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Redetermination of the Structure of 1,6-Hexamethylenediamine Dihydrochloride

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Abstract. $C_6H_{18}Cl_2N_2$, $M_r = 189{\cdot}14$, monoclinic, $P2_1/c$, $a = 4{\cdot}594\ (1)$, $b = 14{\cdot}123\ (3)$, $c = 15{\cdot}624\ (4)$ Å, $\beta = 90{\cdot}660\ (9)°$, $Z = 4$, $V = 1013{\cdot}63$ Å^3, λ(Cu $K\alpha_1$) = 1·5405 Å, μ(Cu $K\alpha$) = 51·23 cm^{-1}, $F(000) = 408$ e, $D_c = 1{\cdot}239$, $D_m = 1{\cdot}201$ g cm^{-3}. The structure has been determined by Patterson methods, using Cu $K\alpha$ diffractometer data, and has been refined by full-matrix least-squares calculations to $R = 0{\cdot}059$ using 1984 observed reflections. In the chain molecule the C—C bond lengths alternate between average values of 1·508 (4) and 1·538 (4) Å; the mean C—N distance is 1·484 (4) Å. The N atoms are protonated and form hydrogen bonds with the Cl ion, the average N···Cl distance being 3·164 Å.

Introduction. Crystals of 1,6-hexamethylenediamine dihydrochloride were used as a pedagogical example for initiating students into two-dimensional X-ray analysis. In the course of the preliminary investigation it was discovered that in the earlier work of Binnie & Robertson (1949) the X-ray reflections had been misindexed, hkl being consistently interchanged with $hk\bar{l}$ (possibly because $\beta \simeq 90°$). This observation prompted the more detailed three-dimensional analysis reported here.

The title compound crystallizes as needles elongated along a. A crystal of dimensions 0·42 × 0·39 × 0·33 mm was used for the data collection. Unit-cell and space-group data were obtained from rotation, Weissenberg and precession photographs. (See Fig. 1 for prominent faces.) Accurate cell parameters were determined by a least-squares refinement of the θ values of 20 reflections measured on an automatic Hilger & Watts Y290 four-circle diffractometer, using Cu $K\alpha$ radiation. Systematic absences $h0l$ where $h = 2n + 1$ and $0k0$ where $k = 2n + 1$ were obtained. Integrated intensities were measured on the same instrument using the ω–2θ step scanning technique, with Ni-filtered radiation and a scintillation counter connected to a pulse-height analyser (φ axis: a). The counting time per step was 1 s and steps of 0·01° were used with a scan width of 0·70° plus a dispersion correction. The background on both sides of the peak was measured in a single step count of a tenth of the time required to scan the peak. Periodic checks on three reference reflections showed only very small fluctuations. The intensities were later scaled to the reference measurements. A reflection was classified as observed if $I > 3\sigma(I)$. 3104 reflections were measured, including 2109 unique and 125 with insignificant intensity. Lorentz, polarization and absorption corrections were applied. Corrections for absorption were applied using the program *SHELX* (Sheldrick, 1975).

The structure was determined by the heavy-atom method. The coordinates of both the Cl atoms were determined from a three-dimensional Patterson synthesis computed with coefficients sharpened with the function $1/\sum n_i f_i \exp(-8\pi^2 U_i \sin^2\theta/\lambda^2)$, where U_i, an overall isotropic thermal parameter, was arbitrarily assessed as 0·03 Å^2, for each of the i atom types. An

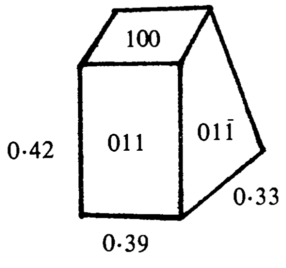

Fig. 1. Prominent faces of the crystal.

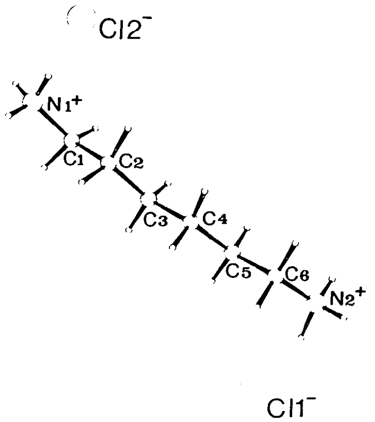

Fig. 2. Diagram of the molecule viewed along the a axis. The circles, in increasing order of size, represent H, C, N and Cl.

electron density map computed with phases based on the two Cl atom coordinates showed the positions of all ten remaining non-hydrogen atoms. A structure factor calculation using estimated isotropic temperature factors $\overline{U^2} = 0{\cdot}06$ Å^2 for C and N, and $0{\cdot}04$ Å^2 for Cl gave an R value of 0·35 at this stage.

The structure was refined by full-matrix least-squares calculations using the program *SHELX*. Isotropic refinement converged at $R = 0{\cdot}110$, with a further reduction to 0·078 with anisotropic temperature factors for the non-H atoms only. All the H atoms were located on a difference electron density map in stereochemically acceptable positions. H atoms were then included in the structure factor calculations, but not in the refinement. The H atoms were assigned temperature factors corresponding to those of the heavy atoms to which they are bonded. Weights used were: $w(hkl) = 1/\sigma^2_{F(hkl)}$.

The final R value was 0·059. The final positional parameters are given in Table 1.*

Discussion. Fig. 2 is a drawing of the asymmetric unit of the structure and shows the atom labelling. Fig. 3 gives the dimensions of the 1,6-hexamethylenediamine chain and further details of the molecular geometry are given in Table 2.

Table 1. *Atomic parameters*

The origin is at $(0,\frac{1}{2},\frac{1}{2})$ with respect to that of Binnie & Robertson (1949) but the same numbering scheme is used.

(*a*) Positional parameters for non-hydrogen atoms, with e.s.d.'s in parentheses

	x	y	z
Cl(1)	0·0772 (2)	0·2741 (1)	0·2835 (1)
Cl(2)	0·8745 (1)	−0·0402 (1)	0·8893 (1)
C(1)	0·2994 (6)	−0·0584 (2)	0·6940 (2)
C(2)	0·5299 (6)	0·0092 (2)	0·6575 (2)
C(3)	0·3626 (6)	0·0806 (2)	0·5990 (2)
C(4)	0·5583 (6)	0·1559 (2)	0·5628 (2)
C(5)	0·3858 (6)	0·2306 (2)	0·5131 (2)
C(6)	0·5784 (6)	0·3068 (2)	0·4765 (2)
N(1)	0·4255 (6)	−0·1277 (2)	0·7553 (2)
N(2)	0·4036 (6)	0·3820 (2)	0·4334 (2)

(*b*) Positional and thermal parameters of hydrogen atoms

	x	y	z	$\overline{U^2}$ (Å^2)*
H(11)	0·2062	−0·1071	0·6485	0·0458
H(12)	0·1389	−0·195	0·7252	0·0458
H(21)	0·6187	0·0428	0·7142	0·0414
H(22)	0·6730	−0·0283	0·6229	0·0414
H(31)	0·2627	0·0464	0·5464	0·0411
H(32)	0·1984	0·1128	0·6336	0·0411
H(41)	0·6707	0·1891	0·6128	0·0385
H(42)	0·7187	0·1250	0·5214	0·0385
H(51)	0·2625	0·1964	0·4642	0·0382
H(52)	0·2250	0·2571	0·5535	0·0382
H(61)	0·6812	0·3392	0·5321	0·0370
H(62)	0·7187	0·2750	0·4285	0·0370
H(10)	0·5169	−0·0901	0·8063	0·0433
H(110)	0·5750	−0·1678	0·7321	0·0433
H(111)	0·2815	−0·1607	0·7857	0·0433
H(20)	0·2562	0·4107	0·4714	0·0405
H(220)	0·2961	0·3529	0·3806	0·0405
H(222)	0·5312	0·4285	0·4107	0·0405

*$\overline{U^2}$ = mean-square amplitude of atomic vibration.

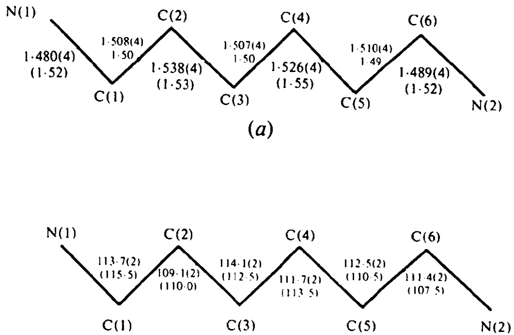

Fig. 3. Dimensions of the 1,6-hexamethylenediamine chain, showing (*a*) bond distances (Å) and (*b*) bond angles (°). Figures in parentheses indicate values obtained by Binnie & Robertson (1949).

Table 2. *Torsion angles* (°) *and hydrogen-bond distances* (Å) *and angles* (°)

The sign of the angle $A-B-C-D$ is positive when a clockwise rotation about $B-C$ is required to bring $A-B-C$ into coincidence with $B-C-D$, viewed along $B-C$.

A B C D	
N(1)–C(1)–C(2)–C(3)	−177
C(1)–C(2)–C(3)–C(4)	177
C(2)–C(3)–C(4)–C(5)	−174
C(3)–C(2)–C(1)–N(1)	−177
C(4)–C(3)–C(2)–C(1)	177
C(5)–C(4)–C(3)–C(2)	−174
C(6)–C(5)–C(4)–C(3)	180
N(2)–C(6)–C(5)–C(4)	−176

Atom A	Atom B	Atom C	$A\cdots B$	$A\cdots C$	$A\cdots B\cdots C$
Cl(1^{i})	H(220^{i})	N(2^{i})	2·125	3·160 (3)	171·3
Cl(1^{i})	H(111^{ii})	N(1^{ii})	2·531	3·155 (3)	123·8
Cl(1^{i})	H(110^{iv})	N(1^{iv})	2·208	3·145 (3)	163·8
Cl(2^{i})	H(10^{i})	N(1^{i})	2·198	3·172 (3)	155·0
Cl(2^{i})	H(222^{iii})	N(2^{iii})	2·256	3·191 (2)	166·2

Symmetry code

(i) x,y,z

(ii) $-x, -y, 1-z$

(iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$

(iv) $1-x, -y, 1-z$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33659 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

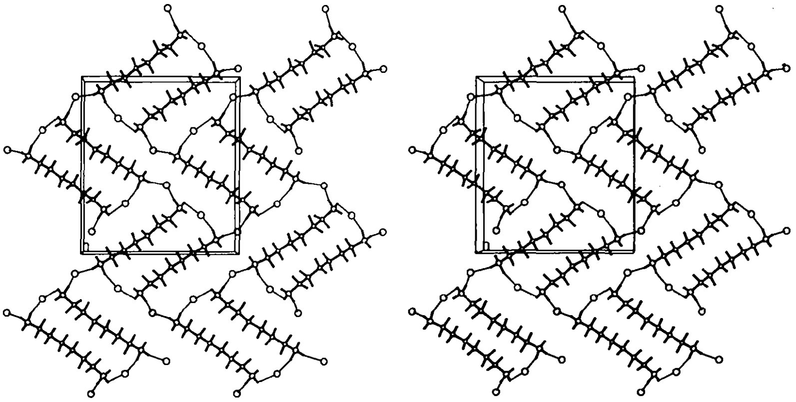

Fig. 4. The structure seen in projection down *a*. *b* is horizontal, *c* vertical (origin bottom left corner). Hydrogen bonds forming sheets approximately parallel to (100) are indicated.

The C—C distances in the hexamethylene chain range between 1·507 (4) and 1·538 (4) Å, with an average value of 1·518 (4) Å. The two C—N distances are 1·480 (4) and 1·489 (3) Å, as would be expected for C—N single bonds. Average values of the C—H and N—H bond lengths are 1·05 and 0·99 Å respectively. The C—C—C angles range from 109·1 (2) to 114·1 (2)°, average value 111·4 (2)°, and the N—C—C angles are 113·7 (2) and 111·4 (2)°. Average values of the bond angles involving H are H—C—C = 109°, H—C—N = 105°, H—N—C = 108° and H—C—H = 110°.

The geometry of the compound is in reasonable agreement with the findings of Binnie & Robertson (1949) who also noted the alternation of the C—C bond lengths in the present compound and in 1,6-hexamethylenediamine itself (Binnie & Robertson, 1950) although the precision of their analysis is much less than the present work. The largest discrepancies between the two determinations occur for the C—N bond lengths.

The C—C distances in the chain are alternately short [average 1·505 (4) Å] and long [average 1·532 (4) Å], the difference being significant at the 6σ level. No significant alternation is observed for example in *n*-hexatriacontane (Shearer & Vand, 1956), average C—C = 1·534 (6) Å, or in the methyl ester of 12-D-hydroxyoctadecanoic acid (Lundén, 1976), average C—C = 1·510 (8) Å.

Torsion angles along the chain are given in Table 2. The chain has a pronounced curvature with the N atoms displaced on the same side of the least-squares plane defined by the chain.

The Cl$^-$ ions at either end of the chain have different environments. There is evidence of N···Cl$^-$ hydrogen bonding, there being three such bonds to N(1) and two to N(2), Table 2. The crystal structure is thus composed of hydrogen-bonded sheets approximately parallel to (100), Fig. 4, with further hydrogen bonding between the sheets (not shown). A network of hydrogen bonds links the chain molecules together.

Table 3. *Comparison of* $|F_o|_{(h0l)}$ *values from diffractometer data and data supplied in paper by Binnie & Robertson* (1949)

	$\lvert F_o\rvert_{(h0l)}$	
h k l	Diffractometer (This work)	Binnie & Robertson (1949)
1 0 12	63	6
1 0 $\overline{12}$	<3	73
1 0 10	27	46
1 0 $\overline{10}$	39	29
1 0 8	15	11
1 0 $\bar{8}$	12	14
2 0 6	35	68
2 0 $\bar{6}$	50	37
2 0 4	19	66
2 0 $\bar{4}$	50	24
4 0 10	<3	38
4 0 $\overline{10}$	29	6
5 0 10	<3	10
5 0 $\overline{10}$	10	<3
1 0 2	80	24
1 0 $\bar{2}$	21	105

Table 3 gives a selection of $|F_o|$ values for the two investigations and shows that the $|F_o|$ values given for the *h*0*l* reflections by Binnie & Robertson (1949) were actually the values for the *h*0$\bar{l}$ reflections. This undoubtedly accounts for some of the differences in the two structure determinations.

All calculations were performed on the CDC 6600 computer at the University of London Computer Centre.

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