

Hexamethylenetetramine at 298 K: New Refinements

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Abstract

New refinements of the crystal structure of hexamethylenetetramine (HMT, $C_6H_{12}N_4$) have been carried out using previously reported neutron and X-ray diffraction data collected at 298 K. A new feature in the structure model is the inclusion of third-order Gram-Charlier coefficients for the description of the anharmonic C–H bond stretching, which is found to be significant. The charge-density distribution is analyzed in terms of the pseudoatom model of Stewart [*Acta Cryst.* (1976). A32, 565–574]. Our experimental determination of the molecular octapole moment gives $\langle xyz \rangle = +1.0(3) |e| \text{ \AA}^3$. The refinement involving HMT provides a worst-case example of a general deficiency in the application of the multipole model to noncentrosymmetric structures. Strong least-squares correlations occur involving the electron population parameters of all atoms for certain of the multipole terms, namely those odd-order terms that are invariant under the symmetry operations of the space group.

Introduction

The crystal structure of hexamethylenetetramine (HMT, $C_6H_{12}N_4$), first determined by Dickenson & Raymond (1923), has attracted much interest because it is a simple molecular structure with unusually high symmetry. In the crystal structure, the full molecular symmetry ($43m$) of this cage-like molecule (Fig. 1) is utilized in the cubic space group $I43m$. Thus, the repeating unit in the structure consists of only the three-atom fragment $>CH-N<$ and all atoms in the crystal lie in special positions involving symmetry constraints. This structure would appear to offer advantages for carrying out diffraction studies with high accuracy, but there is a drawback. Although there is an abundance of other symmetry, the crystal structure is noncentrosymmetric. As a result, the overall symmetry of the HMT structure imposes interesting limitations on the detailed analysis of the Bragg

diffraction data. These affect the determination of the anharmonic nuclear thermal displacements and also the electronic charge-density distribution.

Among previous studies of HMT, that of Becka & Cruickshank (1963) is outstanding for its time because it involved not only the collection of X-ray data for a molecular crystal over a wide range of temperatures (298, 100 and 34 K) but also the use of two different X-ray wavelengths (Cu $K\alpha$ and Mo $K\alpha$). From Weissenberg photographic data, accurate values were obtained for bond lengths and angles and for the carbon and nitrogen anisotropic mean-square (m.s.) displacement parameters.

Neutron diffraction data were collected for HMT at 298 K by Duckworth, Willis & Pawley (1970; subsequently DWP). Their data were corrected for absorption, extinction and thermal diffuse scattering. Nuclear positional and thermal vibrational parameters were then determined assuming the cumulant expansion formalism of Johnson (1970). DWP reported that their least-squares refinements revealed a complete parameter correlation among the third cumulant terms κ^{123} for the C, N and H nuclei. Later, it was shown that this correlation is an example of a general problem which arises when the cumulant formalism is applied in the case of a noncentrosymmetric crystal structure (Hazell & Willis, 1978). In order to resolve the phase-angle ambiguity arising from the effects of crystal symmetry, DWP arbitrarily

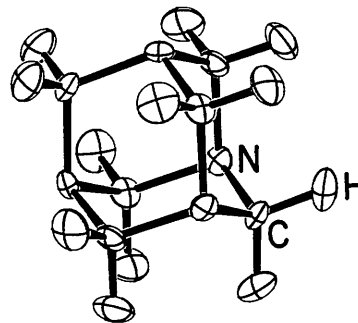


Fig. 1. Molecular structure for HMT (298 K) with harmonic vibrations of the atomic nuclei represented as thermal ellipsoids at the 15% probability level (Johnson, 1976).

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fixed κ^{123} for carbon at zero. In concluding their study, DWP calculated a residual ($X-N$) difference Fourier synthesis using X-ray data from Becka & Cruickshank (1963) and found charge-density features that they attributed to the lone-pair electrons for nitrogen.

Stevens & Hope (1975; subsequently SH) collected high-resolution diffractometer X-ray data (Mo $K\alpha$, $\sin\theta/\lambda < 1.10 \text{ \AA}^{-1}$), which were corrected for thermal diffuse scattering (Stevens, 1974) and extinction. They carried out a series of refinements including a model with third cumulant terms as used by DWP and obtained very good agreement with the results from neutron diffraction. SH used their X-ray data to obtain ($X-N$) and ($X-X$) maps that were essentially indistinguishable. These maps indicated the nitrogen lone-pair density and also electron density in the C-N and C-H bonding regions.

We have undertaken to collect new neutron and X-ray data over a range of temperatures (20 to 200 K) in order to obtain further details concerning the nuclear vibrations and the charge-density distribution in HMT. As a preliminary and a benchmark, we have carried out new refinements with the highly accurate data for 298 K already obtained by DWP and SH. These are different from previous refinements because they make use of the Gram-Charlier expansion (Johnson & Levy, 1974; Kuhs, 1983), for the treatment of anharmonic nuclear vibrations, and the pseudoatom model of Stewart (1976), for the treatment of the charge-density distribution.

The refinement with neutron data

Our refinement is based on the neutron structure amplitudes and their e.s.d.'s reported by DWP and taken from the two right-hand columns of their Table 1. The list consists of 49 reflections with $\sin\theta/\lambda < 0.76 \text{ \AA}^{-1}$ corrected for absorption, extinction and thermal diffuse scattering. Neutron coherent scattering lengths 6.648, 9.360 and -3.741 fm for carbon, nitrogen and hydrogen, respectively, were taken from Koester (1977). We assumed the unit-cell dimension $a_o = 7.028 \text{ \AA}$ for HMT at 298 K as determined from X-ray diffraction by SH. Full-matrix least-squares refinement minimized the residual $\sum w\Delta^2$ with $\Delta = |F_o| - |F_c|$ and $w = \sigma^{-2}(F_o)$ and was carried out with the computer program *NOOT* (Craven & Weber, 1987). Initially, we attempted the refinement of 26 independent variables consisting of one scale factor, four nuclear positional parameters, nine anisotropic m.s. displacement parameters and 12 third-order displacement parameters from the Gram-Charlier expansion. However, we encountered a problem very similar to that reported by DWP, namely a singular normal equation matrix owing to the correlation of the c^{123} coefficients for carbon, nitrogen and hydrogen.

As explained by DWP and by Hazell & Willis (1978), the structure factor for reflection $h_1h_2h_3$ is a sum over individual atom contributions where, in the cumulant expansion, each contribution contains phase factors $\exp(-i\kappa^{jkl}h_jh_kh_l)$. All symmetry-related atoms in HMT contribute with an identical phase term involving κ^{123} . Therefore, common phase terms $\exp(i\varphi_C)$, $\exp(i\varphi_N)$ and $\exp(i\varphi_H)$ can be factored out from the contribution of each atom type. In a structure-factor diagram, the vector representing the atomic contribution from each type of atom is subject to a phase rotation (φ_C , φ_N or φ_H) in order to give the resultant structure factor. If the same arbitrary increment is applied to all κ^{123} values, the result is a change affecting the phase of the structure factor but not its magnitude. It is only possible to determine the values of κ^{123} under a suitable constraint, such as fixing the value of κ^{123} for a selected atom. In their refinements, DWP chose to set $\kappa^{123} = 0$ for the C atoms, and this procedure was later followed by SH in their refinements using X-ray data. Thus, in both studies, the coefficients κ^{123} for the N and H atoms have values relative to the value assigned for the C atom.

In the Gram-Charlier expansion, the third-order coefficients occur in a temperature factor of the form $T = 1 - (4/3)\pi^3 i \sum_{j,k,l} c^{jkl} h_j h_k h_l$. As in the cumulant expansion, the terms involving c^{123} are unchanged by the symmetry operations for HMT and provide a common factor for each atom type. It should be noted that, in the Gram-Charlier formalism, third- and higher-order temperature factors are not the arguments of exponential functions as is the case in the cumulant expansion. Each term in c^{123} occurs in the structure-factor diagram as a vector with magnitude proportional to c^{123} and with a phase which is necessarily $\pi/2$ different from the vector representing the sum of other contributing terms for the particular atom type. Therefore, the inclusion of the c^{123} term produces a change in the magnitude of the atomic contribution as well as a change in phase. This important advantage over the cumulant formalism has been emphasized by Nelmes & Tun (1987). For HMT, if the coefficients c^{123} are sufficiently large, it should be possible to determine all three without difficulty by least-squares fitting. However, if the coefficients are small, the Gram-Charlier formalism becomes almost indistinguishable from the cumulant formalism and there will be very high least-squares correlations among the c^{123} values.

Using the Gram-Charlier expansion as far as the third order, our refinement was successfully carried out by assigning arbitrarily large starting values for the three c^{123} coefficients. They turned out to be two orders of magnitude greater than the final values. As refinement progressed and the values of c^{123} decreased, the least-squares correlations among these parameters increased. At convergence

($R = 0.012$, $R_w = 0.013$ and $S = 2.31$), the correlation factors were 0.97 between c^{123} for carbon and nitrogen, 0.82 between those for carbon and hydrogen and 0.85 between those for nitrogen and hydrogen.

We find that only the H atom has c^{jkl} values significantly different from zero. Thus, for carbon, the symmetry-independent terms are $c^{111} = -49$ (35), $c^{122} = -35$ (26) and $c^{123} = 26$ (74); for nitrogen they are $c^{111} = 22$ (43), $c^{112} = 2$ (11) and $c^{123} = 29$ (79), with all values $\times 10^{-7}$. Subsequently, the C and N atoms were assumed to be vibrating harmonically and we retained third-order terms only for hydrogen. Refinement was then completed with 20 variables, including the six independent c^{jkl} for hydrogen, and this gave our final result with $R = 0.014$, $R_w = 0.015$ and $S = 2.37$. Final nuclear parameters are given in Table 1. The total probability density functions (p.d.f.'s) for the displacements of the C and H nuclei, which are shown in Fig. 2, were obtained using a computer program by Craven & He (1987).

Although in the final result we have circumvented the difficulty concerning the large correlation of c^{123} coefficients, we have described the problem in detail because it recurs, although somewhat differently, in our refinement using the X-ray data.

The refinements with X-ray data

Our refinements are based on the X-ray structure amplitudes $|F_o|$ and reciprocal e.s.d.'s given by SH in their Table 3. The list consists of 148 independent reflections with $\sin\theta/\lambda < 1.11 \text{ \AA}^{-1}$ and with structure amplitudes corrected for absorption, extinction and thermal diffuse scattering (Stevens, 1974). Parallel full-matrix least-squares refinements were carried out using the *POP* computer program (Craven, Weber & He, 1987) in order to minimize the residual $\sum w\Delta^2$ with $\Delta = |F_o| - |F_c|$ and $w = \sigma^{-2}(F_o)$ and also using

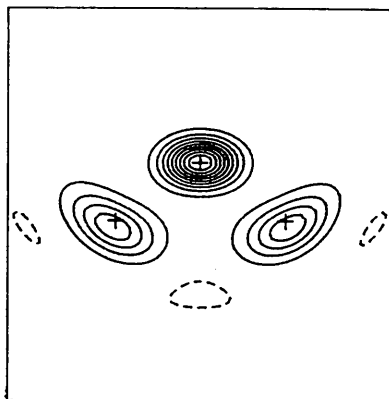


Fig. 2. Total p.d.f.'s for the thermal vibrations of the nuclei in the plane of a CH_2 group. For carbon, elliptical contours (arbitrary contour level) describe the harmonic p.d.f. For hydrogen, there is also an anharmonic component. A cross marks the center of the harmonic contribution to each p.d.f.

Table 1. Final nuclear parameters with e.s.d.'s

The thermal displacement factor is given by

$$T = \exp \left[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij} \right] \left[1 - (4/3)\pi^3 i \sum_{jkl} c^{jkl} h_j h_k h_l \right],$$

with coefficients in \AA^2 for U_{ij} and $\times 10^7$ for c^{jkl} . For hydrogen, $c^{111} = -159$ (53), $c^{222} = -c^{333} = 158$ (65), $c^{112} = -c^{113} = -92$ (30), $c^{122} = c^{133} = -149$ (39), $c^{223} = -c^{233} = -9$ (35), $c^{123} = 11$ (40). The hydrogen-atom parameters are different from those of DWP and SH because we have chosen our asymmetric unit to consist of bonded atoms N-C-H.

	Carbon	Nitrogen	Hydrogen
x	0.2379 (4)	0.1222 (6)	0.3229 (11)
y	0	0.1222	-0.0894 (9)
z	0	0.1222	0.0894
U_{11}	0.0262 (12)	0.0497 (8)	0.0501 (29)
U_{22}	0.0648 (13)	0.0497	0.1109 (23)
U_{33}	0.0648	0.0497	0.1109
U_{12}	0	-0.0101 (6)	0.0246 (15)
U_{13}	0	-0.0101	-0.0246
U_{23}	0.0004 (19)	-0.0101	0.0049 (26)

an updated version of the computer program *VALRAY* (Stewart & Spackman, 1983), for which the residual involved was $\Delta = |F_o|^2 - |F_c|^2$ with $w = \sigma^{-2}(F_o^2)$. This was done as a cross check after we encountered highly correlated charge-density parameters in the initial *POP* refinement. It was found that, although the assumed structure models differed slightly as described below, the final results obtained in the two refinements were not significantly different.

The *POP* refinement was based on the pseudoatom model of Stewart (1976), with the assumption that pseudoatom cores consist of neutral spherical Hartree-Fock atoms. Corresponding atomic scattering factors were taken from Cromer & Waber (1974) for Hartree-Fock carbon and nitrogen and from Stewart, Davidson & Simpson (1965) for spherical-bonded hydrogen. Pseudoatom deformation terms were derived with angular functions from a multipole expansion up to octapole for carbon and nitrogen and dipole for hydrogen and with each multipole having a single Slater-type radial function. Standard values for radial exponents (6.42, 7.37 and 4.69 \AA^{-1} for carbon, nitrogen and hydrogen, respectively) were taken from Hehre, Stewart & Pople (1969). All deformation terms allowed by crystal symmetry were included in the refinement. In addition to the monopole term for each atom type, these consist of: one dipole, two quadrupole and two octapole terms for carbon (site symmetry $2mm$); one dipole, one quadrupole and two octapole terms for nitrogen (site symmetry $3m$); and two dipole terms for hydrogen (site symmetry m). By rotation from a local axial system for each atom type to a common crystallographic axial system (Cromer, Larson & Stewart, 1976), the relationships given in Table 2 were determined for the various electron-population parameters.

For the *VALRAY* refinement, inner and outer localized density functions (van der Wal & Stewart,

Table 2. Relationships between electron population parameters in HMT

Values are referred to the common cubic crystallographic axial system and the coefficients are for parameters normalized according to Hansen & Coppens (1978). The population parameters are for the deformations as defined by Epstein, Ruble & Craven (1982).

	Carbon	Nitrogen	Hydrogen
d_1	d_1	d_1	d_1
d_2	0	d_1	$-d_3$
d_3	0	d_1	d_3
q_1	q_1	0	q_1
q_2	0	q_2	q_2
q_3	0	q_2	$-q_2$
q_4	q_4	q_2	q_4
q_5	$-0.605q_1$	0	$-q_1$
o_1	o_1	o_1	
o_2	0	$-o_1$	
o_3	0	0	
o_4	o_4	o_4	
o_5	$-0.795o_1$	$-1.793o_1$	
o_6	0	$-1.793o_1$	
o_7	0	$1.387o_1$	

1984) were used for the spherically symmetric components of each pseudoatom. The inner *K*-shell density was constrained to have the same number of electrons for both carbon and nitrogen. The number of electrons in the outer *L* shells was unconstrained. Dipole and higher multipole terms were as described for the POP refinement, except that the three symmetry-allowed quadrupole terms were included for the H atoms.

Variables in the initial structure model for POP refinement consisted of a scale factor for the structure amplitudes and the 14 electron-population parameters described above. All atomic positional and thermal displacement parameters (including c^{123} for hydrogen) were assigned fixed values from neutron diffraction (Table 1). This model gave convergence with $R_w = 0.024$, $R = 0.028$, $S = 5.86$. The agreement improved when four anisotropic m.s. displacement parameters for carbon and nitrogen were included as variables ($R_w = 0.022$, $R = 0.027$, $S = 5.30$) and there was considerable further improvement when the two positional parameters for carbon and nitrogen were also varied ($R_w = 0.016$, $R = 0.023$, $S = 3.99$). Final values for the 21 parameters from this refinement are given in Table 3, column (a). The final scale factor, 1.011 (8), was not significantly different from the scale of the structure amplitudes listed by SH. However, the sum of pseudoatom monopole population parameters taken over a complete molecule indicated an excess of 4.5 electrons over the number (76) required for a neutral molecule. All population parameters have been rescaled to correspond to a neutral molecule.

A feature of special interest in these refinements was the very large least-squares correlation (0.97) between the octapole population parameters o_4 for carbon and nitrogen. In the structure-factor expression (see Epstein, Ruble & Craven, 1982), these

parameters occur in the sum of octapole terms in the form $-io_4 f_{\text{oct}} s_x s_y s_z$, where f_{oct} is the octapole radial scattering factor and s_x , s_y , s_z are the components of a unit vector along the Bragg vector. It can be seen that the octapole terms in o_4 and the Gram-Charlier terms in c^{123} have the same angular symmetry properties and differ only in their radial dependence on $\sin \theta/\lambda$. As is the case for the terms in c^{123} , the o_4 terms provide contributions to the structure factor that are unchanged by the symmetry operations of the HMT structure. They give rise to a vector for each atom type that has a phase $\pi/2$ different from the remainder of the atomic contribution. The large least-squares correlation observed between the o_4 variables is analogous to the correlations between c^{123} for carbon and nitrogen in refinements with the neutron data and arises because the deformation terms do not cause a sufficiently large change in the magnitudes of the overall X-ray structure amplitudes.

The terms in o_4 form a chemically important component of the deformation density in HMT because each describes a regular tetrahedral distribution of deformation density about carbon or nitrogen with lobes that are directed very nearly along the lines joining all C, N and H nuclei in the molecule. A negative o_4 population for carbon directs positive deformation density towards the two neighboring N and two neighboring H atoms. A positive o_4 for nitrogen has a similar effect in directing positive deformation density towards its three neighboring C atoms, overlapping the contributions from the C atoms, and with a fourth lobe directed into the region where nitrogen lone-pair density is expected. A negative value of o_4 for nitrogen has the opposite effect, conferring negative rather than positive density in these regions. As can be seen from Table 3, column (a), o_4 is negative for carbon and almost zero for nitrogen, but with large e.s.d.'s that arise because of the strong correlation. Thus, the unconstrained values for o_4 do not provide an accurate estimate for the tetrahedral character of the bonds formed at the C and N atoms. The value $o_4 = -5.1$ (13) for carbon is considerably greater in magnitude than that observed for the methylene C atoms in γ -aminobutyric acid (Craven & Weber, 1983) and phosphoryl-ethanolamine (Swaminathan & Craven, 1984), where five C atoms have comparable tetrahedral deformations with populations ranging from 3.1 (2) to 3.5 (2).

Because there is nearly a redundancy when both o_4 variables are included, we have carried out a refinement in which carbon was assigned a fixed value $o_4 = -2.5$ (becoming $o_4 = -2.36$ after final scaling of all population parameters). This gave $R = 0.024$, $R_w = 0.017$, $S = 4.05$ with the final parameter values listed in Table 3, column (b). There are no significant changes from the values of column (a) except $o_4 = 2.9$ (3) for nitrogen. Thus, the constrained model more nearly fulfils conventional expectations for the tetra-

Table 3. Atomic parameters from refinements with X-ray data

Values of U_{ij} (\AA^2) are as defined in Table 1. The population parameters, which have been normalized (Hansen & Coppens, 1978) are as defined by Epstein, Ruble & Craven (1982). The columns are: (a) POP refinement, no constraint on o_4 ; (b) POP refinement with o_4 for carbon fixed; (c) VALRAY refinement, no constraint on o_4 .

		(a)	(b)	(c)	
Carbon	x	0.23813 (14)	0.23810 (15)	0.23813 (18)	
	U_{11}	0.0258 (4)	0.0259 (4)	0.0263 (4)	
	U_{22}	0.0652 (6)	0.0651 (6)	0.0646 (7)	
	U_{23}	0.0006 (8)	0.0005 (8)	0.0010 (9)	
	p_v	5.98 (8)	5.97 (8)	6.01 (15)	
	d_1	0.00 (25)	-0.07 (24)	-0.24 (46)	
	q_1	1.05 (24)	1.00 (23)	0.66 (20)	
	q_4	-1.54 (50)	-1.51 (50)	-1.45 (57)	
	o_1	1.39 (23)	1.35 (23)	1.04 (17)	
	o_4	-5.06 (130)	[-2.36]	-6.75 (162)	
Nitrogen	x	0.12250 (14)	0.12256 (13)	0.12251 (14)	
	U_{11}	0.0475 (4)	0.0477 (4)	0.0475 (4)	
	U_{12}	-0.0105 (3)	-0.0107 (3)	-0.0110 (4)	
	p_v	7.00 (12)	6.99 (12)	7.24 (8)	
	d_1	-0.13 (62)	-0.25 (56)	-0.11 (20)	
	q_2	0.03 (71)	0.19 (65)	0.72 (25)	
	o_1	0.97 (49)	0.93 (49)	0.63 (8)	
	o_4	0.22 (127)	2.85 (28)	-1.58 (170)	
	Hydrogen	p_v	1.01 (3)	1.02 (3)	0.91 (4)
		d_1	-1.32 (21)	-1.26 (20)	-0.79 (22)
d_3		-0.43 (29)	-0.29 (28)	-0.62 (26)	
q_1				-0.14 (20)	
q_2				-0.82 (40)	
q_4				-0.30 (38)	

hedral deformation density of both carbon and nitrogen.

The residual electron density (Fig. 3) was obtained from a difference Fourier map involving subtraction of the density for the constrained model [see Table 3, column (b)]. The range of values (0.03 to

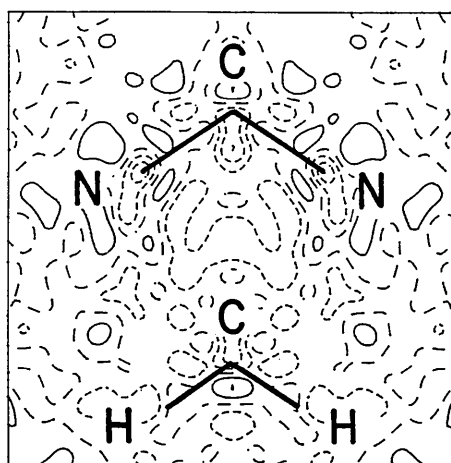


Fig. 3. Difference Fourier synthesis showing the residual electron density after the POP refinement with a constrained value for o_4 of the C atoms. The section passes through six atomic nuclei from the same molecule so that the central region of the section cuts through the molecular cage. Contours are at intervals of 0.03 e \AA^{-3} with the zero contour shown as extended dashes.

$-0.099 \text{ e \AA}^{-3}$) indicates that this model accounts satisfactorily for the total thermally averaged electron-density distribution. Maps of static deformation density (Figs. 4 and 5) were constructed as direct sums of the deformation terms.*

Final parameters from the VALRAY refinement are given in Table 3, column (c). The least-squares fitting involved the second derivatives of the variables. In this way, it was shown that proper convergence was obtained for the model without constraint on the o_4 population parameters. The refinement, based on 25 variables, gave $R_w(F^2) = 0.0341$, $R(F^2) = 0.0401$ and $S = 4.223$. Corresponding values based on F were

* A static deformation map was also calculated following a POP refinement using fixed values from neutron diffraction for all positional and thermal parameters. This map was not significantly different from Fig. 5.

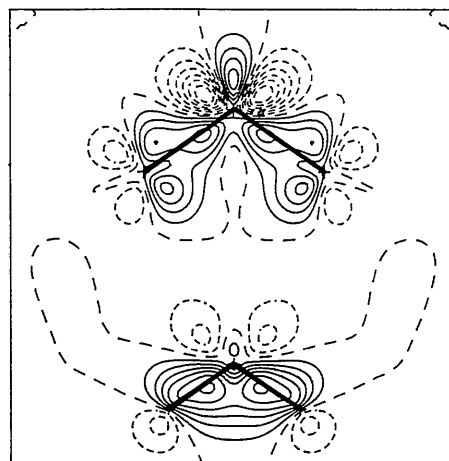


Fig. 4. Static deformation density map derived from the POP refinement with no constraints on o_4 . Contours are at intervals of 0.1 e \AA^{-3} .

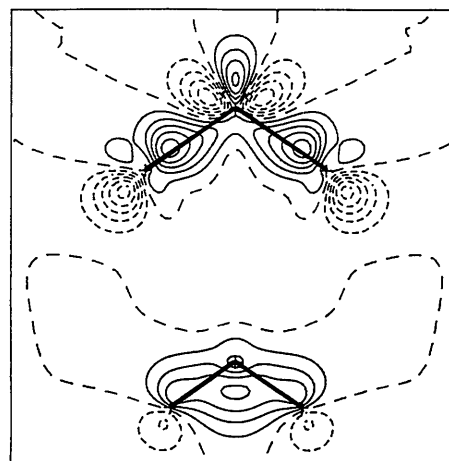


Fig. 5. Static deformation density map derived from the POP refinement using a constrained value for o_4 of the C atom. Contours are at intervals of 0.1 e \AA^{-3} .

$R_w = 0.017$, $R = 0.025$. As in the *POP* refinement, the least-squares correlation between o_4 population parameters for carbon and nitrogen was very high (0.97). The sum of monopole population parameters for the molecule gave the value 76.2 electrons, corresponding to a neutral molecule within the estimated error ($\sigma = 0.4$ electrons). Nevertheless, the population parameters have been rescaled by the factor 1.0024.

Discussion

(i) *The results from neutron diffraction*

The bond lengths obtained from the parameters in Table 1 are 1.462 (5) Å for C–N and 1.071 (7) Å for C–N. Bond angles are 112.4 (3)° for N–C–N, 108.0 (3)° for C–N–C, 112.2 (6)° for H–C–H and 108.1 (5)° for N–C–H. Bond torsion angles are ± 58.3 (4)° for N–C–N–C, ± 60.9 (5)° and ± 177.4 ° for H–C–N–C.

A rigid-body analysis (Schomaker & Trueblood, 1968) for the C–N molecular frame gave good agreement between observed and calculated U^{ij} ($R_w = 0.009$, $S = 1.57$). As pointed out by DWP, there are only two variables in this fit. We obtain $T = 0.0263$ (2) Å² for the isotropic translational vibration and $L = 46.1$ (3)⁰² for the isotropic libration. After correction for rigid-body libration, the C–N bond lengths become 1.482 Å.

When the H atoms are considered to be carried rigidly on the C–N framework and the resulting m.s. displacements are subtracted from the observed values, the resulting ΔU^{ij} tensor has principal components 0.0048, 0.0061 and 0.0234 Å². The CH₂ group has crystallographic symmetry $2mm$ about the C atom and, therefore, two of the principal displacements for the H atom lie on a mirror plane and the other is perpendicular to the mirror. The 0.0061 Å² displacement is perpendicular to the mirror. The others are twisted within the mirror plane so that the minimum displacement (0.0048 Å²) is 12° from the C–H bond direction. The twist is in the sense which avoids the region of the twofold axis. The C–H bond stretching and CH₂ in-plane displacements are in reasonable agreement with m.s. amplitudes of internal vibration obtained in a similar way for other methylene groups (see Table 6 of Weber, Craven, Sawzik & McMullan, 1991). However, the out-of-plane motion is considerably less (0.006 versus 0.015 Å²).

In Fig. 2 it can be seen that the total p.d.f. for the vibrating H nucleus has its maximum displaced from the centroid of the harmonic contribution. The displacement is approximately along the C–H bond and on the opposite side of the H atom from the C atom. This p.d.f. indicates a highly significant C–H anharmonic bond-stretching vibration. The skewed component of the p.d.f. for hydrogen does not exhibit the alternating pattern of maxima and minima associated with curvilinear librational motion (Johnson, 1970).

(ii) *The results from X-ray diffraction*

For the HMT molecule with $\bar{4}3m$ symmetry, the molecular dipole and quadrupole moments are zero. The molecular octapole moment derived from the results of the VALRAY refinement (monopole through octapole terms) is $\langle xyz \rangle = +1.0$ (3) |e| Å³ or, as defined by Buckingham (1970), $\Omega = 5\langle xyz \rangle / 2 = -4.0$ (14) $\times 10^{-49}$ C m³. The determination of a molecular octapole moment including its sign has rarely been reported, either from a theoretical charge distribution or from experiment. The experimental estimate obtained from Bragg diffraction data that we report here appears to be the first of its kind.

In Figs. 4 and 5, we show deformation charge-density maps for pseudoatoms at rest that have been derived from the two *POP* refinements (Table 3). In Fig. 4, corresponding to the unconstrained model in which o_4 was refined for both carbon and nitrogen, there is a region of charge deficiency where nitrogen lone-pair density might be expected. However, the deformation density around the N atom in Fig. 4 has marginal significance because of the large e.s.d.'s in the unconstrained population parameters. Fig. 5 corresponds to the model in which o_4 for carbon is constrained to a value similar to that obtained for methylene groups in other crystal structures. Here, the deformation density at the N atom is more concentrated in the C–N bonding region but there is no significant density in the lone-pair region. Fig. 5 is in contrast to the ($X-N$) and ($X-X$) Fourier maps of DWP and SH, which indicate positive density in this region. For a more direct comparison with the DWP and SH maps, we calculated a difference Fourier synthesis (Fig. 6) in which ρ_{obs} was phased with the multipole model (constrained version) and ρ_{calc} was derived and phased from the neutral-spherical-atom component of the model. All reflections were included

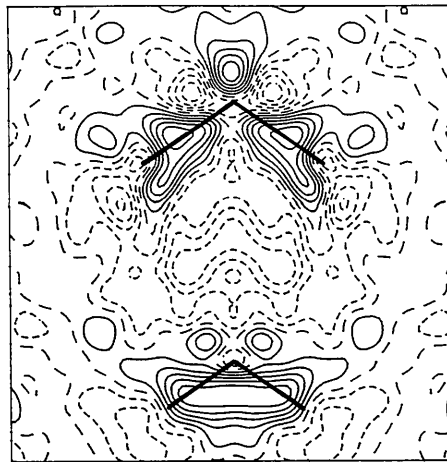


Fig. 6. Difference Fourier synthesis showing the dynamic deformation density which corresponds to the static density in Fig. 5. Contours are at intervals of 0.03 e Å⁻³.

in the Fourier synthesis. We point out that previous ($X-N$) and ($X-X$) maps were derived in the same way as Fig. 6, except that both ρ_{obs} and ρ_{calc} were phased by a spherical-atom model. It can be seen that, when the static deformation density is reconvoluted with the atomic thermal vibrations, we obtain a dynamic deformation density (Fig. 6), which agrees well with the maps of DWP and SH.

It might be concluded that the apparent lone-pair density in Fig. 6 and in the ($X-X$) and ($X-N$) maps is largely an artifact arising from the thermal vibrational averaging of the static deformation-density distribution (Fig. 5). At 298 K, the r.m.s. (root-mean-square) thermal displacement of nitrogen is large (0.24 Å) in the direction perpendicular to [111] and tangential to the molecular surface. Alternatively, the structure refinement which gave rise to Fig. 5, owing to the large atomic displacements, may not have provided a reliable deconvolution of the charge-density distribution from thermal vibrational effects. Our proposed analysis of X-ray and neutron diffraction data collected at reduced temperature should allow a clear distinction between these alternative explanations.

(iii) Concluding remarks

We believe that both the neutron (DWP) and the X-ray (SH) data used in our refinements are of the highest quality. The agreement factors which we obtain are unusually small. Nevertheless, we conclude that because of the crystal symmetry of HMT, in particular the absence of a center of symmetry, and because of the large m.s. atomic displacements at 298 K chemically important features of the charge-density distribution remain uncertain.

An important difficulty arises because a multipole term (the o_4 octapole in HMT) is invariant under the operations of the space group and thereby makes a vector contribution to the structure factor which is common for all symmetry-related atoms. In principle, such vectors contribute to a change both in the magnitude and phase of the overall structure factor but, in fact, the effect on the magnitude of the structure factor is small. Effectively, these vectors cause a phase uncertainty, which for HMT introduces a large least-squares correlation between o_4 for carbon and nitrogen.

The difficulty that we encounter with HMT is an example of a general problem, present in some degree whenever the multipole model is applied in the charge-density study of a noncentrosymmetric structure. Depending on the space group, the correlations between population parameters will involve selected dipole or octapole deformation terms. For space group $P2_1$, the affected terms are the dipole d_2 and the octapoles o_2 , o_4 and o_6 . Indeed, in a study of adenosine (Klooster & Craven, unpublished work) in which the space group is $P2_1$, these particular

population parameters have e.s.d.'s that are systematically almost twice the e.s.d.'s of the other dipoles and octapoles. The structure of HMT provides a worst-case example because the o_4 deformation, owing to its symmetry and orientation in the cell, is important for describing the tetrahedral bonding of both carbon and nitrogen. Fortunately, the correlation problem does not arise for centrosymmetric structures, because all odd-order multipoles then contribute to the structure factor as paired terms with equal and opposite phase. Furthermore, the overall phase of the structure factor is usually well established from a knowledge of the rest of the crystal structure.

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The Absorption-Correction Factor of Multifaceted Crystals

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Abstract

A mathematical analysis of the evaluation of the absorption-correction factors in convex polyhedral crystals is made. Formulae are given that permit the exact evaluation of the factors and their derivatives and that do not depend on the subdivision of the crystal into tetrahedra. A new method of defining the Howells polyhedra as the included volume of a set of planes is also described. The method allows additional constraints to be introduced, which could be used to deal with inhomogeneities in either the crystal or the incident beam. Computation based on these ideas gives rapid and exact evaluation of both the absorption-correction factor and its derivatives, with negligible rounding-error problems. In addition, a formula is given for scattering by a general tetrahedron with a wide range of orientations that can be used as a test of computer programs.

Introduction

The transmission (or absorption-correction) factor of a multifaceted crystal has been found in the past either by a numerical method (Busing & Levy, 1957; Hamilton, 1963) or by subdivision of the crystal into elemental tetrahedra (de Meulenaer & Tompa, 1965) and analytic evaluation of the absorption over a tetrahedron. Similar methods that use triangles and parallelograms have been used in the case of two-dimensional crystals (Howells, 1950; Braibanti & Tiripicchio, 1965). The two techniques have been compared many times, most recently by Blanc, Schwarzenbach & Flack (1991). In principle, the analytic method should give an exact answer but the subdivision into tetrahedra leads to problems with rounding errors and to extended computing time for

multifaceted crystals. The rounding-error problems have been largely overcome by the improvements suggested by Alcock (1970, 1974) and by Blanc, Schwarzenbach & Flack (1991). Nevertheless, the subdivision into tetrahedra is totally unnecessary because analytic expressions for the transmission factor can be found for any simple shape. In this paper, mathematical expressions are provided that avoid this unnecessary subdivision. All that is required is the evaluation of geometric factors for the edges of each Howells polyhedron. In addition, a method of finding these edges is described that results in an unambiguous determination of each edge. The expressions given in this paper allow the volume of the whole crystal and that of each of the Howells polyhedra to be evaluated separately.

This paper is divided into three sections. The first section derives the mathematical expressions. The one following that explains how the concept of the included volume of a set of planes can be used to simplify the definitions of the Howells polyhedra. Finally, a simple way of deriving the transmission factors for crystals that each consist of a single Howells polyhedron is given.

The transmission factor

The transmission factor is defined by

$$T = V^{-1} \int_V d\tau \exp[-\mu L(\mathbf{r})], \quad (1)$$

where $L(\mathbf{r})$ is the total path length within the crystal of a ray that is scattered once at \mathbf{r} . Because $L(\mathbf{r})$ is a linear function of the scattering position \mathbf{r} , one can write

$$-\mu L(\mathbf{r}) = -\mu(\mathbf{a} \cdot \mathbf{r} + c) \quad (2)$$