{\cdot}160$ A.

The co-ordinates assigned to the atoms from the final Fourier projections are indicated by small crosses in Figs. 4 and 5, which cover the areas of the asymmetric units. The values derived from these plots are tabulated in Table 1.

From the final values of the co-ordinates, including those of the hydrogen atoms, the F values were recalculated with the results tabulated in Table 5, where the overall discrepancy between measured and calculated values amounts to 15%. For these calculations a single composite atomic scattering factor curve was employed, derived from the experimental measurements with the carbon, nitrogen and hydrogen coefficients weighted in the ratio of 7 : 6 : 1.

In conclusion we desire to express our thanks to Imperial Chemical Industries Ltd. for a grant and a supply of hexamethylenediamine, and also to the Department of Scientific and Industrial Research for a further grant to one of us (W. P. B.).

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Die vollständige und eindeutige Kennzeichnung der Raumsysteme durch Charakterentafeln. II.

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The method of representing space groups by tables of characters given in a previous communication is now extended to space groups with face- or body-centred translation groups and to those of the tetragonal, hexagonal and cubic systems.

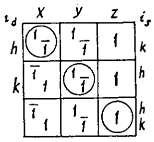
(*a*) Digonale Raumsysteme mit mehrfach primitiver Translationsgruppe

In diesem zweiten Teil erfolgt die Erweiterung der Raumsystemscharakterisierung auf Raumsysteme mit mehrfach primitiven Translationsgruppen und mit höher als zweizähligen Achsen. Wiederum dienen die holoedrischen Raumsysteme mit einem Symmetriezentrum im Nullpunkt als Ausgangssysteme, aus denen sich die hemiedrischen und tetartoedrischen als Untergruppen ergeben, eventuell vermehrt um jene Untergruppen, die Schraubenachsenscharen enthalten, welche mit Holoedrie unverträglich sind. Mit wenigen Ausnahmen umfasst bereits Tabelle 2 (Niggli, 1949, S. 268–9) alle notwendigen quadratischen Grundsymbole. Zu den als Raumsystemscharakteren bezeichneten Werten, die sich auf x, y, z beziehen, kommen bei basisflächenzentriertem Gitter Werte hinzu, die in den entsprechenden Kolonnen operativ mit $\bar{1}, \bar{1}, 1$ multipliziert werden müssen; bei innenzentriertem Gitter treten als solche Operatoren $\bar{1}\ \bar{1}\ \bar{1}$ und bei allseitig flächenzentriertem Gitter $\bar{1}\ \bar{1}\ 1$, $\bar{1}\ 1\ \bar{1}$, $1\ \bar{1}\ \bar{1}$ hinzu. Ein Beispiel D_{2h}^{21}-*Cmma* diene zur Erläuterung für orthorhombisch basisflächenzentriert: D_{2h}^{21} geht aus D_{2h}^{3} und (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0) hervor und ergibt als vollständiges Gruppensymbol:

D_{2h}^{21}	x	y	z
	$\bar{1}$	$\bar{1}$	1
	①	1	1
	$\bar{1}$	①	1
	$\bar{1}$	1	①

Aus ihm lassen sich wiederum alle Symmetrieelemente, die Auswahlregeln, Punktsymmetrien und Untergruppen ablesen. Zum Beweis wollen wir die Multiplikationen durchführen und die Ergebnisse jeweilen in einer zweiten Horizontalzeile anführen.

D_{2h}^{21}



		x, y, z; $x+\frac{1}{2}, y+\frac{1}{2}, z$
$(100)_0$ SE	$[100]_{00}$ Digyre	$\bar{x}, y, z$; $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, z$
$(100)_{\frac{1}{4}}$ GSE $\frac{1}{2}b$	$[100]_{\frac{1}{4}0}$ Schraubenachse	$x, \bar{y}, \bar{z}$; $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$
$(010)_0$ GSE $\frac{1}{2}a$	$[010]_{\frac{1}{4}0}$ Digyre	$x+\frac{1}{2}, \bar{y}, z$; $x, \bar{y}+\frac{1}{2}, z$
$(010)_{\frac{1}{4}}$ SE	$[010]_{00}$ Schraubenachse	$\bar{x}+\frac{1}{2}, y, \bar{z}$; $\bar{x}, y+\frac{1}{2}, \bar{z}$
$(001)_0$ GSE $\frac{1}{2}b$	$[001]_{\frac{1}{4}0}$ Digyre	$x+\frac{1}{2}, y, \bar{z}$; $x, y+\frac{1}{2}, \bar{z}$
$(001)_0$ GSE $\frac{1}{2}a$	$[001]_{0\frac{1}{4}}$ Digyre	$\bar{x}+\frac{1}{2}, \bar{y}, z$; $\bar{x}, \bar{y}+\frac{1}{2}, z$
0,0,0 und $\frac{1}{4},\frac{1}{4},0$	Symmetriezentren	$\bar{x}, \bar{y}, \bar{z}$; $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$

Die (nach den in der ersten Mitteilung angegebenen Regeln) aus den Charakteren ableitbaren Symmetrieelemente und Koordinatentripel sind rechts des Quadrates angeführt, wobei das Einzelelement jeweilen durch die ganze Schar zu ergänzen ist. Nach den erläuterten Gesetzen (Niggli, 1949) ergeben sich auch sofort die Auswahlregeln:

Integral: (hkl) nur mit $h+k=2n$ vorhanden,
($0kl$) mit $k=2n$, ($h0l$) mit $h=2n$, ($hk0$) mit $h=2n$, $k=2n$, usw.

Die speziellen Auslöschungsgesetze sind besser durch diejenigen der massgebenden geometrischen Oerter zu ersetzen und nach den Regeln ableitbar, die von Niggli (1950) erläutert wurden. Der Strukturfaktor (mit $B=0$) lässt sich unmittelbar hinschreiben. Die normalen