

Crystal and Molecular Structure of Hexamethylmelamine [2,4,6-tris(dimethylamino)-1,3,5-triazine]

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Crystals of the title compound are hexagonal, $a = 9.99 \pm 0.01$, $c = 7.11 \pm 0.01$ Å, space group $P6_3/m$, $Z = 2$. The atomic positions have been determined by least-squares refinement from diffractometer data, the final R being 0.073 for 255 reflexions. The molecule is planar (apart from the hydrogen atoms). It occupies a crystallographic site of symmetry $3/m$ ($\bar{6}$, C_{3h}) but within experimental error the molecular symmetry is $\bar{6}2m$ (D_{3h}). Mean bond lengths corrected for molecular oscillations are: C-N(cyclic) 1.345, C-N(exocyclic) 1.366, and C(methyl)-N 1.466 Å. The C-N-C and N-C-N angles in the ring are 112.7 and 127.3°. The atomic thermal vibrations have been analysed to show that at 24 ± 2 °C the molecule is undergoing translational vibrations with root-mean-square amplitudes of 0.25–0.26 Å combined with angular oscillations of root-mean-square amplitude 4.2°. The van der Waals distances between the molecules are normal (3.7–3.8 Å) except in the region of the 6_3 screw axis where the molecules are further apart leaving a channel through the structure with a free diameter of 1.5 Å.

THE formation of molecular complexes between hexamethylmelamine [2,4,6-tris(dimethylamino)-1,3,5-triazine] and a variety of other molecules including 1,3,5-trinitrobenzene, chloranil, and cyanuric chloride has been reported.¹⁻³ In the 1:1 complex with trinitrobenzene the hexamethylmelamine molecules are planar (apart from the hydrogen atoms) and are stacked alternately with the trinitrobenzene molecules.⁴ We decided to examine the crystal structure of hexamethylmelamine itself to find whether the planarity of the molecule is maintained where complex formation with other molecules is not involved.

¹ S. K. Das, R. A. Shaw, B. C. Smith, W. A. Last, and F. B. G. Wells, *Chem. and Ind.*, 1963, 866.

² S. K. Das, R. A. Shaw, and B. C. Smith, *Chem. Comm.*, 1965, 176.

EXPERIMENTAL

Crystal Data.— $C_9H_{18}N_6$, $M = 210.285$, hexagonal, $a = 9.99 \pm 0.01$, $c = 7.11 \pm 0.01$ Å, $U = 614.5$ Å³, $D_m = 1.10$ (by flotation), $Z = 2$, $D_c = 1.14$, $F(000) = 228$. Space group $P6_3/m$ (C_{6h}^2 , No. 176) from systematic absences: 000 l for l odd; Laue symmetry $6/m$. Mo- K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 0.91$ cm⁻¹. Optically uniaxial negative.

Acicular crystals were produced by cooling a hot solution in methanol. They are prisms elongated along the c axis and showing the forms {1000} and {0001}. Unit-cell parameters were determined from diffractometer measurements. X-ray intensity data comprising the ten layers of re-

³ S. K. Das, T. Gündüz, R. A. Shaw, and B. C. Smith, *J. Chem. Soc. (A)*, 1969, 1403.

⁴ R. M. Williams and S. C. Wallwork, *Acta Cryst.*, 1966, **21**, 406.

reflexions $hki0=9$ and the layer $h0\bar{h}l$ were measured at 22–26 °C on a Phillips PAILRED diffractometer using monochromatised Mo- K_{α} radiation. Intensities were measured for all reflexions with $\sin \theta/\lambda \leq 0.62 \text{ \AA}^{-1}$ and some with $\sin \theta/\lambda$ in the range 0.62–0.70 \AA^{-1} . Groups of three (and occasionally four) symmetry-related reflexions were measured and the intensities averaged. The 000 l reflexions were measured once only from the $h0\bar{h}l$ layer which was collected by use of a different crystal from that used to obtain the rest of the data. The same applies to the reflexions 10 $\bar{1}4$, 10 $\bar{1}5$, 10 $\bar{1}6$, and 10 $\bar{1}7$ which were taken from the $h0\bar{h}l$ layer in preference to the other data. In all, 519 independent reflexions were recorded of which 256 gave reliable intensities with a relative counting error $\sigma(I)/I < 0.5$. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, Didcot, Berkshire, using a computer programme written by O. S. Mills, L. I. Hodgson, and F. S. Stephens and the 'X-Ray 63' set of programmes.^{5a} The atomic scattering factors were taken from ref. 5b.

Determination of the Structure.—The systematic absences of X-ray reflexions and the Laue symmetry indicate the space group to be either $P6_3/m$ or $P6_3$. Since there are only two molecules in the unit cell they must occupy special positions and the molecular symmetry must be either $3/m$ for the former space group or 3 for the latter with the molecules related to each other by a 2_1 axis. The layers of X-ray reflexions with l even all show a very similar intensity distribution; the layers with l odd are also similar to each other but different from the even layers. This indicates that all or nearly all the atoms in one molecule possess identical z co-ordinates, as would be the case if the space group was $P6_3/m$ and the molecular symmetry $3/m$. This choice was therefore accepted provisionally.

The orientation of the triazine ring was deduced from the projection of the Patterson function on the (0001) plane. There are three possible sets of positions for the centre of the ring which are consistent with the symmetry:⁶

$$\begin{array}{l} (2a) \quad 0, 0, \frac{1}{4}; \quad 0, 0, \frac{3}{4} \\ (2c) \quad \frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \quad \frac{2}{3}, \frac{1}{3}, \frac{3}{4} \\ \text{or } (2d) \quad \frac{2}{3}, \frac{1}{3}, \frac{1}{4}; \quad \frac{1}{3}, \frac{2}{3}, \frac{3}{4} \end{array}$$

(2c) is equivalent to (2d), differing only in choice of origin, and was therefore disregarded. (2a) seemed unlikely because it produced clustering together of the molecules near $x = y = 0$ but a large space at the centre of the unit cell. It was tested further by calculating structure factors for a model based on the known orientation of the ring and likely values for the C–N bond lengths. Agreement with the observed intensity data was poor and so (2a) was rejected, leaving (2d) only.

There remained an ambiguity in that the molecules could be placed as in Figure 1 or alternatively by turning them through 60° about their triad axes. This could not be resolved from the Patterson function because the two arrangements have a large number of vectors in common. Structure factors were calculated for both arrangements and better agreement was found for that shown in Figure 1 although the decision was not at this stage entirely conclusive. This arrangement was refined by Fourier and full-

matrix least-squares methods using at first 168 stronger reflexions. In the least-squares refinement the function minimised was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$.

When R for the 168 reflexions had reached 0.094 a difference Fourier synthesis was calculated and from this the hydrogen atoms were located. Refinement was then resumed with the hydrogen atoms included but not refined and anisotropic temperature factors applied to the carbon and nitrogen atoms. The intensity data were expanded by the inclusion of 87 weaker reflexions, making 255 in all. The weighting scheme used in the later cycles of least-squares put $w = 3/|F_o|$ if $|F_o| > 3$ (on absolute scale) but otherwise $w = 1$, except that $w = 0$ if $|F_c| < 0.3|F_o|$. This gave similar average values of $w\Delta^2$ for ranges of increasing $|F_o|$ and $\sin \theta/\lambda$ except for a few of the strongest reflexions whose $w\Delta^2$ values were high. The refinement terminated at

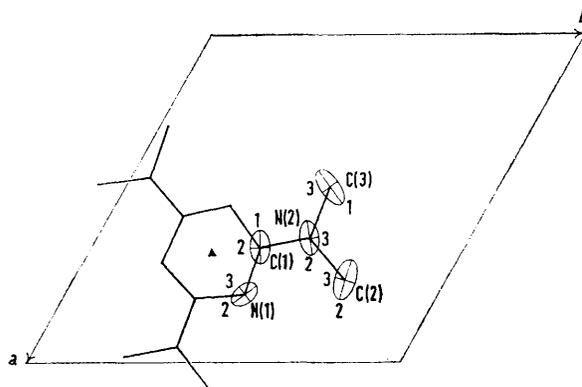


FIGURE 1 Position of the molecule and orientation of the thermal vibration ellipsoids in the ab plane. The principal axes are labelled (1), (2), or (3) according to the size of the vibration amplitudes. The elongation of the ellipses has been exaggerated to make the difference between the amplitudes clearer

R 0.073 for 255 reflexions. In the final cycle of refinement all parameter shifts were $< 0.08\sigma$. The reflexion 0002, which was very strong and almost certainly suffered from extinction, was not included in the refinement. Its $|F_c|$ was always some 70% higher than its $|F_o|$.

An attempt was made to refine the structure using the noncentrosymmetric space group $P6_3$ at a stage before the hydrogen atoms were inserted. This produced no improvement in the agreement index R and the shifts in the z co-ordinates oscillated considerably in successive cycles of refinement. It was therefore concluded that the correct space group was $P6_3/m$.

RESULTS

The final atomic co-ordinates and thermal parameters with their estimated standard deviations are listed in Tables 1–3. For the hydrogen atoms an isotropic temperature factor with B 8.0 \AA^2 , equivalent to $\langle u^2 \rangle^{\frac{1}{2}} = 0.32 \text{ \AA}$, was used. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20322 (2 pp., 1 microfiche).*

* (a) 'X-Ray 63' system of programmes compiled by J. M. Stewart and D. F. High; (b) 'International Tables for X-Ray Crystallography', vol. III, Kynoch Press, Birmingham, 1962, pp. 202, 203.

⁶ Ref. 5b, vol. 1, 1952, p. 283.

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses, and root-mean-square standard deviations

	x/a	y/b	z/c	σ_{rms} (10^{-3} Å)
N(1)	0.7915(4)	0.4825(4)	0.25	4
N(2)	0.6195(6)	0.5713(5)	0.25	6
C(1)	0.6446(6)	0.4496(5)	0.25	6
C(2)	0.7480(8)	0.7299(7)	0.25	8
C(3)	0.4634(8)	0.5483(8)	0.25	8

TABLE 2

Fractional co-ordinates of hydrogen atoms used for structure-factor calculations

	x/a	y/b	z/c
H(21)	0.846	0.731	0.25
H(22)	0.739	0.785	0.365
H(31)	0.376	0.435	0.25
H(32)	0.442	0.597	0.365

TABLE 3

Anisotropic thermal parameters ($\times 10^4$) with estimated standard deviations in parentheses.* For all atoms $b_{13} = b_{23} = 0$

	b_{11}	b_{22}	b_{33}	b_{12}
N(1)	183(6)	181(7)	300(10)	86(6)
N(2)	255(9)	200(7)	439(14)	139(7)
C(1)	216(8)	183(8)	226(10)	109(7)
C(2)	359(15)	203(10)	561(23)	137(11)
C(3)	291(11)	326(13)	443(18)	230(10)

* The temperature factor is in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$.

Bond lengths are listed in Table 4 and bond angles are shown in Figure 2. The lengths in Table 4(a) were calculated from the co-ordinates in Table 1 which were derived from the least-squares refinement. Table 4(b) contains the

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses

(a) Derived from the least-squares refinement			
C(1)-N(1)	1.334(7)	C(1)-N(2)	1.359(8)
C(1)-N(1')	1.342(7)	C(2)-N(2)	1.458(10)
		C(3)-N(2)	1.458(10)
(b) Corrected for molecular oscillations			
C(1)-N(1)	1.341(7)	C(1)-N(2)	1.366(8)
C(1)-N(1')	1.349(7)	C(2)-N(2)	1.465(10)
		C(3)-N(2)	1.466(10)

bond lengths corrected for the effect of molecular oscillations. The estimated standard deviations of both lengths and angles were obtained using the formulae given in ref. 7.

The vibration ellipsoids calculated from the anisotropic thermal parameters in Table 3 are shown in Figure 1. For each atom the principal axes are aligned in either radial or tangential directions with respect to the centre of the molecule, and in all cases except C(1) the radial vibration is the smallest. For C(1) the amplitude perpendicular to the molecular plane (0.24 Å) is just smaller than in the radial direction (0.25 Å). It is clear from the orientations of the ellipsoids that the vibrations of the individual atoms may be expressed in terms of a rigid-body motion of the

⁷ G. A. Jeffrey and D. W. J. Cruickshank, *Quart. Rev.*, 1953, **7**, 335.

⁸ D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

molecule. The thermal vibration tensor \mathbf{U} referred to the orthogonal crystal axes a' , b , and c was calculated for each atom from the b_{ij} values [Table 5(a)]. Since the molecule

TABLE 5

Components of the thermal vibration tensors \mathbf{U} (in 10^{-3} Å²) referred to the orthogonal crystal axes a' , b , and c . For all atoms $U_{13} = U_{23} = 0$

	U_{11}	U_{22}	U_{33}	U_{12}
(a) Found				
N(1)	69	71	77	-2
N(2)	97	63	112	5
C(1)	82	64	58	0
C(2)	136	79	144	-19
C(3)	110	85	113	37
(b) Calc. from \mathbf{T} and $\boldsymbol{\omega}$				
N(1)	70	72	72	-5
N(2)	103	67	99	6
C(1)	75	66	70	1
C(2)	134	68	132	-14
C(3)	120	83	132	30

occupies a site with symmetry $3/m$, its translational vibration tensor \mathbf{T} and angular oscillation tensor $\boldsymbol{\omega}$ will be equivalent to ellipsoids of rotation (with c as unique axis). This

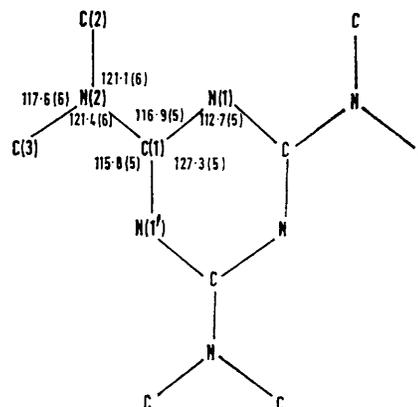


FIGURE 2 Bond angles (deg.) with estimated standard deviations in parentheses

has the consequences (i) that $T_{11} = T_{22}$ and $T_{12} = T_{13} = T_{23} = 0$, and similar conditions for ω_{ij} , and (ii) that any pair of orthogonal directions in the molecular plane may be chosen as axes for the \mathbf{T} and $\boldsymbol{\omega}$ tensors. For this latter reason it was unnecessary to recalculate the \mathbf{U} tensors with reference to special molecular axes (other than c as axis 3). The tensors \mathbf{T} and $\boldsymbol{\omega}$ were evaluated from the U_{ij} values by use of the least-squares procedure of ref. 8: $T_{11} = 0.066(2)$ Å², $T_{33} = 0.061(8)$ Å², $\omega_{11} = 0.0054(11)$ radian², $\omega_{33} = 0.0054(2)$ radian². The estimated standard deviations of T_{33} and ω_{11} are large because these quantities are derived solely from the U_{33} values, of which there are only five observations. In contrast T_{11} and ω_{33} are derived from a larger group of 15 U_{ij} observations. In addition the agreement between observed and calculated values was poorer for U_{33} than for the other U_{ij} . The U_{ij} values calculated from \mathbf{T} and $\boldsymbol{\omega}$ are shown for comparison in Table 5(b). The root-mean-square amplitudes of angular oscillation about the three principal axes (*i.e.* $\omega_{ii}^{\frac{1}{2}}$) are all equal to 4.2° .

To correct the atomic positions obtained from the least-squares refinement for the effect of the angular

oscillations, the distance of each atom r from the molecular centre must be increased by an amount $\Delta r = \frac{1}{2}r(\omega_{11} + \omega_{33})$.⁹ This results in the C-N bond lengths all being enlarged by 0.007–0.008 Å (see Table 4). The corrections have little effect on the bond angles.

DISCUSSION

Bond Lengths and Angles.—The hexamethylmelamine molecule is planar with the exception of the hydrogen atoms. There are no significant differences between either chemically equivalent bond lengths or bond angles, and therefore no significant departure from the maximum possible molecular symmetry $\bar{6}2m$ (D_{3h}). The positions assigned to the hydrogen atoms also obey this symmetry. The mean molecular dimensions are:

C_r-N_r	1.345(5) Å	$C_r-N_r-C_r$	112.7(5)°
C_r-N_o	1.366(8)	$N_r-C_r-N_r$	127.3(5)
N_o-CH_3	1.466(7)	$N_r-C_r-N_o$	116.4(4)
		$C_r-N_o-CH_3$	121.2(4)
		$CH_3-N_o-CH_3$	117.6(6)

where subscript r denotes an atom in the ring and subscript o an atom outside the ring. The parameters for

TABLE 6
Molecular dimensions of azine derivatives

	$C_r-N_r/\text{Å}$	$C_r-N_o/\text{Å}$	$C_r-N_r-C_r/\text{deg}$	Method †
Hexamethylmelamine	1.345(5)	1.366(8)	112.7(5)	X-ray ^a
HMM-TNB*	1.30–1.39	1.41, 1.44	112, 115	X-ray ^b
Melamine	1.34 ± 0.01	1.37 ± 0.03	117 ± 3	E.d. ^c
Melamine	1.33–1.35	1.35–1.36	115–117	X-ray ^d
Trisodium tri-cyanomelamine trihydrate	1.34, 1.35	1.40		X-ray ^e
Cyanuric chloride	1.33 ± 0.02		115 ± 3	E.d. ^c
1,3,5-Triazine	1.319(5)		113.2(4)	X-ray ^f
1,3,5-Triazine	1.317 ± 0.009		114.8	N.d. ^g
2,4,6-Triphenyl-1,3,5-triazine	1.321–1.359		115.5	X-ray ^h
Pyrazine	1.334 ± 0.015		115.1	X-ray ⁱ
α -Pyrazinamide	1.331–1.356		115.7	X-ray ^j
1,2,4,5-Tetrazine	1.334(7)		116.0	X-ray ^k
α -Phenazine	1.345(9)		(\angle CNN) 116.6	X-ray ^l

* Hexamethylmelamine-trinitrobenzene complex. † E.d. = electron diffraction, N.d. = neutron diffraction.

^a This work. ^b Ref. 4. ^c Y. Akimoto, *Bull. Chem. Soc. Japan*, 1955, **28**, 1. ^d E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737. ^e J. L. Hoard, *J. Amer. Chem. Soc.*, 1938, **60**, 1194. ^f P. J. Wheatley, *Acta Cryst.*, 1955, **8**, 224. ^g P. Coppens, *Science*, 1967, **158**, 1577. ^h A. Damiani, E. Giglio, and A. Ripamonti, *Acta Cryst.*, 1965, **19**, 161. ⁱ P. J. Wheatley, *Acta Cryst.*, 1957, **10**, 182. ^j Y. Takaki, Y. Sasada, and T. Watanabé, *Acta Cryst.*, 1960, **13**, 693. ^k F. Bertinotti, G. Giacomello, and A. M. Liquori, *Acta Cryst.*, 1956, **9**, 510. ^l F. H. Herbstein and G. M. J. Schmidt, *Acta Cryst.*, 1955, **8**, 399.

other azine derivatives are shown in Table 6 for comparison, but unfortunately the comparison cannot be

⁹ D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757; 1961, **14**, 896; Conference on Accuracy and Automation in X-Ray Analysis, Inst. Phys. and Phys. Soc., 1968, Abstracts, Paper IV 4.

very critical because the accuracy of several of the previous measurements is low. For example, the only X-ray determinations in Table 6 in which the bond lengths were corrected for molecular oscillations are those of pyrazine and α -pyrazinamide. The cyclic C-N bond length usually lies in the range 1.33–1.35 Å but is shorter in triazine and for four of the bonds in triphenyltriazine.

The planarity of the whole hexamethylmelamine molecule and the shortness of the C_r-N_o bonds show that the π system of the ring extends over these exocyclic bonds. Although the difference in length between the C_r-N_r and C_r-N_o bonds is of doubtful statistical significance, it probably does indicate a smaller π character for the exocyclic bond as expected. There is a suggestion of a similar trend in the published data for melamine. In *NN*-dimethyl-*p*-nitroaniline¹⁰ where the

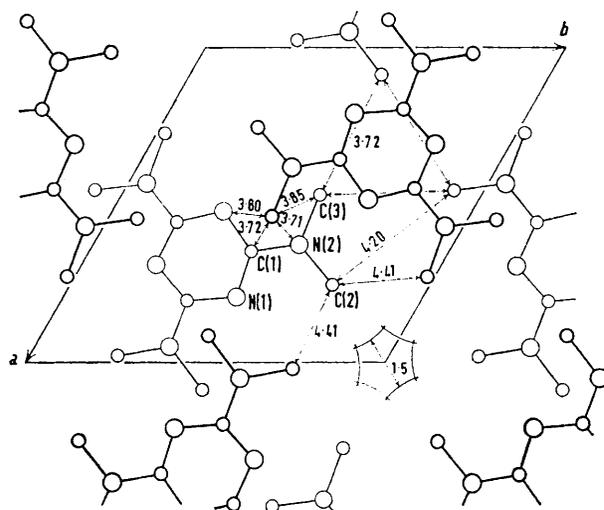


FIGURE 3 The structure viewed in projection down the c axis. Molecules at a height $z = \frac{1}{4}$ are drawn in thin lines and those at a height $z = \frac{3}{4}$ in thick lines. Intermolecular distances are marked in Å.

C_r-N_o bond has a length [1.358(16) Å] similar to that in hexamethylmelamine, the dimethylamino-group is again planar but is twisted out of the plane of the benzene ring by 7.3°. It is difficult to understand why in the complex with trinitrobenzene⁴ the C_r-N_o bonds are not shorter than 1.41 Å although the hexamethylmelamine molecule is planar. The N_o-CH_3 length in hexamethylmelamine is close to the standard value for a single C-N bond.¹¹

A common feature of triazine molecules is that the endocyclic angles at nitrogen are smaller than 120° (Table 6); hexamethylmelamine conforms to this pattern.

Packing of the Molecules.—The arrangement of the molecules in the crystal is shown in Figure 3. The structure is made up of layers parallel to (0001) at heights $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Within one layer the closest approach between molecules (3.72 Å) is between sets of

¹⁰ T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68.

¹¹ *Chem. Soc. Special Publ.*, No. 11, 1958, p. S16.

C(3) atoms related by a triad axis. The shortest contacts between layers (Figure 3) are from atom C(3) in one molecule to atoms N(1), C(1), N(2), and C(3) in the neighbouring molecule, ranging from 3.71 to 3.85 Å. Atom C(2) makes no close intermolecular contacts, the nearest being 4.20 Å to atom C(3) in the next molecule within the same layer and 4.41 Å to an atom C(2) in another layer. This results in a very loose packing of the molecules around $x = 0$, $y = 0$, leaving a channel running parallel to c . However, this channel has a free diameter of only *ca.* 1.5 Å and is therefore too narrow to

accommodate other molecules. The loose packing probably accounts for the rather large thermal vibrations in this structure, which are greatest for atom C(2).

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