Qualitative estimates of the intensity changes which would accompany such disorder indicate that either of these explanations is plausible. However, in connection with the latter suggestion, it may be noted that no appreciable peak broadening or peak shift was observed.

The samples used for refinement of parameters at room temperature had of course been ground, but the diffraction patterns were run a few weeks later. The question arises whether the values of the intensities in the cured sample are indeed the correct ones for an ideally imperfect crystal. It may be noted in this connection that the changes in intensity summarized in Table 2 have relatively little effect on atomic positions. A least-squares treatment similar to that described above was carried out on one of the worst samples described here (Sample 3, line 4 in Table 2), and the parameter values obtained lay within one standard deviation of those obtained above. However, the fit to the data is here rather poor, the estimates of error being about four times as great as those derived above. This would seem to add further weight to the disorder hypothesis suggested, i.e. the intensities cannot be fitted well on the basis of variation in atomic positions and temperature factors alone. The goodness of the fit in the least-squares treatment in § 4 would seem to indicate that the samples there are more nearly perfect. However, it would perhaps be best not to have complete confidence in the parameter values derived there until they are confirmed by measurements on a single, unstrained crystal. This investigation was undertaken not for precise determination of atomic positions (the standard deviations quoted are evidence of this) but rather to shed some light on the rotation of the nitrate groups.

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Investigation of Hexamethylene Tetramine by Neutron Diffraction

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Hexamethylene tetramine has been re-investigated by neutron diffraction in order to determine the exact positions of the hydrogen atoms. The space group is found to be $I\bar{4}3m$, and the parameters lead to C–H bonds of lengths 1·13 Å forming angles of 110° 6′. An anisotropic temperature factor is introduced, based on the assumption of the molecule rotating as a rigid constellation. This leads to a remarkably good agreement between observed and calculated structure factors.

Introduction

Despite the fact that hexamethylene tetramine was one of the first organic structures to be solved (Dickinson & Raymond, 1923), reports of new investigations have appeared at regular intervals. The main reasons for this continuing interest have been the location of the hydrogen atoms, which are assumed to play an important part in the structure and determine the space group, and lack of agreement between observed and calculated intensities.

Hexamethylene tetramine, $C_6N_4H_{12}$, crystallizes, as far as the C and N atoms are concerned, in a body-centred cubic lattice with $a = 7{\cdot}02$ Å. The 6 C atoms are placed octahedrally on the edges and the 4 N atoms tetrahedrally on the space diagonals of the unit cell, leaving two possible space groups: T_d^3–$I\bar{4}3m$ and T_d^4–$P\bar{4}3n$. In the former case the hydrogen atoms must be in the diagonal planes, and the molecule at the centre of the unit cell will be identical with that at the corner. In the latter case the hydrogen atoms are displaced from these planes, in opposite directions for the molecule at the centre and that at the corner. The unit cell is then primitive.

The first determination of the hydrogen positions was carried out with X-rays by Brill, Grimm, Hermann & Peters (1939) in their painstaking investigations on chemical bonding by Fourier methods. More recently Lobatchev (1954) has employed electron diffraction by thin films, and his parameters for all atoms deviate somewhat from those previously found. A low-temperature X-ray study of hexamethylene tetramine has been undertaken by Schaffer (1947), who found some anomalies in the variation of a few intensities with temperature. These he could explain by introducing an anisotropic temperature factor due to rotation-oscillations of the approximately spherical molecule around its centre of gravity. A splitting-up of the temperature factor into an isotropic and an anisotropic part resulted in better agreement between observed and calculated intensities for reflexions in the [001] zone, which he considered.

With the possibility offered by neutron diffraction of making an exact determination of the hydrogen positions, it was considered to be of interest to utilize this method. The greater contribution of scattering from the hydrogen atoms, together with increased possibility of exact intensity determination, was expected to throw further light on the question of anisotropic oscillations.

Experimental

Single crystals were grown from alcoholic solutions, as the solubility in water was too large. Seeds were suspended on hairs in saturated solutions in 96% alcohol, which were allowed to evaporate slowly at constant temperature in desiccators filled with calcium chloride. The crystals used were rhombic dodecahedra of size 4–7 mm. To increase the mosaic spread all were dipped in liquid air three times.

The problem was found suitable for trying out a new single-crystal goniometer constructed at the Norwegian Defence Research Establishment by Barstad & Andresen (1956). This is based on a new principle utilizing a macromodel of the unit cell for orienting. The crystal is aligned with its unit cell parallel to the macromodel, and by turning both, any crystallographic plane can be set to reflect in the equator plane. To intercept an equal amount of the primary beam for all positions, the crystal should be of spherical shape. A rhombic dodecahedron represents a good approximation to this.

The exact alignment of the crystal to the macromodel was exceedingly difficult as a suitable goniometer head had not been constructed at the time of the experiments. This caused the determination of the high-angle reflexions to be rather uncertain. Neutrons of wavelength 1·15 Å, with a rather large wavelength spread to gain intensity, were used. In order to check the observed intensities and get enough reflexions for making two Fourier projections, cylindrical crystals with axes [001] and [1$\bar{1}$0] were put up on the automatic diffractometer at Kjeller, set for a wavelength of 1·015 Å. Fifteen different reflexions of type ($hk0$) and twenty-five of type (hhl) were measured.

If the space group were $P\bar{4}3n$, reflexions with $h+k+l = 2n+1$ should exist, but, being due only to small displacements of the hydrogen atoms, these would be very weak. Still they should be detectable by single-crystal measurements, at least at low angles where the Lorentz factor increases rapidly. As none was found, we conclude that the space group is $I\bar{4}3m$, as previously assumed. Thus the atomic positions are:

$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$
12 C in 12(e): $v, 0, 0;\ 0, v, 0;\ 0, 0, v;\ \bar{v}, 0, 0;$
$0, \bar{v}, 0;\ 0, 0, \bar{v}.$
8 N in 8(c): $u, u, u;\ u, \bar{u}, \bar{u};\ \bar{u}, u, \bar{u};\ \bar{u}, \bar{u}, u.$
24 H in 24(g): $x, x, z;\ z, x, x;\ x, z, x;\ \bar{x}, x, \bar{z};$
$\bar{z}, x, \bar{x};\ \bar{x}, z, \bar{x};\ x, \bar{x}, \bar{z};\ z, \bar{x}, \bar{x};$
$x, \bar{z}, \bar{x};\ \bar{x}, \bar{x}, z;\ \bar{z}, \bar{x}, x;\ \bar{x}, \bar{z}, x.$

Calculations

The observed structure factors (F_o in Table 2) were used for making Fourier diagrams of the [001] and [1$\bar{1}$0] projections. As the molecule contains no centre of symmetry, phase angles had to be calculated for the (hhl) reflexions. For the ($hk0$) reflexions, on the other hand, only signs were needed, since the projection along the axes will have a centre of symmetry. Signs and phases were calculated for the parameters given by Brill *et al.* (Table 1).

For finding the hydrogen positions, difference syntheses were made after subtracting the contribution of the C and N atoms, whose parameters were considered well determined. The values used for the temperature factors were rather decisive. By considering separately reflexions mainly dependent on C or N and on H atoms, the best values found for B in the isotropic temperature factor $\exp\left[-B\,(\sin^2\theta/\lambda^2)\right]$ were: $B_{\mathrm{C,N}} = 4{\cdot}0$ Å^2 and $B_{\mathrm{H}} = 7{\cdot}5$ Å^2. In Table 2 the cal-

Table 1. *Parameters*

	C	N	H	
Authors	v	u	x	z
Brill *et al.*	0·2353	0·1204	0·095	0·335
Schaffer	0·235	0·122	—	—
Lobatchev	0·228	0·118	0·090	0·328
This paper	0·235	0·122	0·093	0·327

culated structure factors for these values, when using the final parameters of Table 1, are given as F_1.

New parameters deduced from these diagrams did not improve the agreement between observed and calculated structure factors appreciably, and it became evident that no reasonable changes of the parameters would bring about agreement for reflexions like (220), (310), (332), (422) and (600). A marked ellipticity of the peaks (see Fig. 1), especially for atoms projected perpendicular to their radius vectors from the centre of gravity of the molecule, indicated the existence of rotation-oscillations as found by Schaffer.

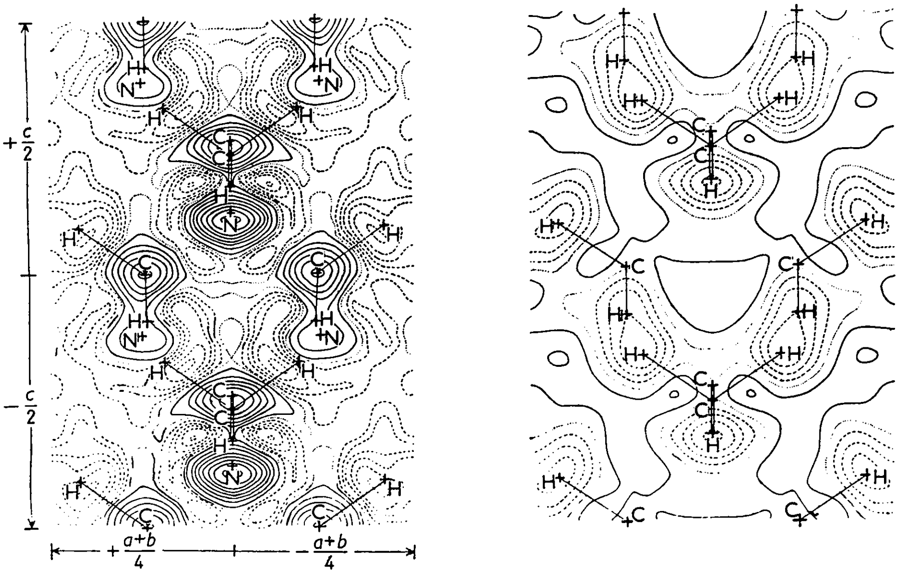
To take account of these oscillations Schaffer introduced a two-dimensional Gaussian probability distribution of the atoms around their equilibrium position. Applied to our three-dimensional data this would lead to a rather complicated correction factor. Besides, with the hydrogen atoms giving a considerable contribution to the scattering, it was desirable to introduce different parameters for the different kinds of atoms, depending on their distance from the centre of rotation. For simplicity, therefore, we assume the molecule to rotate as a rigid constellation, and the atoms to be evenly distributed over circular discs perpendicular to the radius vector from the centre. The radius of each disc will then be proportional to the length of this vector. For an atom distributed over such a disc the average scattering power is (King & Lipscomb, 1950):

$$\bar{g} = b.\exp\,(2\pi i\mathbf{h}.\mathbf{k})(2/a)J_1(a)\,.$$

Here b is the coherent scattering amplitude, $\mathbf{h}$ the reciprocal-lattice vector of the reflexion considered and $\mathbf{k}$ the above-mentioned radius vector to the centre of the disc. $J_1(a)$ is the first-order Bessel function of $a = 2\pi|\mathbf{h}|.r\sin\psi$, where r is the radius of the disc and ψ the angle between $\mathbf{h}$ and $\mathbf{k}$.

By applying this correction factor, the agreement between observed and calculated structure factors was considerably improved. The best fit was obtained for $r = 0{\cdot}35$ Å for the N atoms, corresponding to 0·39 Å for the C atoms and 0·58 Å for the H atoms. The parameter for the isotropic temperature factor could then be reduced to $B = 1{\cdot}8$ Å^2 for all atoms.

It was now possible to obtain better Fourier diagrams using new phase angles and re-calculated values for the contribution of the C and N atoms. The diagrams for the $[1\bar{1}0]$ projection are shown in Fig. 1. Parameters derived from these diagrams were not considered very accurate because of the large temperature motion and the few reflexions available. There is also a strong overlap of the peaks, which in the difference synthesis makes the position of some of the hydrogen peaks strongly dependent on the temperature factor assigned to the N atoms. A last refinement was therefore done by trial, and resulted in the parameters given in Table 1. The final calculated structure factors are tabulated as F_2 in Table 2, where the deviations Δ from the observed F's are also given. F_1 and F_2 are absolute values in units of 10^{-12} cm. and F_o are normalized values. It is seen that by introducing the anisotropic temperature factor all the large deviations have been taken care of, and the reliability factor R for the 27 well-determined reflexions in the [001] and $[1\bar{1}0]$ zones is reduced from 15·1% to 3·2%. Here weak reflexions at high angles and the (110) reflexion, which was affected by extinction, have been omitted. Reflexions marked with



(a) (b)

Fig. 1. The final $[1\bar{1}0]$ Fourier projections; (a) total synthesis, (b) difference synthesis for the H atoms. Contours are drawn at intervals of 100 units except in the positive peaks of (a), where the intervals are 200. The crosses show the final atomic positions. The bonds of the methylene groups are indicated.

Table 2. *Structure factors*

hkl	F_o	F_1	Δ	F_2	Δ
110	3·28	3·50	—	3·50	—
200	1·09	1·08	0·01	1·07	0·02
211	2·45	2·39	0·06	2·45	0
220	1·05	0·75	0·30	1·03	0·02
310	1·73	1·38	0·35	1·70	0·03
222	3·07	2·94	0·13	3·15	0·08
321*	2·51	2·36	—	2·51	—
400	1·52	1·55	0·03	1·48	0·04
411	1·0	1·02	0·02	1·05	0·05
330	1·66	1·81	0·15	1·71	0·05
420	1·04	0·75	0·29	0·92	0·12
332	1·08	1·33	0·25	1·11	0·03
422	0·67	1·0	0·33	0·65	0·02
510	0·66	0·49	0·17	0·64	0·02
431*	2·46	2·08	—	2·38	—
521*	0·94	1·19	—	1·25	—
440	3·80	3·46	0·34	3·96	0·16
530	2·04	2·03	0·01	2·04	0
433	0·50	0·81	0·31	0·71	0·21
600	0·28	0·88	0·60	0·40	0·12
442	0·88	0·73	0·15	0·85	0·03
611	1·80	1·40	0·40	1·83	0·03
532*	1·06	1·25	—	1·40	—
620	0·99	0·67	0·32	0·92	0·07
541*	1·18	1·62	—	1·57	—
622	2·49	2·34	0·15	2·53	0·04
444	0·46	0·36	0·10	0·51	0·05
550	0·99	1·20	0·21	1·01	0·02
710	0·91	0·91	0	0·78	0·13
633	1·19	1·06	0·13	1·20	0·01
800	2·52	2·09	0·43	2·54	0·02
811	1·34	0·90	0·44	1·40	0·06
822	0·36	0·37	0·01	0·35	0·01

an asterisk have been determined only on the new goniometer, and show large deviations at high angles because of bad alignment.

Discussion of the structure

For the C and N atoms our parameters confirm the values given by Brill *et al.*, with the modification for the N atoms found by least-squares treatment of their data by Schaffer. The parameters for the H atoms lead to a C–H distance of 1·13 Å, much shorter than the value 1·175 Å found by them; they agree more with those of Lobatchev, which lead to a C–H distance of 1·137 Å. (The value 1·17 kX. given by him must be due to an arithmetical error.) From the effect on the reliability index we assume the error in the parameters of the H atoms to be within the limits ±0·002. As the parameter for the C atoms is very well determined by X-rays (Brill *et al.* give ±0·0004), we assume the error in the calculated C–H bond length to be less than ±0·02 Å. The value deduced from the most reliable peaks of the Fourier diagrams lies within these limits.

The stability of the hexamethylene tetramine crystals can, as pointed out by Schaffer, be attributed to the formation of weak hydrogen bonds between the methylene C atoms and the nearest N atoms of adjacent molecules. Each C atom will then be bonded to two N atoms and each N atom to three C atoms. Our parameters lead, however, to the angle 110° 6′ between the C–H bonds of a methylene group, i.e. only slightly larger than the tetrahedral angle, while the angle between the C–N directions is 150° 3′. Thus the hydrogen bonds are, as one might expect, not strong enough to deform the tetrahedral angle to any considerable extent.

Another indication of a weak bonding to the N atoms is the fact that our assumption of the molecule, including the hydrogen atoms, rotating as a rigid constellation leads to a satisfactory temperature factor. Still, the effect of these weak hydrogen bonds might be appreciable, as every molecule is linked to its neighbours by 24 bonds. Being at a larger distance from the centre of rotation, the H atoms have been ascribed a larger oscillation amplitude than the other atoms. In view of the relatively larger scattering amplitude of hydrogen for neutrons than for X-rays, this explains the greater effect of introducing the anisotropic temperature factor here.

The isotropic temperature factor corresponds to a root-mean-square amplitude of oscillation for each atom of 0·15 Å in the direction of the molecular centre of gravity. In a direction normal to this the oscillations will, in addition, have a rotational contribution, which for the C atoms corresponds to a linear root-mean-square oscillation amplitude of 0·20 Å. The values used by Schaffer are 0·18 and 0·19 Å respectively. It should be kept in mind that, whereas he used a Gaussian probability distribution, we have here assumed an even distribution over the circular discs.

The remarkably good agreement obtained, $R = 3{\cdot}2\,\%$, justifies the simplifications made in introducing the anisotropic temperature factor. Thus we have also ignored, as did Schaffer, the fact that the molecules will not rotate independently, and that there will be coherence of the atomic displacements within a molecule.

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