

(Küppers, 1973) the group is non-centrosymmetric while in $(\text{NH}_4)_4\text{UO}_2(\text{C}_2\text{O}_4)_3$ (Alcock, 1973) the ends of the oxalate groups are twisted relative to each other by 37° . The oxalate groups in the present compound are almost planar [the sums of the angles at C(1) and C(2) are 360° within experimental error and the dihedral angle between the plane containing O(1), C(1), and O(2) and the plane containing O(3), C(2) and O(4) is 176.1°] but non-centrosymmetric. The bond distances and angles for the oxalate groups in $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$ are very similar to those found in other crystal structures. It is, however, interesting that the longest C–O bonds are to the oxygen atoms forming the longer of the two Sn–O bonds.

One of us (M. T. D.) is grateful to the International Tin Research Council for a studentship.

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The Crystal and Molecular Structure of Trihydrazinotriazine

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(Received 24 December 1975; accepted 9 February 1976)

The crystal structure of trihydrazinotriazine, $\text{C}_3\text{N}_3(\text{NHNH}_2)_3$, has been determined by Patterson and trial-and-error methods and refined to a conventional R of 0.087 for 632 observed reflexions. Crystals are monoclinic, Cc , with $a = 3.625$ (1), $b = 17.603$ (4), $c = 11.026$ (2) Å and $\beta = 101.93$ (2)°; $Z = 4$. Individual molecules are hydrogen-bonded to neighbouring molecules to form a planar ribbon-like structure with the ribbons connected to one another by normal van der Waals contacts. One particularly close N–H...N hydrogen bond of 2.83 (2) Å is reported.

Introduction

Trihydrazinotriazine (THT) is used commercially as a blowing agent for producing plastic foams since its thermal decomposition yields gaseous products. As part of a kinetic study of the decomposition of a number of blowing agents, the crystal structure of

THT has been determined in order to provide structural evidence for the mechanism of decomposition.

Experimental

Commercial THT (Fisons) was recrystallized from aqueous solution to give colourless crystals in the

form of small platelets. Many of these crystals were twinned but eventually a single crystal suitable for X-ray analysis was found.

Crystal data

Formula $C_3H_9N_9$, M.W. 171.17

Unit cell: monoclinic

$a = 3.625$ (1) Å $Z = 4$

$b = 17.603$ (4) $D_m = 1.645$ g cm⁻³ (by flotation)

$c = 11.026$ (2) $D_x = 1.651$

$\beta = 101.93$ (2)° $F(000) = 360$

$U = 688.45$ Å³

Space group: Absent reflexions: hkl when $h+k$ odd, $h0l$ when l odd. $C2/c$ (No. 15) or Cc (No. 9). Since the $\bar{1}$ or 2 point group symmetry in the molecule required by $C2/c$ is theoretically impossible, Cc was chosen.

Radiation: Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 1.36$ cm⁻¹.

Crystal size: $0.50 \times 0.27 \times 0.02$ mm.

Intensities

The intensities and refined cell dimensions were obtained from a Hilger and Watts four-circle diffractometer using an $\omega/2\theta$ scan and Mo $K\alpha$ radiation. Reflexions were measured to $\sin \theta \leq 0.5$. Out of the 1008 reflexions measured, 376 had intensities less than 3σ of the background and were classed as unobserved. Lorentz and polarization corrections were applied to the net intensity counts but no corrections were made for absorption or extinction.

Structure determination

The orientation of the six-membered triazine ring was found from the $0kl$ weighted reciprocal lattice and from a three-dimensional Patterson synthesis. The position of the ring along the y axis was determined from the minimum R obtained when the molecule was moved in small increments along y . Full-matrix

least-squares refinement of the positional and isotropic thermal parameters of the six ring atoms yielded a conventional R of 0.303. The positions of the three pairs of nitrogen atoms constituting the side groups were found from a three-dimensional Fourier synthesis. Inclusion of these six atoms in the structure reduced R to 0.196, and further refinement, allowing anisotropic motion for the atoms, converged at $R = 0.102$. At this stage a difference map was computed which, although showing rather diffuse features, led to the placing of the nine hydrogen atoms in regions of high electron density (ca 0.6 e Å⁻³). These positions were also compatible with theoretical considerations. The hydrogen atoms with estimated isotropic temperature factors were included in the final rounds of refinement (but not refined) and convergence was reached with $R = 0.087$. The following weighting scheme was used

Table 1. Atomic coordinates ($\times 10^4$) and their *e.s.d.*'s

The x and y coordinates of C(1) were fixed in order to define the origin.

	x	y	z
N(1)	6285 (62)	3523 (5)	3296 (13)
N(2)	6963 (60)	2275 (5)	2459 (15)
N(3)	5301 (54)	2424 (5)	4452 (12)
N(10)	7928 (54)	3345 (5)	1413 (12)
N(20)	5831 (58)	1241 (6)	3646 (13)
N(30)	4687 (57)	3601 (6)	5224 (13)
N(11)	8505 (63)	4128 (5)	1246 (14)
N(22)	6636 (64)	705 (6)	2786 (15)
N(33)	3819 (66)	4377 (6)	5065 (14)
C(1)	7052	3035 (6)	2430
C(2)	6006 (70)	2006 (7)	3486 (15)
C(3)	5446 (54)	3174 (6)	4280 (14)
H(11)	8562	3074	924
H(12)	10214	4270	1895
H(13)	6478	4364	1453
H(21)	5609	1059	4438
H(22)	8927	795	2752
H(23)	4815	782	2005
H(31)	3334	3320	5794
H(32)	1289	4369	4522
H(33)	5677	4653	4765

Table 2. Thermal parameters ($\times 10^4$) and their *e.s.d.*'s

The parameters refer to the equations $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$ and $\exp[-8\pi^2U \sin^2 \theta/\lambda^2]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	548 (40)	148 (24)	218 (27)	-128 (27)	146 (26)	-65 (22)
N(2)	465 (40)	195 (25)	192 (24)	-35 (28)	163 (26)	-21 (22)
N(3)	673 (52)	222 (26)	179 (26)	-16 (30)	201 (30)	22 (21)
N(10)	773 (56)	185 (24)	219 (28)	-63 (32)	281 (33)	-41 (22)
N(20)	888 (65)	270 (32)	227 (32)	-92 (36)	273 (35)	-46 (26)
N(30)	724 (51)	224 (27)	191 (28)	10 (29)	213 (31)	-29 (25)
N(11)	773 (61)	217 (29)	352 (34)	5 (32)	228 (38)	14 (26)
N(22)	830 (60)	268 (33)	361 (35)	-19 (36)	300 (39)	-44 (28)
N(33)	977 (72)	240 (32)	396 (42)	38 (36)	340 (44)	-12 (28)
C(1)	375 (44)	311 (34)	137 (27)	140 (34)	46 (27)	59 (28)
C(2)	389 (43)	250 (32)	239 (31)	44 (31)	131 (29)	6 (27)
C(3)	470 (51)	198 (29)	241 (31)	66 (33)	126 (31)	55 (27)
	U		U		U	
H(11)	400		H(21)	400	H(31)	400
H(12)	500		H(22)	500	H(32)	500
H(13)	500		H(23)	500	H(33)	500

in the final stages: $w=1/\{1+[(F_o-B)/A]^2\}$, with $A=7.0$ and $B=12.0$. Unobserved reflexions calculating less than their measured value and reflexions with weighted differences greater than 4.0 were not included in the least-squares matrix. There were 692 reflexions contributing to the matrix in the final cycle of refinement. Out of the 376 unobserved reflexions, 61 calculated greater than the observed values and only 3 calculated 1.5 times the observed values. A final difference map showed a maximum electron density of $0.4 \text{ e } \text{Å}^{-3}$.

The scattering factors used for carbon, nitrogen and oxygen were those of Cromer & Mann (1968) and for hydrogen, those of Stewart, Davidson & Simpson (1965). Calculations were carried out using the LUX system of programs (Lee, 1971) on the Loughborough University ICL 1904A and X-RAY system (1972) as implemented at the University of Manchester Regional Computer Centre.

Results

The final atomic positional and thermal parameters together with their standard deviations are listed in Tables 1 and 2.* Fig. 1 shows the numbering systems for atoms in the asymmetric unit and Table 3 gives a key denoting the positions of symmetry-related atoms relative to their equivalents at x, y, z . Intramolecular bond lengths and angles are listed in Tables 4 and 5 and intermolecular contacts in Table 6.

Discussion

The crystal structure of THT comprises individual molecules which are linked to adjacent coplanar mol-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31676 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Key to symmetry relations with respect to the asymmetric unit x, y, z

i	$x+\frac{1}{2}$	$\frac{1}{2}-y$	$z-\frac{1}{2}$	vi	$x-1$	y	$1+z$
ii	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$z+\frac{1}{2}$	vii	$x-\frac{1}{2}$	$y+\frac{1}{2}$	$1+z$
iii	x	$1-y$	$z+\frac{1}{2}$	viii	x	$1-y$	$z-\frac{1}{2}$
iv	$x+\frac{1}{2}$	$y+\frac{1}{2}$	z	ix	$x-\frac{1}{2}$	$y+\frac{1}{2}$	z
v	$x+\frac{1}{2}$	$1-y$	$z+\frac{1}{2}$				

Table 7. Some close reported values of N...N intermolecular contacts

Compound	N...N (Å)	Reference
Imidazole	2.86	Martínez-Carrera (1966)
Purine	2.85	Watson, Sweet & Marsh (1965)
Hydrazinium hydrogen oxalate	2.85	Ahmed, Liminga & Olovsson (1968)
Triazole	2.82	Goldstein, Ladell & Abowitz (1969)
9-Ethylguanine	2.85, 2.78	Destro, Kistenmacher & Marsh (1974)
DL-Histidine	2.85	Eding & Harding (1974)
1-(4-Imidazolylsulphonyl)-4-phenylimidazole	2.87	Guggenberger (1975)

Table 4. Intramolecular bond lengths (Å) and their e.s.d.'s

C(1)—N(1)	1.355 (16)	N(20)—H(21)	0.949
C(1)—N(2)	1.339 (14)	N(20)—N(22)	1.410 (21)
C(1)—N(10)	1.343 (16)	N(30)—H(31)	1.004
C(2)—N(2)	1.338 (26)	N(30)—N(33)	1.405 (16)
C(2)—N(3)	1.362 (22)	N(11)—H(12)	0.880
C(2)—N(20)	1.361 (16)	N(11)—H(13)	0.913
C(3)—N(1)	1.336 (23)	N(22)—H(22)	0.854
C(3)—N(3)	1.336 (14)	N(22)—H(23)	0.980
C(3)—N(30)	1.357 (22)	N(33)—H(32)	0.986
N(10)—H(11)	0.789	N(33)—H(33)	0.944
N(10)—N(11)	1.412 (14)		

Table 5. Intramolecular bond angles (°) and their e.s.d.'s

C(1)—N(1)—C(3)	113.3 (9)
C(1)—N(2)—C(2)	112.7 (1.2)
C(2)—N(3)—C(3)	113.8 (1.4)
C(1)—N(10)—N(11)	124.9 (1.3)
C(1)—N(10)—H(11)	118.5
N(11)—N(10)—H(11)	115.4
C(2)—N(20)—N(22)	123.6 (1.6)
C(2)—N(20)—H(21)	117.9
N(22)—N(20)—H(21)	117.5
C(3)—N(30)—N(33)	121.2 (1.4)
C(3)—N(30)—H(31)	114.2 (1.1)
N(33)—N(30)—H(31)	115.6
N(10)—N(11)—H(12)	105.6
N(10)—N(11)—H(13)	105.2
H(12)—N(11)—H(13)	97.8
N(20)—N(22)—H(22)	104.1
N(20)—N(22)—H(23)	107.6
H(22)—N(22)—H(23)	114.9
N(30)—N(33)—H(32)	102.6
N(30)—N(33)—H(33)	112.7
H(32)—N(33)—H(33)	115.8
N(1)—C(1)—N(2)	127.4 (1.0)
N(1)—C(1)—N(10)	116.7 (1.1)
N(2)—C(1)—N(10)	115.9 (1.0)
N(2)—C(2)—N(3)	126.5 (1.1)
N(2)—C(2)—N(20)	119.1 (1.5)
N(3)—C(2)—N(20)	114.3 (1.5)
N(1)—C(3)—N(3)	126.3 (1.4)
N(1)—C(3)—N(30)	118.9 (1.0)
N(3)—C(3)—N(30)	114.7 (1.5)

Table 6. Hydrogen bonds and closest intermolecular contacts

	A—B	Distance (Å)	$\angle AHB(^{\circ})$
1	N(20)—N(11 ⁱⁱ)	3.22 (2)	162
2	N(3)—N(10 ⁱⁱ)	2.83 (2)	168
3	N(30)—N(2 ⁱⁱ)	3.23 (2)	163
4	N(33)—N(22 ⁱⁱ)	3.26 (3)	107
5	N(11)—N(22 ^{iv})	3.33 (2)	127
6	N(11)—N(33 ^{viii})	3.25 (2)	116
7	N(33)—N(22 ^{ix})	3.40 (2)	103

ecules by hydrogen bonds to form infinite ribbons. These ribbons run parallel to *c* and perpendicular to *b* and they are inclined to (100) at an angle of 16.8°. The molecules themselves are approximately planar as evidenced by the least-squares plane through the non-hydrogen atoms [Table 8(a)]. A least-squares plane was also calculated through non-hydrogen atoms in the asymmetric unit and those in the adjacent molecule at $x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$ (ii) as shown in Table 8(b). There is no significant difference between this plane and that calculated for the asymmetric unit alone. Fig. 2 shows a projection of the structure down *a*; the intermolecular contacts linking the molecules to form the ribbons are numbered 1–4. Reference to Table 6 indicates that three of these contacts are definite hydrogen bonds with the hydrogen atoms lying close to the line joining the two nitrogen atoms. The contact between N(3) and N(10ⁱⁱ) of 2.83 (2) Å is one of the closest N...N contacts reported, although it agrees well with some other values quoted in the literature as shown in Table 7. The position of the hydrogen atom in the fourth contact between N(33) and N(22ⁱⁱ) appears to be unfavourably placed for hydrogen bonding and therefore one must conclude that this constitutes a normal van der Waals interaction.

The ribbons are held together by close contacts between terminal NH₂ groups, each group being in-

Table 8(a). *Least-squares plane through the non-hydrogen atoms of the molecule in the asymmetric unit*

The equation is expressed as:

$$3.180X + 0.028Y + 3.178Z = 3.034,$$

where *X*, *Y* and *Z* refer to the real cell dimensions.

Delta (Å)		Delta (Å)	
N(1)	0.016	N(11)	0.078
N(2)	-0.032	N(22)	-0.037
N(3)	0.073	N(33)	-0.198
N(10)	-0.055	C(1)	-0.011
N(20)	-0.018	C(2)	-0.011
N(30)	0.127	C(3)	0.067

Table 8(b). *Least-squares plane through the non-hydrogen atoms of the molecule in the asymmetric unit and the molecule at $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$ (ii)*

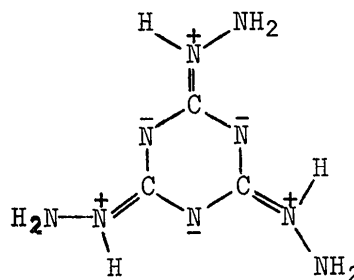
The equation is expressed as:

$$3.180X + 0.000Y + 3.180Z = 3.027.$$

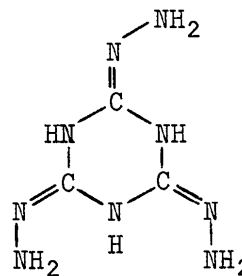
Delta (Å)		Delta (Å)	
N(1)	0.013	N(1 ⁱⁱ)	0.014
N(2)	-0.031	N(2 ⁱⁱ)	-0.031
N(3)	0.075	N(3 ⁱⁱ)	0.075
N(10)	-0.057	N(10 ⁱⁱ)	-0.057
N(20)	-0.013	N(20 ⁱⁱ)	-0.013
N(30)	0.125	N(30 ⁱⁱ)	0.125
N(11)	0.074	N(11 ⁱⁱ)	0.074
N(22)	-0.031	N(22 ⁱⁱ)	-0.031
N(33)	-0.202	N(33 ⁱⁱ)	-0.202
C(1)	-0.011	C(1 ⁱⁱ)	-0.011
C(2)	-0.008	C(2 ⁱⁱ)	-0.008
C(3)	0.066	C(3 ⁱⁱ)	0.066

involved in two contacts. There are three crystallographically unique contacts of this type and these are numbered 5–7 in Table 6. The positions of the hydrogen atoms attached to the NH₂ groups are restricted by bonding considerations and no hydrogen atoms are favourably positioned for hydrogen bonding.

Intramolecular bond lengths and angles are summarized in Tables 4 and 5. The C–N bond lengths are very similar to those found in melamine by Hughes (1941). The C–N bond lengths of the side groups are of the same order as those in the ring, suggesting contributions from structures of the type:



There were no regions of high electron density near to the ring nitrogen atoms to suggest the possibility of the imide form, *viz*:



The N–N bond lengths are slightly shorter than the normally accepted value of 1.45 Å for a N–N single bond (Sidgwick, Millar & Springall, 1966; *Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965) although shorter values have been found (Tomiie, Koo & Nitta, 1958; Lepicard, Berthou, Deletré, Laurent & Mornon, 1973). The apparent shortening observed in the present case presumably derives from the reduction in lone-pair repulsive forces caused by the slight positive charge on the NH group.

The structure is characterized by an abnormal amount of anisotropic thermal motion, with the greatest amount of thermal vibration in the *a** direction. This direction corresponds to that where there are the least number of close contacts, thus allowing greatest freedom for molecular libration in this direction.

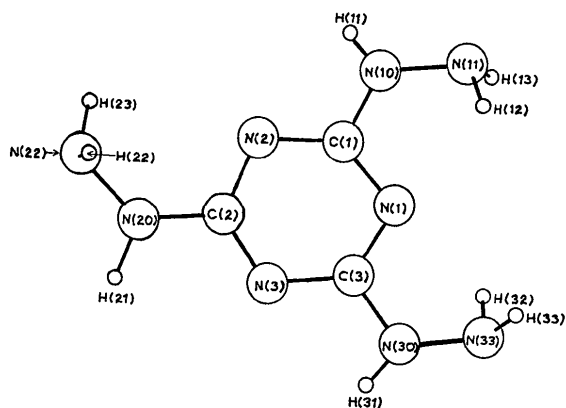


Fig. 1. Numbering system of the atoms in trihydrazinotriazine.

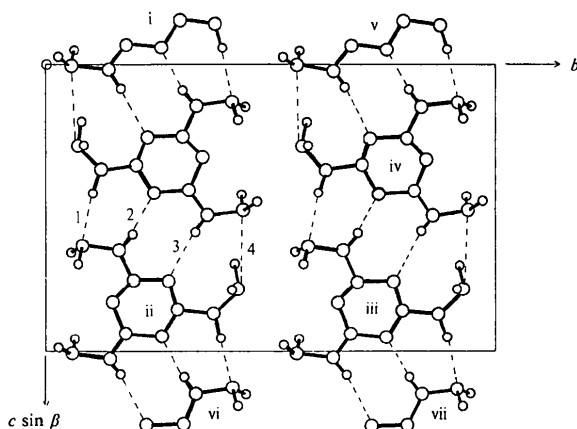


Fig. 2. Projection of the structure down a showing molecules hydrogen-bonded together to form a ribbon-like structure.

We are extremely grateful to Professor T. J. King for assistance in the data collection and for the use of the diffractometer at Nottingham University, and to Fisons Ltd for a support grant (to P.R.R.).

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