

A. Cousson,^a B. Nicolai^{b*} and F. Fillaux^c^aLaboratoire Léon Brillouin, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France, ^bLaboratoire de Chimie Physique, Faculté de Pharmacie, Université Paris 5, 4 avenue de l'Observatoire, 75006 Paris, France, and ^cLADIR-CNRS—Université Pierre et Marie Curie, 2 rue Henry Dunant, 94320 Thiais, FranceCorrespondence e-mail:
beatrice.nicolai@univ-paris5.fr

Key indicators

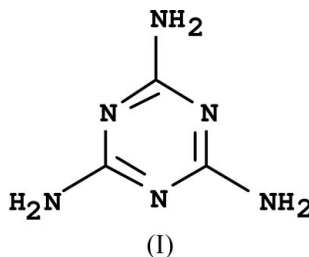
Single-crystal neutron study
 $T = 14$ K
Mean $\sigma(\text{N}-\text{C}) = 0.001$ Å
 R factor = 0.047
 wR factor = 0.043
Data-to-parameter ratio = 13.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Melamine (1,3,5-triazine-2,4,6-triamine): a neutron diffraction study at 14 K

The single-crystal neutron diffraction technique was used to determine the crystal structure of melamine, $\text{C}_3\text{H}_6\text{N}_6$, at 14 K. The molecule is nearly planar. There are three crystallographically inequivalent amine groups with different geometries, the asymmetric unit being the complete molecule.

Comment

Melamine (1,3,5-triazine-2,4,6-triamine; Fig. 1), (I), is of industrial interest in the production of melamine-formaldehyde resins with high surface hardness, and good heat and flame resistance.



The compound has been studied extensively with spectroscopy techniques, either in the solid state or in the gas phase, with Raman and IR (Schneider & Schrader, 1975; Meier *et al.*, 1995; Wang *et al.*, 1997) and inelastic neutron scattering (Fernandez-Liencrens *et al.*, 2001). Recently, there has been a growing interest in theoretical studies of the geometry of the isolated molecule. Different methods of molecular modelling, including *ab initio* and molecular dynamics calculations, have been used (Wang *et al.*, 1993; Meier & Coussens, 1990). The triazine ring was found to be nearly planar and the three amine groups are pyramidal. The calculated barrier of inversion is very low (< 1 kcal mol⁻¹), indicating possible disorder of NH_2 groups at room temperature.

The crystal structure of melamine has been determined at room temperature using both single-crystal X-ray and neutron diffraction techniques (Shanker *et al.*, 1939; Hughes, 1941; Cromer *et al.*, 1976; Larson & Cromer, 1974; Varghese *et al.*, 1977; Price *et al.*, 1978) and under pressure (Ma *et al.*, 2003).

In order to better understand the dynamics of the NH_2 groups, we needed to know the position of the H atoms at low temperature. We have thus determined the structure by the single-crystal neutron diffraction technique at 14 K, after a preliminary study at 293 K.

The space group is monoclinic $P2_1/a$, with four molecules per unit cell (Fig. 1). There is no evidence for any phase transition between 293 and 14 K. The lattice parameters are only slightly changed [$a = 10.433$ (6) Å, $b = 7.458$ (6) Å, $c =$

Received 28 October 2004
Accepted 16 December 2004
Online 8 January 2005

7.238 (5) Å and $\beta = 113.3 (2)^\circ$, cf. $a = 10.573 (6) \text{ \AA}$, $b = 7.463 (6) \text{ \AA}$, $c = 7.268 (5) \text{ \AA}$ and $\beta = 112.4 (2)^\circ$ at 293 K]. The ring is nearly planar. There are three crystallographically inequivalent amine groups bound to the triazine ring. The three C–N bonds are nearly coplanar with the ring. No disorder was observed. However, the amine groups have different configurations and destroy the D_{3h} symmetry of the isolated molecule indicated by *ab initio* calculations (Fig. 2).

The N3/H5/H6 amine group is pyramidal, with an N3–C3–N5–C1 torsion angle of $176.64 (8)^\circ$, and H–N–H and C–N–H angles of 114° . The two other amine groups, N1/H1/H2 and N2/H3/H4, are almost trigonal, with torsion angles close to 180° [C3–N5–C1–N1 = $178.32 (8)^\circ$ and C3–N4–C2–N2 = $178.66 (8)^\circ$] and H–N–H and C–N–H angles close to 119° (see Table 1). Atoms H2 and H3 are almost in the molecular plane. Atoms H1 and H4 deviate significantly from coplanarity with the triazine ring, with torsion angles greater than 10° .

The principal direction of maximum amplitude of each atom is approximately perpendicular to the molecular plane (Fig. 2). The U_{iso} values of the ring N atoms are about 14% greater than those of the C atoms. This is in accordance with the flexibility of the molecule proposed by molecular calculations (Meier & Coussens, 1990).

Experimental

White single crystals were obtained by slow evaporation of saturated aqueous solutions.

Crystal data

$\text{C}_3\text{H}_6\text{N}_6$	Neutron radiation
$M_r = 126.12$	$\lambda = 0.831 \text{ \AA}$
Monoclinic, $P2_1/a$	Cell parameters from 15 reflections
$a = 10.433 (1) \text{ \AA}$	$\theta = 32\text{--}44^\circ$
$b = 7.458 (1) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 7.238 (1) \text{ \AA}$	$T = 14 \text{ K}$
$\beta = 113.30 (2)^\circ$	Prism, white
$V = 517.26 (14) \text{ \AA}^3$	$3.50 \times 3.00 \times 3.00 \text{ mm}$
$Z = 4$	
$D_x = 1.619 \text{ Mg m}^{-3}$	

Data collection

Orphée reactor (Saclay, France): 5-C2 four-circle diffractometer	$\theta_{\text{max}} = 42.6^\circ$
ω scans	$h = -16 \rightarrow 16$
Absorption correction: none	$k = -4 \rightarrow 12$
2714 measured reflections	$l = -11 \rightarrow 11$
2327 independent reflections	450 standard reflections
1819 reflections with $I > 3\sigma(I)$	frequency: 2 min
$R_{\text{int}} = 0.08$	intensity decay: none

Refinement

Refinement on F^2	1982): $w = [\text{weight}][1 - (\ F_o\ - F_c)/6\sigma F_o]^2$, 1.42, -1.26, 0.982, -0.228
$R = 0.047$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR = 0.043$	$\Delta\rho_{\text{max}} = 1.81$
$S = 1.11$	$\Delta\rho_{\text{min}} = -1.67$
1819 reflections	Extinction correction: Larson (1970)
137 parameters	Extinction coefficient: 17.2 (5)
All H-atom parameters refined	
Prince modified Chebychev polynomial (Watkin, 1994; Prince,	

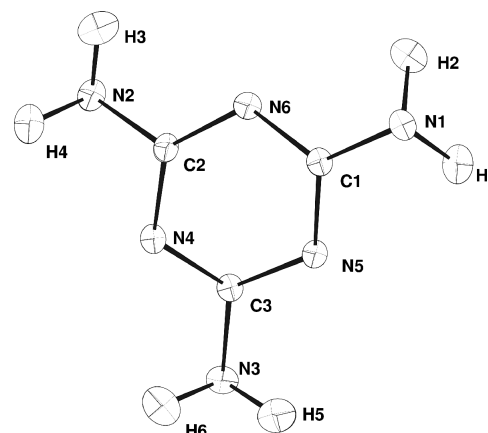


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

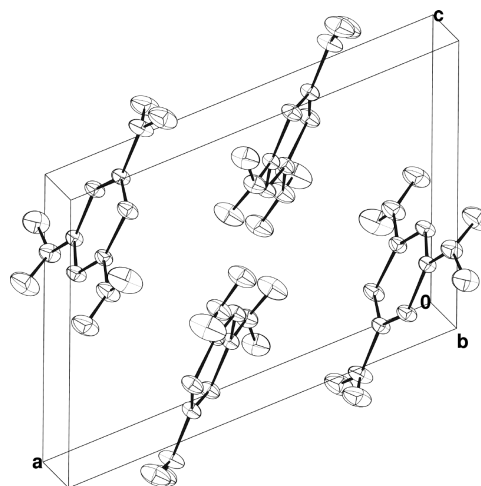


Figure 2
The packing of molecules in the unit cell.

Table 1
Selected geometric parameters (Å, °).

C1–N1	1.3376 (12)	C3–N5	1.3420 (12)
C1–N5	1.3539 (12)	N1–H1	1.017 (3)
C1–N6	1.3475 (12)	N1–H2	1.013 (3)
C2–N2	1.3420 (12)	N2–H3	1.003 (3)
C2–N4	1.3497 (12)	N2–H4	1.022 (3)
C2–N6	1.3457 (12)	N3–H5	1.022 (3)
C3–N3	1.3618 (12)	N3–H6	1.013 (3)
C3–N4	1.3382 (12)		
N1–C1–N5	117.02 (8)	H1–N1–H2	119.6 (2)
N1–C1–N6	118.30 (8)	C2–N2–H3	118.49 (18)
N5–C1–N6	124.68 (8)	C2–N2–H4	119.59 (17)
N2–C2–N4	116.94 (8)	H3–N2–H4	119.0 (2)
N2–C2–N6	117.77 (8)	C3–N3–H5	114.42 (17)
N4–C2–N6	125.28 (8)	C3–N3–H6	115.30 (17)
N3–C3–N4	117.88 (8)	H5–N3–H6	113.9 (2)
N3–C3–N5	116.34 (8)	C2–N4–C3	114.53 (7)
N4–C3–N5	125.76 (8)	C1–N5–C3	114.76 (7)
C1–N1–H1	118.42 (17)	C1–N6–C2	114.87 (7)
C1–N1–H2	118.91 (17)		
N3–C3–N5–C1	176.64 (8)	H3–N2–C2–N6	−7.47 (17)
C3–N5–C1–N1	178.32 (8)	H4–N2–C2–N4	13.01 (17)
C3–N4–C2–N2	178.66 (8)	H5–N3–C3–N5	25.12 (17)
H1–N1–C1–N1	−94.89 (7)	H6–N3–C3–N4	−21.30 (17)
H2–N1–C1–N5	176.29 (17)		

H atoms were refined anisotropically.

Data collection: *DIF4N* (modified Linux version of *DIF4*; Stoe & Cie, 2000); cell refinement: *DIF4N*; data reduction: *PRON* (modified version of *REDU4*; Stoe & Cie, 2000); program(s) used to solve structure: *CRYSTALS* (Watkin *et al.*, 2001); program(s) used to refine structure: *CRYSTALS*; molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

The authors thank J. Godard of the Parc d'Orsay, France, for providing the single crystals.

References

- Cromer, D. T., Larson, A. C. & Stewart, R. F. (1976). *J. Chem. Phys.* **65**, 336–349.
- Fernandez-Liencres, M. P., Navarro, A., Lopez-Gonzalez, J. J., Fernandez-Gomez, M., Kearley, G. J. & Fernandez-Diaz, M. T. (1997). Spectroscopy of Biological Molecules: Modern Trends. Seventh European Conference on Spectroscopy of Biological Molecules, Madrid.
- Fernandez-Liencres, M. P., Navarro, A., Lopez-Gonzalez, J. J., Fernandez-Gomez, M., Tomkinson, J. & Kearley, G. J. (2001). *Chem. Phys.* **266**, 1–17.
- Hughes, E. W. (1941). *J. Am. Chem. Soc.* pp. 63–70.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Larson, A. C. & Cromer, D. T. (1974). *J. Chem. Phys.* **60**, 185–192.
- Ma, H. A., Jia, X., Cui, Q. L., Pan, Y. W., Zhu, P. W., Liu, B. B., Liu, H. J., Wang, X. C., Liu, J. & Zou, G. T. (2003). *Chem. Phys. Lett.* **368**, 668–672.
- Meier, J. & Coussens, B. (1990). *J. Mol. Struct. Theochem.* **209**, 303–312.
- Meier, R. J., Maple, J. R., Hwang, M. J. & Hagler, A. T. (1995). *J. Phys. Chem.* **99**, 5445–5456.
- Price, P. F., Varghese, J. N. & Maslen, E. N. (1978). *Acta Cryst.* **A34**, 203–216.
- Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
- Schneider, J. R. & Schrader, B. J. (1975). *J. Mol. Struct.* **29**, 1–14.
- Shanker, J., Baljekar Prabhakar, N. & Prasad, M. (1939). *J. Indian Chem. Soc.* pp. 16–20.
- Stoe & Cie (2000). *DIF4* and *REDU4*. Stoe & Cie, Darmstadt, Germany.
- Varghese, J. N., O'Connell, A. M. & Laslen, E. N. (1977). *Acta Cryst.* **B33**, 2102–210.
- Wang, Y., Mebel, A. M., Wu, C., Chen, Y., Lin, C. & Liang J. (1997). *J. Chem. Soc. Faraday Trans.* **93**, 3445–3451.
- Wang, Y., Pittman, C. U. & Saebo, S. (1993). *J. Org. Chem.* **58**, 3085–3090.
- Watkin, D. J. (1994). *Acta Cryst.* **A50**, 411–437.
- Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper, R. I. (2001). *CRYSTALS*. Issue 11. Chemical Crystallography Laboratory, Oxford, England.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.