

Do the Ellipsoids of Thermal Vibration Mean Anything?—Analysis of Neutron Diffraction Measurements on Hexamethylenetetramine

BY B. T. M. WILLIS

A.E.R.E., Harwell, Oxfordshire OX11 0RA, England

AND J. A. K. HOWARD*

School of Chemistry, The University, Bristol, England

(Received 13 May 1974; accepted 21 December 1974)

The anisotropic thermal parameters of the atoms in crystalline hexamethylenetetramine (HMT), which were determined from the neutron-diffraction study of Duckworth, Willis & Pawley [*Acta Cryst.* (1970). A26, 263–271], are shown to be in close agreement with those calculated independently from lattice-dynamical and spectroscopic data. Although HMT is probably the only molecular crystal for which there is sufficient information for such a comparison to be made, this result may give comfort to those crystallographers who wonder whether their thermal parameters really mean anything. Tests are also made of various procedures for modifying the rigid-body model of thermal motion (as applied to the structure refinement of HMT) to take into account the internal modes of vibration.

1. Introduction

The results of a crystal-structure determination are often presented as a list of atomic coordinates for each atom in the asymmetric unit of the unit-cell, together with a corresponding list of anisotropic temperature-factor coefficients. Although a crystallographer may be confident of the essential correctness of his positional parameters, he is usually much less certain about his thermal parameters. This uncertainty has been described in the following way by Zachariasen (1969): '... Looking at the many structures which have been published in *Acta Crystallographica* during the last few years, it is evident that the positional parameters are reasonably good ... [but that] the thermal parameters are all nonsense and must all be done again in a sensible way'.

It is the purpose of this paper to show that the situation in crystallography may not be quite as gloomy as that depicted by Zachariasen. We show that the anisotropic thermal parameters of hexamethylenetetramine (HMT), as derived from neutron diffraction measurements, are in very close agreement with those calculated entirely independently from lattice-dynamical and spectroscopic data. At the present time, HMT is probably the only molecular crystal for which there is sufficient information (in the form of diffraction, lattice-dynamical and spectroscopic measurements) for such a comparison to be made.

2. Modes of vibration of an HMT crystal

The HMT molecule has $\bar{4}3m$ point symmetry [see Fig. 1(a)] and crystallizes in the cubic space group $I\bar{4}3m$. Each molecule in the crystal is surrounded by eight

others, which are in identical orientations and lie along the eight $\langle 111 \rangle$ directions. Thus the body-centred unit-cell, Fig. 1(b), is equivalent to that of a b.c.c. metal such as sodium, with each sodium atom replaced by a single molecule of HMT. The carbon atoms are in positions 12(e): $(u', 0, 0)$ with $u' \approx 0.24$; the nitrogen atoms in positions 8(c): (v, v, v) with $v \approx 0.12$; and the hydrogen atoms in positions 24(g): (x, x, z) with $x \approx 0.09$ and $z \approx -0.33$.

Now the thermal motion of the atoms in a crystal composed of N primitive unit cells, each containing n atoms, can be described in terms of $3nN$ independent modes of vibration. Corresponding to any of the N distinct wave vectors \mathbf{q} in the first Brillouin zone, there are $3n$ modes of (circular) frequency $\omega_j(\mathbf{q})$, $j = 1, 2, \dots, 3n$. For large N , $\omega_j(\mathbf{q})$ is practically a continuous function of \mathbf{q} , and a plot of $\omega_j(\mathbf{q})$ versus \mathbf{q} gives the so-called phonon dispersion relations for the direction in reciprocal space defined by \mathbf{q} . In general, there are $3n$ branches of the dispersion relations (with the index j labelling an individual branch), but along symmetry directions degeneracies can occur and so the number of branches may be less than $3n$. For HMT, the primitive unit-cell contains one molecule of composition $C_6H_{12}N_4$, so that n is equal to 22 and there are $3 \times 22 = 66$ branches of the dispersion relations for general directions of \mathbf{q} .

The description of the nature of the thermal vibrations of HMT is simplified by recalling that the interaction forces between different molecules in the crystal are much weaker than the forces between atoms within a single molecule. This allows the normal modes of vibration to be divided into internal and external vibrations. For the internal vibrations, the atoms of the molecule move relative to one another without shifting the centre of gravity of the molecule or causing the molecule to rotate as a whole. The frequencies of these

* Née Duckworth.

internal modes are much higher than the external-mode frequencies and are practically independent of the wave vector \mathbf{q} . For the external vibrations, each molecule undergoes a rotational and translational motion which is correlated with the motions of the other molecules and gives rise to a \mathbf{q} dependence of the frequencies. The number of external branches is $6n'$, where n' is the number of molecules in the primitive unit-cell: $n' = 1$ for HMT so that there are only six branches for a general direction of \mathbf{q} and even fewer (see Fig. 2) along symmetry directions. The wide separation in Fig. 2 between the frequencies of the external and internal modes implies that we are justified in treating the vibrations of the HMT crystal in terms of external modes involving rigid-body oscillations of the molecule and of internal modes which are essentially the same as for the free molecule.

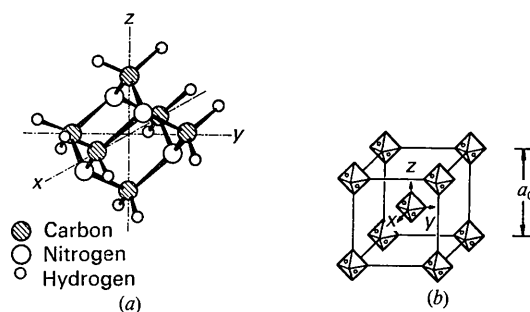


Fig. 1. (a) Molecular structure of HMT. The six carbon atoms lie along the positive and negative directions of the Cartesian axes x, y, z . (b) Cubic unit cell of HMT, with octahedral blocks representing the individual molecules shown in (a). (After Cochran & Pawley, 1964).

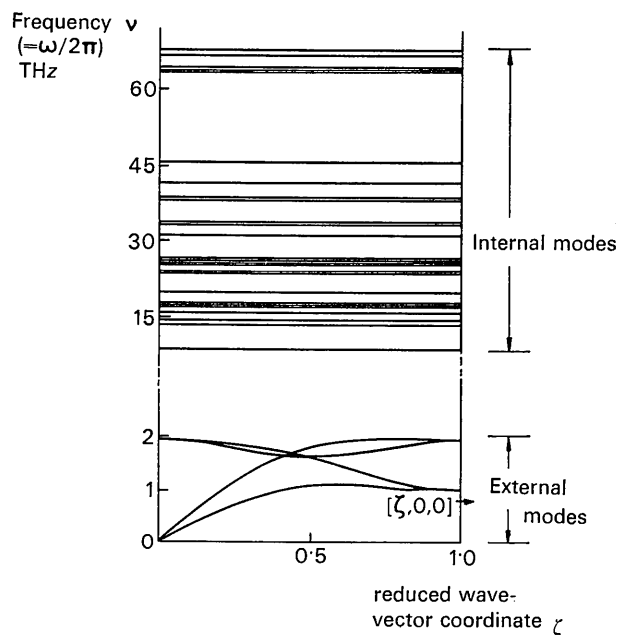


Fig. 2. HMT: dispersionless, high-frequency internal modes and dispersive, low-frequency external modes. (Note the change of scale on the frequency axis.)

Our principal task is to compute (from the known dynamical properties of HMT) the anisotropic temperature parameters β_{rs}^{κ} appearing in the temperature-factor expression

$$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \quad (1)$$

for each atom κ in the unit-cell, and to compare these with the observed values derived from diffraction measurements. The parameters β_{rs}^{κ} are related to the atomic displacements by the expression

$$U_{rs} = \frac{a_0^2}{2\pi^2} \beta_{rs}^{\kappa}, \quad (2)$$

where a_0 is the cubic lattice parameter and U_{rs} is the mean value of the atomic displacement along the Cartesian r axis multiplied by the displacement along the Cartesian s axis. U_{rs} may be subdivided into separate contributions arising from the external and internal modes of motion

$$U_{rs} = U_{rs}^{\text{ext}} + U_{rs}^{\text{int}}. \quad (3)$$

We shall discuss the calculation of the anisotropic mean-square external displacements U_{rs}^{ext} in § 3, and the calculation of the anisotropic mean-square internal displacements U_{rs}^{int} in § 4.

3. External atomic mean-square displacements

The mean-square displacements due to the external modes of motion may be described in terms of three second-rank tensors T , L and S (Schomaker & Trueblood, 1968). Because the centre of the HMT molecule occupies a site in the crystal of $\bar{4}3m$ symmetry, the rigid-body translational tensor T reduces to a scalar quantity $\langle u^2 \rangle$, the librational tensor L reduces to a scalar quantity $\langle \theta^2 \rangle$, and the translational-librational tensor S vanishes. $\langle u^2 \rangle$ is the mean-square translational displacement of the rigid molecule in any direction, and $\langle \theta^2 \rangle$ is its mean-square librational displacement about any axis passing through the molecular centre. Explicit expressions for the individual atomic displacements U_{rs}^{ext} in terms of $\langle u^2 \rangle$ and $\langle \theta^2 \rangle$ are derived by Duckworth, Willis & Pawley (1970) (DWP) and are reproduced in Table 1. We shall calculate the quantities $\langle u^2 \rangle$ and $\langle \theta^2 \rangle$ and then substitute these into the expressions in Table 1 to obtain the external displacements at a given temperature.

Now the mean-square translational displacement, arising from all the $6N$ external modes of vibration, is given by the expression (Cochran & Pawley, 1964)

$$\langle u^2 \rangle = \frac{2 \int E(\omega) \omega^{-2} g_T(\omega) d\omega}{m \int g(\omega) d\omega}. \quad (4)$$

Here $E(\omega)$ is the average energy of a mode of frequency ω , m is the mass of the molecule, and $g(\omega)d\omega$ is the

Table 1. *Tensor components* U_{rs}^{ext} *for HMT expressed in terms of the scalar quantities* $\langle u^2 \rangle$ *and* $\langle \theta^2 \rangle$ (1) Carbon atom at $(u', 0, 0)$

$$\begin{aligned} U_{11}^{\text{ext}} &= \langle u^2 \rangle + u'^2 a_0^2 \langle \theta^2 \rangle^2 \\ U_{22}^{\text{ext}} &= \langle u^2 \rangle + u'^2 a_0^2 \langle \theta^2 \rangle^2 - \frac{1}{2} u'^2 a_0^2 \langle \theta^2 \rangle^2 \\ &= U_{33}^{\text{ext}} \\ U_{12}^{\text{ext}} &= U_{13}^{\text{ext}} = U_{23}^{\text{ext}} = 0. \end{aligned}$$

(2) Nitrogen atom at (v, v, v)

$$\begin{aligned} U_{11}^{\text{ext}} &= \langle u^2 \rangle + 2v^2 a_0^2 \langle \theta^2 \rangle - \frac{1}{6} v^2 a_0^2 \langle \theta^2 \rangle^2 \\ &= U_{22}^{\text{ext}} = U_{33}^{\text{ext}} \\ U_{12}^{\text{ext}} &= -v^2 a_0^2 \langle \theta^2 \rangle + \frac{2}{3} v^2 a_0^2 \langle \theta^2 \rangle^2 \\ &= U_{13}^{\text{ext}} = U_{23}^{\text{ext}}. \end{aligned}$$

(3) Hydrogen atom at (x, x, z)

$$\begin{aligned} U_{11}^{\text{ext}} &= \langle u^2 \rangle + (x^2 + z^2) a_0^2 \langle \theta^2 \rangle - \frac{1}{2} \langle \theta^2 \rangle^2 + x^2 \langle \theta^2 \rangle^2 \\ &= U_{22}^{\text{ext}} \\ U_{33}^{\text{ext}} &= \langle u^2 \rangle + 2x^2 a_0^2 \langle \theta^2 \rangle - \frac{1}{2} \langle \theta^2 \rangle^2 + z^2 \langle \theta^2 \rangle^2 \\ U_{12}^{\text{ext}} &= -x^2 a_0^2 \langle \theta^2 \rangle - \frac{2}{3} x^2 \langle \theta^2 \rangle^2 \\ U_{13}^{\text{ext}} &= -xza_0^2 \langle \theta^2 \rangle - \frac{2}{3} xz \langle \theta^2 \rangle^2 \\ &= U_{23}^{\text{ext}}. \end{aligned}$$

number of modes in the frequency interval $\omega, \omega + d\omega$. The corresponding expression for the mean-square librational displacement is

$$\langle \theta^2 \rangle = \frac{2 \int E(\omega) \omega^{-2} g_L(\omega) d\omega}{mk^2 \int g(\omega) d\omega} \quad (5)$$

with k the radius of gyration of the molecule. The meanings of g_T and g_L in (4) and (5) are discussed in the next paragraph. The average energy $E(\omega)$ is related to the frequency and the temperature T by

$$E(\omega) = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{[\exp(\hbar \omega / k_B T) - 1]}. \quad (6)$$

In the classical (high-temperature) limit, $E(\omega)$ is simply $k_B T$. \hbar is Planck's constant $\div 2\pi$.

The function $g_T(\omega)$ in equation (4) represents the contribution of translational motion to the frequency distribution function $g(\omega)$, and $g_L(\omega)$ in equation (5) represents the librational contribution:

$$g(\omega) = g_T(\omega) + g_L(\omega). \quad (7)$$

Although modes propagating along symmetry directions may be predominantly translational or librational in character, *each* external mode will involve, in general, *both* translations and librations of the molecule and so will contribute to both g_T and g_L . To determine $g_T(\omega)$ and $g_L(\omega)$ we must know the eigenvector $\mathbf{e}(j\mathbf{q})$ of each mode ($j\mathbf{q}$) as well as its frequency ω . The eigenvector determines the pattern of the molecular displacements for a given mode: it has six components e_i ($i=1, 2, \dots, 6$) of which the first three refer to displacements arising from translations of the rigid molecule along the principal cubic axes, and the last three to displacements from librations about these axes. We can say that a fraction

$$\sum_{i=1}^3 e_i^* e_i \div \sum_{i=1}^6 e_i^* e_i$$

of a mode contributes to g_T , and a fraction

$$\sum_{i=4}^6 e_i^* e_i \div \sum_{i=1}^6 e_i^* e_i$$

to g_L . If the eigenvectors are normalized, so that

$$\sum_{i=1}^6 e_i^* e_i = 1,$$

then

$$g_T(\omega) = \sum_{j\mathbf{q}} \sum_{i=1}^3 e_i^*(j\mathbf{q}) e_i(j\mathbf{q}) \quad (8a)$$

and

$$g_L(\omega) = \sum_{j\mathbf{q}} \sum_{i=4}^6 e_i^*(j\mathbf{q}) e_i(j\mathbf{q}). \quad (8b)$$

The first summation on the right-hand side of (8a) and (8b) refers to those modes ($j\mathbf{q}$) lying in the frequency interval $\omega, \omega + d\omega$; the index j labels the six branches of the dispersion relations.

The frequencies and corresponding eigenvectors of the six external modes with a given wave vector \mathbf{q} may be derived by applying the Born-von Kármán theory in the form appropriate to molecular crystals (see, for example, Venkataraman & Sahni, 1970). The main steps in this procedure consist of setting up an appropriate force field to describe the interactions between different molecules and then assembling the 6×6 'dynamical matrix' $D(\mathbf{q})$, which is diagonalized to yield the six eigenvalues $\omega_j^2(\mathbf{q})$ and six eigenvectors $\mathbf{e}(j\mathbf{q})$. The calculation is carried out over a mesh of \mathbf{q} points in the Brillouin zone and interpolation is used to cover points within the mesh.

Dr G. Dolling (private communication, 1973) has kindly carried through this procedure for us on HMT, with the aid of a computer program based on the five-parameter force-constant model of Dolling & Powell (1970). This model was originally derived from the analysis of experimental dispersion relations at 298 K for deuterated hexamine, Fig. 3, but the same model may be applied to HMT as the intermolecular forces are unlikely to change on substituting hydrogen for deuterium. Dolling calculated $g_T(\omega)$ and $g_L(\omega)$ from equations (8a, b) at intervals of 0.001 THz in frequency $\nu (= \omega/2\pi)$ for the frequency range $0 < \nu < 2.5$ THz.

We have used Dolling's tabulation of g_T , g_L and $g (= g_T + g_L)$ to derive $\langle u^2 \rangle$ and $\langle \theta^2 \rangle$ by means of numerical integration of the quantities on the right-hand side of equations (4) and (5). Our results are

$$\left. \begin{aligned} \langle u^2 \rangle &= 0.0244 \text{ \AA}^2 \\ \langle \theta^2 \rangle &= 44.4 \text{ degrees}^2 \end{aligned} \right\} \text{ at } 298 \text{ K,}$$

with a calculated precision for both estimates of less than one unit in the last decimal place.

Inserting these estimates into the expressions for U_{rs}^{ext} in Table 1, together with the DWP positional parameters ($u' = 0.239$ for carbon; $v = 0.124$ for nitrogen; $x = 0.092$, $z = -0.328$ for hydrogen) and the room-temperature lattice constant ($a_0 = 7.019 \text{ \AA}$), yields the re-

sults listed in Tables 2 to 4 in the columns 'external-mode contribution'. Note that U_{23}^{ext} for carbon is zero; this is a consequence of the rigid-body assumption and is not a requirement imposed by the site symmetry of the atom. On the other hand, U_{12}^{ext} and U_{13}^{ext} for the same atom are zero by symmetry and so are not listed separately in Table 2.

Table 2. Anisotropic mean-square displacement of carbon atom at $(u', 0, 0)$

	Calculated (\AA^2)			Observed (\AA^2)
	External-mode contribution	Internal-mode contribution	Total	
U_{11}	0.0249	0.0016	0.0265	0.0262 (13)
U_{22}	0.0617	0.0017	0.0634	0.0652 (15)
U_{23}	zero	-0.0001	-0.0001	0.0005 (24)

Site symmetry is mm , which gives the symmetry restrictions:

$$U_{22} = U_{33}; \quad U_{12} = U_{13} = 0.$$

Coordinate system as in Fig. 1.

Table 3. Anisotropic mean-square displacement of nitrogen atom at (v, v, v)

	Calculated (\AA^2)			Observed (\AA^2)
	External-mode contribution	Internal-mode contribution	Total	
U_{11}	0.0446	0.0013	0.0459	0.0485 (7)
U_{12}	-0.0099	-0.0001	-0.0100	-0.0101 (8)

Site symmetry is $3m$, which gives the symmetry restrictions:

$$U_{11} = U_{22} = U_{33}; \quad U_{12} = U_{13} = U_{23}.$$

Table 4. Anisotropic mean-square displacement of hydrogen atom at (x, x, z)

	Calculated (\AA^2)			Observed (\AA^2)
	External-mode contribution	Internal-mode contribution	Total	
U_{11}	0.1002	0.0135	0.1137	0.1106 (33)
U_{33}	0.0355	0.0168	0.0523	0.0513 (26)
U_{12}	-0.0055	0.0003	-0.0052	-0.0055 (38)
U_{13}	0.0194	0.0058	0.0252	0.0235 (20)

Site symmetry is m , which gives the symmetry restrictions:

$$U_{11} = U_{22}; \quad U_{13} = U_{23}.$$

4. Internal atomic mean-square displacements

The contribution of the internal modes to the mean-square atomic displacements is calculated by carrying out a normal-coordinate analysis for the molecular vibrations of HMT. The FG matrix method of Wilson may be used (see Wilson, Decius & Cross, 1955), in which the elements of the F matrix are the intramolecular force constants and the elements of the G matrix are related to the known atomic masses and atomic coordinates. A suitable force field is obtained by fitting the observed optical frequencies to those calculated from the equation

$$FG - E\lambda = 0, \quad (9)$$

where E is the unit matrix and λ is an eigenvalue related to the frequency ν by

$$\lambda = 4\pi^2 c^2 \nu^2.$$

Equation (9) has 60 non-zero eigenvalues, corresponding to the 60 internal modes of vibration of HMT. [Maximum factorization of equation (9) is achieved by applying group-theoretical methods, which exploit the symmetry properties of the molecule.] The eigenvector associated with a given eigenvalue determines the atomic displacements for that particular mode of vibration, and by adding the appropriate components of the eigenvectors for all 60 modes the quantities U_{rs}^{int} in equation (3) may be derived.

This calculation was first carried out for HMT by Becka & Cruickshank (1963). These authors treated the CH_2 groups as rigid units and used the optical frequencies observed by Couture-Mathieu, Mathieu, Cremer & Poulet (1951) to obtain three force constants: one each for C-N stretching, C-N-C bending and N-C-N bending. The Becka & Cruickshank treatment was limited to a determination of the tensor components U_{rs}^{int} of the carbon and nitrogen atoms only.

More recently, Elvebredd & Cyvin (1973) have calculated the tensor components for all three atoms, by removing the restriction that the CH_2 groups are rigid and by employing both Raman and infrared frequencies

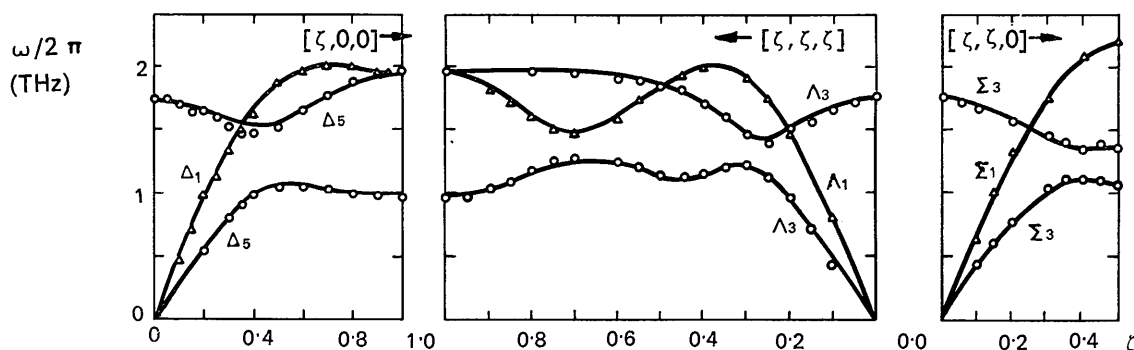


Fig. 3. Dispersion relations for deuterated HMT at 298 K, as measured along the symmetry directions $[100]$, $[111]$ and $[110]$. The solid curves are a best least-squares fit based on a five-parameter force-constant model. The branches labelled Δ_1 , Λ_1 , Σ_1 are purely translational, while Δ_5 , Λ_3 and Σ_3 are mixed branches with modes having both translational and librational character. (After Dolling & Powell, 1970).

(Cheutin & Mathieu, 1956) to obtain the additional force constants involving hydrogen. However, Thomas (1975) has shown that there are several discrepancies between the normal-coordinate analysis of Elvebredd & Cyvin and the observed incoherent inelastic neutron spectrum of HMT. These discrepancies may be removed, without impairing the match between calculated and observed optical frequencies, by re-assigning one of the triply-degenerate T_1 modes of vibration. Thomas has repeated the Elvebredd & Cyvin analysis using this new assignment, and has derived new tensor components U_{rs}^{int} which, in fact, turn out to be very similar to those calculated by Elvebredd & Cyvin. In Tables 2, 3 and 4 we quote only, under 'internal mode contribution', the values calculated by Thomas.

5. Comparison with experiment

The 'observed' displacements in the last column of Table 2 were derived by Duckworth, Willis & Pawley (1970) from the analysis of their room-temperature neutron-diffraction measurements. Estimates were made of 49 structure amplitudes, in which each estimate represented an average over about 12 symmetry-related reflexions. The nine symmetry-independent U_{rs} 's, together with their e.s.d.'s, were then obtained by means of an unconstrained refinement based on equations (1) and (2). (Third and high-order cumulants were set to zero, although DWP showed that the inclusion of third-order cumulants does lead to a small but significant improvement in the refinement.)

If the last two columns of Tables 2 to 4 are compared, the 'calculated' and 'observed' tensor components are in agreement, within a few standard deviations, for all three types of atom. This is particularly encouraging in view of the high precision in the measurement of the original Bragg intensities, which implies a corresponding precision in the measured estimates of the U_{rs} 's. Thus the magnitude and orientation of the ellipsoids of thermal vibration, as deduced from the refinement of diffraction data on HMT, are close to those calculated entirely independently from lattice-dynamical and spectroscopic measurements.

6. Constrained refinements

In Tables 2 to 4 the observed displacements refer to the unconstrained refinement of the diffraction data of Duckworth, Willis & Pawley. In this section we shall describe some results obtained by carrying out refinements in which the thermal parameters of carbon, nitrogen and hydrogen are constrained in various ways. These results are summarized in Table 5.

In model 1 the thermal parameters describing the external motion are fixed at the lattice-dynamical values calculated in § 3, and the parameters describing the internal motion are fixed at the values calculated in § 4 from Thomas's normal-coordinate analysis. There are no variable thermal parameters. The quoted R val-

ues correspond to a second-cumulants refinement employing five variable parameters: four for the atomic positions and one for the overall scale factor. (For the remaining models the same five variable parameters were employed in each refinement.)

Model 2 is the same as model 1 with respect to the external motion but ignores the contribution from internal motion.

In model 3 the parameters for the external motion are fixed once more at the values calculated in § 3, but five variable thermal parameters are allocated for the internal motion. Three of these variable parameters represent the internal mean-square anisotropic displacements of the hydrogen atom. A fourth parameter represents the mean-square isotropic displacement of the carbon atom due to internal motion, and the fifth describes the internal mean-square isotropic displacement of the nitrogen atom.

Model 4 is the traditional TLS rigid-body model, which employs (two) variable parameters for the external motion and ignores the internal motion.

In model 5 the external motion is treated as in model 4, and the internal motion is allowed for using the formula (Scheringer, 1972):

$$U_{\alpha} = \frac{1}{3}(U_{11}^{int} + U_{22}^{int} + U_{33}^{int})_{\alpha} = \frac{(n-2)a}{m_{\alpha}} \quad (10)$$

Here U_{α} is the isotropic mean-square displacement of atom α and m_{α} is its mass number; n is the number of atoms in the molecule (=22 for HMT); and a is a fixed constant = 0.0015 mole \AA^2 .

Model 6 is the same as model 5 except that the quantity a in equation (10) is treated as a variable parameter.

Comparing the R values, listed in the last two columns of Table 5, of the constrained models (1-6) and of the unconstrained model (7), we can draw the following conclusions. All these conclusions have been confirmed by applying the Hamilton (1965) tests to the R -value ratios.

(1) The unconstrained model possesses too many thermal parameters (it has the same R value as model 3 but has more thermal parameters), whereas the strictly rigid-body models (2 and 4) possess too few. The rigid-body models must be modified to allow for the effect of internal motion. The most satisfactory way of doing this (model 3) is to allocate five parameters for the internal motion, one each for the isotropic motion of carbon and nitrogen and three for the anisotropic motion of hydrogen.

(2) The rigid-body model 4, with variable rigid-body parameters $\langle u^2 \rangle$ and $\langle \theta^2 \rangle$, yields a better refinement than the rigid-body model 2, with rigid-body parameters fixed at the lattice-dynamical values. This is because model 4 allows *implicitly* for some degree of internal motion by over-estimating both $\langle u^2 \rangle$ and $\langle \theta^2 \rangle$.

(3) The contribution of the internal modes to the total mean-square atomic displacements is least for carbon and nitrogen and greatest for hydrogen. This

implies that the neglect of internal motion will give rise to special difficulties in refining neutron-diffraction measurements.

(4) Comparison of models 1 and 3 indicates that the internal displacements deduced from diffraction meas-

urements (model 3) differ slightly from those given by a normal-coordinate analysis of spectroscopic measurements (model 1). On the other hand, the thermal and positional parameters for model 3 are in *exact* agreement with those for the unconstrained model (7).

Table 5. *Constrained refinements of diffraction data of DWP*

Model	External-motion parameters		Internal-motion parameters	Number of independent thermal parameters	Number of variable thermal parameters	<i>R</i> (%)	<i>R_w</i> (%)
	$\langle u^2 \rangle$ (Å ²)	$\langle \theta^2 \rangle$ (deg ²)	U_{rs}^{int} (Å ²)				
1 (Fixed external and internal parameters)	0.0244	44.4	$U_{11}(=U_{22}=U_{33})=0.002$ for carbon; $U_{11}(=U_{22}=U_{33})=0.001$ for nitrogen; $U_{11}(=U_{22})=0.014$, $U_{33}=0.017$, $U_{13}(=U_{23})=0.006$ for hydrogen.	7	0	3.06	3.45
2 (Fixed external parameters: no internal motion)	0.0244	44.4	Zero	2	0	4.96	5.14
3 (Fixed external parameters: variable internal parameters)	0.0244	44.4	$U_{11}(=U_{22}=U_{33})=0.002$ (1) for carbon; $U_{11}(=U_{22}=U_{33})=0.004$ (1) for nitrogen; $U_{11}(=U_{22})=0.009$ (2) $U_{33}=0.015$ (2), $U_{13}=0.004$ (2) for hydrogen.	7	5	2.23	2.49
4 (Variable external parameters: no internal motion)	0.0267 (10)	46.8 (1.9)	Zero	2	2	3.35	3.79
5 (Variable external parameters: Scheringer treatment of internal motion)	0.0262 (14)	41.6 (2.6)	$U_{11}(=U_{22}=U_{33})=0.0025$ for carbon $U_{11}(=U_{22}=U_{33})=0.0021$ for nitrogen; $U_{11}(=U_{22}=U_{33})=0.0300$ for hydrogen	3	2	4.32	5.48
6 (Variable external parameters: modified Scheringer treatment of internal motion)	0.0264 (9)	45.1 (1.5)	$U_{11}(=U_{22}=U_{33})=0.0008$ for carbon $U_{11}(=U_{22}=U_{33})=0.0007$ for nitrogen; $U_{11}(=U_{22}=U_{33})=0.0095$ (25) for hydrogen.	3	3	2.47	2.72
7 (No thermal constraints)	—	—	—	9	9	2.23	2.48

Notes: (i) Those tensor components U_{rs}^{int} which are not listed in the fourth column are all zero.

(ii) R_w in the last column is defined by:

$$R_w = \left(\frac{\sum_i w_i (F_{i\text{obs}} - F_{i\text{calc}})^2}{\sum_i w_i (F_{i\text{obs}})^2} \right)^{1/2}.$$

The weights w_i are given by the quantities $1/\sigma^2$ from the last column of Table 1 in the paper by DWP, and $F_{i\text{obs}}$ is given by F_{obs} in the same table.

(iii) In models 1, 2 and 3 the external-mode parameters are fixed at the values calculated from lattice dynamics; in models 4 to 7 they are treated as variable parameters.

(5) The Scheringer model (5) for the internal motion gives an even poorer refinement than one in which there is no explicit internal mode correction at all (model 4). In model 6 the quantity a in Scheringer's formula (10) is refined from an initial value of 0.0015 mole \AA^2 to 0.0005 mole \AA^2 , and the corresponding refinement now represents a considerable improvement on model 4.

7. Conclusions

We have shown that the anisotropic components of the temperature factors of the atoms in crystalline hexamethylenetetramine, as determined from an unconstrained refinement of the neutron-diffraction measurements of Duckworth, Willis & Pawley (1970), are in close agreement with those calculated independently from lattice-dynamical and spectroscopic data.

Constrained refinements of the DWP structure factors illustrate the need to extend the TLS rigid-body model to take into account the effect of internal molecular motion. The TLS model implicitly allows for some degree of internal motion, but this allowance is insufficient, especially for the hydrogen atoms. However, internal motion parameters derived from formula (10), proposed by Scheringer (1972), lead to a gross overestimate of the internal motion. A modified Scheringer approach, employing a single variable parameter for the internal motion, proves to be somewhat more satisfactory.

We are deeply indebted to Professor D. W. J. Cruickshank who first suggested that the rigid-body

analysis for HMT should be extended to include the influence of internal motion, to Dr G. Dolling who supplied the eigenvector and eigenfrequency data needed for calculating the external-mode displacements, and to Dr M. W. Thomas who helped us substantially in the calculations of § 3.

References

- BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc. A* **273**, 45–454.
- CHEUTIN, A. & MATHIEU, J. P. (1956). *J. Chim. Phys.* **53**, 106–107.
- COCHRAN, W. & PAWLEY, G. S. (1964). *Proc. Roy. Soc. A* **280**, 1–22.
- COUTURE-MATHIEU, L., MATHIEU, J. P., CREMER, J. & POULET, H. (1951). *J. Chim. Phys.* **48**, 1–12.
- DOLLING, G. & POWELL, B. M. (1970). *Proc. Roy. Soc. A* **319**, 209–235.
- DUCKWORTH, J. A. K., WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 263–271.
- ELVEBREDD, I. & CYVIN, S. J. (1973). *Molecular Structures and Vibrations*, edited by S. J. CYVIN, Chap. 17. Amsterdam: Elsevier.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- SCHERINGER, C. (1972). *Acta Cryst.* **A28**, 516–522.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- THOMAS, M. W. (1975). To be published.
- VENKATARAMAN, G. & SAHNI, V. C. (1970). *Rev. Mod. Phys.* **42**, 409–470.
- WILSON, E. B., DECIUS, J. C. & CROSS, P. C. (1955). *Molecular Vibration. The Theory of Infrared and Raman Vibrational Spectra*. New York: McGraw-Hill.
- ZACHARIASEN, W. H. (1969). *Acta Cryst.* **A25**, 276.