parison of this pattern with those found for other halogenated purines (Bugg, 1972).

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The X-ray and Neutron Crystal Structure of 2,4,6-Triamino-1,3,5-triazine (Melamine)

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The crystal structure of 2,4,6-triamino-1,3,5-triazine has been investigated with extensive three-dimensional X-ray ($\sin\theta/\lambda < 0\cdot91$) and neutron ($\sin\theta/\lambda < 0\cdot84$ Å^{-1}) diffraction data. The structure is significantly non-planar with the amine groups deviating by up to 0·10 Å from the mean plane through the ring. The molecule does not behave like a rigid body, the out-of-plane mean-square amplitudes of the ring nitrogens being about 12% greater than those of the C atoms. The positional parameters for the C and N atoms from the X-ray refinement are generally similar to the neutron values, but the thermal parameters for these atoms show a systematic bias as a result of the neglect of the non-spherical symmetry of the valence density. The X-ray H positions are displaced along the N–H bonds by amounts which, while generally similar to those reported for similar systems, are also related to the internal modes of vibration in the structure. The internal motions of the H atoms, as indicated by the differences between thermal ellipsoids for the H and amine N atoms, are related to the hydrogen bonding. The amplitudes for the hydrogen-bonded atoms are relatively lower normal to the N–H bonds, and larger in the directions corresponding to the N–H stretching mode. This exaggerates the foreshortening of the N–H bonds, as has been predicted by Coulson & Thomas [*Acta Cryst.* (1971), B**27**, 1354–1359].

Introduction

The crystal structure of melamine was previously determined by Hughes (1941) from projection data. The present reinvestigation, with both X-ray and neutron diffraction data, was undertaken to obtain more accurate structural information prior to a study of the valence-electron distribution. Larson & Cromer (1974) have refined an X-ray structure of the molecule which included parametrization of the electron density. However, that work was concerned mainly with the relationship between the redistribution of electron density as a result of bonding and structural parameters. Electron density models for molecular crystals have improved considerably since that time, and detailed discussion of the earlier results is not warranted. Two properties of the melamine structure make it ideal for such an analysis. Crystals of melamine grow as hard three-dimensional prisms, with low thermal parameters at room temperature, so that Bragg reflexions are observed at high angles. The free molecule of melamine has $\bar{6}m2$ symmetry which is not utilized in the packing in the crystal. The symmetry is approximately conserved within the molecular unit of the structure, which provides an internal check on the consistency of the results, and a guide to the magnitude of the effects resulting from intermolecular force.

X-ray analysis

Crystals of melamine, prepared by evaporation of a water solution in a temperature-controlled environment, were monoclinic prismatic with development of (011), (110) and (001) faces. The space group determined as $P2_1/a$ by Hughes was confirmed, and the original cell constants are also in fairly good agreement with those determined (Table 1) by a least-squares analysis of the angular coordinates for twelve reflexions measured on a Picker FACS-1 diffractometer (λ = 0·71069 Å).

The intensity measurements were made with Zr-filtered Mo $K\alpha$ radiation, the $\omega/2\theta$ scan technique and a continuous scan rate of 0·5° min^{-1}. The scan range at low Bragg angles ($2\theta < 7°$) was set at 0·9° and for larger angles was increased from a minimum of 1·3° to account for the increased α_1–α_2 dispersion at higher Bragg angles. Stationary background counts of 40 s were made at the beginning and end of each scan. 3316 reflexions having $2\theta < 80°$ ($\sin\theta/\lambda < 0{\cdot}91$) were recorded.

The dimensions of the crystal listed in Table 2 were used to estimate absorption corrections by the Gaussian integration method (Busing & Levy, 1957), with 48 sample points and an absorption coefficient of 1·2733 cm^{-1} (*International Tables for X-ray Crystallography*, 1962).

Table 1. *Melamine crystal data*

$C_3N_6H_6$, 2,4,6-triamino-1,3,5-triazine (melamine)
Space group $P2_1/a$ (monoclinic)
Unit-cell constants: a = 10·606 (1), b = 7·495 (1), c = 7·295 (1) Å, β = 112·26 (2)°
U = 536·68 Å^3
Z = 4
μ = 1·273 cm^{-1} for Mo $K\alpha$
μ = 2·161 cm^{-1} for neutrons, λ = 0·981 Å

Table 2. *Melamine crystal dimensions*

Face indices	D* (neutron)	D* (X-ray)
$0\;1\;1$ $0\;\bar{1}\;\bar{1}$	0·1905 cm	0·0144 cm
$0\;1\;\bar{1}$ $0\;\bar{1}\;1$	0·1803	0·0144
$1\;\bar{1}\;0$ $\bar{1}\;1\;0$	0·2159	0·0160
$1\;1\;0$ $\bar{1}\;\bar{1}\;0$	0·3149	0·0152
$1\;0\;\bar{1}$ $\bar{1}\;0\;1$	–	0·0296
$\bar{5}\;0\;1$	0·3822	–

* Distance from crystal centre.

The structure was refined with block-diagonal least-squares techniques to minimize the function $\Sigma w(F_o^2 - F_c^2)^2$. Weights were calculated directly from counting statistics according to Evans (1961). Scattering factors of Cromer & Mann (1968) were used for C and N, and the bonded atomic-scattering factors of Stewart, Davidson & Simpson (1965) were used for H. After locating the H atoms, the parameters varied were the positions and anisotropic thermal parameters for C and N, and the positions and isotropic thermal parameters for H. During the final stages of the structure refinement, the isotropic extinction factor (Zachariasen, 1969) was varied, together with anisotropic H thermal parameters. The refinement was well behaved throughout and the H thermal parameters are physically reasonable, although the standard deviations are large, as expected. After convergence, the residual $R(F) = \Sigma\, w|F_o - F_c|/\Sigma|F_o|$ was 0·056.† The final extinction factor r^* was 0·696 × 10^{-4} cm. The resulting atomic positional parameters are listed in Table 3.

Neutron analysis

The large crystal needed for a neutron diffraction study was prepared by slow cooling of a saturated solution in water, starting at about 60°C and reducing the temperature by 0·25°C at half-hourly intervals. The dimensions of the crystal used are listed in Table 2. The ($\bar{5}01$) face corresponds to a portion of the sample that was cut away with an air abrasive unit.

The intensity profiles were measured with an auto-

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† Lists of structure factors for both X-ray and neutron determinations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32405 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

matic four-circle diffractometer situated at post 2TAN of the reactor HIFAR operated by The Australian Atomic Energy Commission at Lucas Heights, New South Wales. The incident neutron beam, obtained by reflexion from the (111) planes of a Cu crystal, had a measured wavelength of 0·981 Å and a flux of approximately 5 × 10^5 neutrons cm^{-2} s^{-1}. The profiles were recorded by the $\omega/2\theta$ scan technique in the symmetric configuration, with the detector stepped in increments of 0·04° of arc over a range of 5°. 160 steps were taken over the peak, increasing to 200 steps at higher 2θ angles. Two separate background counts were taken on either side of the peak for a time sufficient to ensure reliable statistics. Careful analysis of 20 reflexions showed that the cell parameters from the X-ray analysis (Table 1) were acceptable within the precision of the settings of the diffractometer circles. These cell parameters were adopted throughout the analysis.

5473 reflexions were collected, of which 2647 were unique and in the range $0·0741 < \sin\theta/\lambda < 0·8401$. The reflexion $8\bar{5}1$ was measured after every 20 reflexions as a standard during the data collection. Results showed that the counting system was effectively stable during the data collection, indicating that little radiation degradation of the crystal took place. Higher-angle data were inaccessible as a result of limitations imposed by the reactor-shield wall. A linear absorption coefficient of 2·161 cm^{-1} was determined experimentally with a flat crystal specimen of known thickness. The background appeared to be little affected by thermal diffuse scattering, and was an approximately linear function of 2θ. After subtracting the background and correction for the Lorentz factor, the absorption corrections were determined by the Gaussian integration method with 125 points in a volume enclosed by the faces listed in Table 2.

The equivalent reflexions were averaged and the final estimate of variance, $\sigma(F^2)$, for F^2 was determined from $\sigma^2(F^2) = \sigma_1^2(F^2) + \sigma_2^2(F^2) + \Delta\sigma_3^2(F^2)$, where $\sigma_1^2(F^2)$ is the variance purely from counting statistics, $\sigma_2^2(F^2)$ is the variance arising from error in the absorption coefficient, and $\Delta\sigma_3^2(F^2)$ is obtained from the dif-

Table 3. *X-ray coordinates and thermal parameters* (× 10^4)

$$T=\exp\{-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)\}.$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1728 (1)	6540 (1)	738 (1)	266 (3)	198 (3)	265 (3)	24 (2)	159 (2)	31 (2)
C(2)	1213 (1)	5154 (1)	3132 (1)	263 (3)	193 (3)	264 (3)	12 (2)	153 (2)	40 (2)
C(3)	634 (1)	8049 (1)	2400 (1)	241 (3)	185 (3)	242 (3)	12 (2)	130 (2)	11 (2)
N(4)	2238 (1)	6496 (1)	−681 (1)	469 (4)	252 (3)	370 (4)	86 (3)	314 (3)	77 (2)
N(5)	1232 (1)	3697 (1)	4213 (1)	437 (4)	224 (3)	414 (4)	76 (2)	295 (3)	118 (2)
N(6)	118 (1)	9611 (1)	2771 (1)	377 (3)	206 (3)	327 (3)	67 (2)	215 (3)	27 (2)
N(7)	602 (1)	6626 (1)	3492 (1)	317 (3)	197 (3)	293 (3)	26 (2)	201 (2)	38 (2)
N(8)	1164 (1)	8094 (1)	993 (1)	312 (3)	190 (2)	283 (3)	38 (2)	194 (2)	50 (2)
N(9)	1813 (1)	5043 (1)	1808 (1)	348 (3)	191 (3)	329 (3)	53 (2)	231 (3)	57 (2)
H(1)	2285 (17)	7426 (17)	−1223 (21)	1130 (129)	585 (82)	454 (86)	420 (87)	584 (91)	67 (68)
H(2)	2669 (12)	5518 (13)	−777 (18)	760 (94)	127 (49)	571 (77)	85 (62)	518 (73)	65 (57)
H(3)	1511 (18)	2652 (15)	3841 (24)	1547 (169)	259 (71)	1117 (139)	296 (94)	1108 (137)	437 (85)
H(4)	764 (15)	3689 (13)	4980 (18)	1149 (132)	374 (68)	471 (83)	453 (82)	718 (93)	281 (64)
H(5)	−485 (15)	9383 (18)	3386 (18)	730 (109)	861 (98)	466 (83)	−339 (82)	503 (82)	−296 (72)
H(6)	121 (16)	10431 (15)	1745 (19)	957 (123)	314 (70)	382 (73)	223 (76)	318 (79)	152 (63)

Table 4. *Neutron coordinates and thermal parameters* (× 10^4)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1729 (1)	6538 (1)	743 (2)	266 (5)	188 (4)	245 (5)	31 (3)	164 (4)	43 (3)
C(2)	1213 (1)	5152 (1)	3139 (2)	259 (6)	160 (4)	249 (5)	24 (3)	153 (3)	39 (3)
C(3)	635 (1)	8047 (1)	2400 (2)	240 (4)	161 (4)	220 (4)	13 (3)	133 (3)	18 (3)
N(4)	2242 (1)	6499 (1)	−682 (2)	457 (6)	249 (4)	358 (5)	84 (3)	304 (4)	66 (3)
N(5)	1231 (1)	3697 (1)	4211 (2)	414 (5)	223 (4)	409 (5)	73 (3)	283 (4)	118 (3)
N(6)	116 (1)	9601 (1)	2765 (1)	368 (5)	201 (4)	304 (4)	66 (3)	197 (3)	19 (2)
N(7)	604 (1)	6623 (1)	3491 (1)	318 (4)	192 (4)	269 (4)	27 (2)	197 (3)	36 (2)
N(8)	1164 (1)	8095 (1)	993 (1)	296 (4)	177 (4)	274 (4)	31 (2)	189 (3)	49 (2)
N(9)	1812 (1)	5043 (1)	1808 (1)	335 (4)	181 (4)	317 (4)	59 (2)	224 (3)	59 (2)
H(1)	2409 (1)	7695 (4)	−1239 (5)	622 (12)	349 (12)	489 (15)	88 (12)	403 (14)	130 (11)
H(2)	2712 (4)	5376 (4)	−852 (6)	592 (18)	356 (17)	529 (17)	108 (12)	370 (15)	27 (11)
H(3)	1610 (6)	2558 (5)	3913 (8)	952 (31)	296 (12)	755 (26)	238 (16)	585 (25)	183 (15)
H(4)	646 (4)	3647 (4)	5050 (6)	532 (16)	377 (13)	488 (15)	62 (11)	338 (13)	132 (11)
H(5)	−538 (4)	9487 (5)	3449 (6)	615 (20)	434 (15)	569 (19)	112 (13)	436 (17)	33 (13)
H(6)	−186 (4)	10509 (4)	1630 (5)	567 (17)	313 (11)	470 (15)	140 (11)	287 (13)	102 (10)

ferences ΔF^2 between equivalent reflexions measured in the form $(\alpha + \beta F^2 + \gamma F^4)$ by a least-squares fit of the quadratic to $[(\pi/2)(\Delta F^2)^2 - \sigma_1^2(F^2)]$. The fit was poor when very strong reflexions were included in the refinement (this probably arises from extinction effects), but on removing them from the fit, effects arising from error in the absorption coefficient were predominant. The values of the quadratic were determined as: $\alpha = -0{\cdot}2846$, $\beta = 0{\cdot}00435$ and $\gamma = -0{\cdot}00023$.

The scattering lengths for C, N and H were fixed at 6·61, 9·41 and −3·78 fm respectively (Bacon, 1962). The atomic parameters of the X-ray structure were used as starting parameters for the minimization of the quantity $\Sigma\, w(F_o^2 - F_c^2)^2$, where the weights w are set equal to $1/\sigma^2(F^2)$. All the unique reflexions were included in the refinement.

The scale, positions and anisotropic thermal parameters were refined with full-matrix techniques in the final stages of the refinement. The Zachariasen extinction correction was applied, with the extinction factor r^* refined, and, as expected, considerable extinction was present in the data. The final refinement statistics were $R(F) = 0{\cdot}050$ and $\chi^2 = 3{\cdot}15$. The final atomic positional parameters with their e.s.d.'s obtained from the least-squares matrix are listed in Table 4.† The extinction parameter was refined to a value of 0·467 (5) × 10^{-4} cm.

Discussion

The molecular geometry is broadly in agreement with that previously reported by Hughes, but the increased accuracy of the present work allows a more detailed analysis of the molecular dimensions. The neutron (NR) parameters are preferred to the X-ray parameters, because they are not affected by systematic errors arising from the non-spherical symmetry of the valence electrons.

The locations of the four molecules in the unit cell are indicated (with atom labels) in Fig. 1. Least-squares planes through the molecule are given in Table 5. The molecule is significantly non-planar. The ring has a small amount of boat character and the amine groups deviate from the least-squares plane through the six ring atoms by up to 0·10 Å. The three C—N bonds to each of the ring C atoms are approximately coplanar with the ring, but in each case the H atoms deviate significantly from the ring plane. The best planes through the amine groups are inclined at angles between 0·7° and 3·0° to the ring plane. The amine groups at N(4) and N(5) are close to trigonal, but the group at N(6) has a large amount of pyramidal character, which is clearly illustrated in Fig. 1. For the last group the H atoms deviate from the plane through N(6), C(3), N(7) and N(8) by about 0·33 Å and the mean angle subtended at N(6) is 114°.

Bond lengths and angles for the X-ray and neutron structures are shown in Figs. 2 and 3 respectively. The ring is significantly distorted from the ideal hexagonal form. Within the ring the mean N—C—N and C—N—C angles are 114·6 and 125·4° respectively. In *s*-triazine (Coppens, 1967) the corresponding angles are both 113·2°. The lengths of the C—NH_2 bonds appear to depend on the configuration of the amine groups. The two C—N bonds associated with N(4) and N(5) are

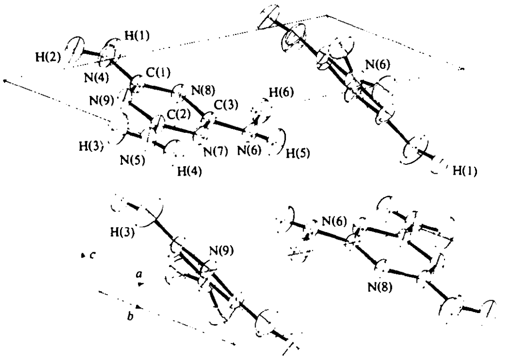

Fig. 1 Molecules in the melamine unit cell (neutron parameters).

Table 5. *Displacements from least-squares planes* (Å)

Equations of planes in direct space

Plane 1 $7{\cdot}029X + 2{\cdot}189Y + 2{\cdot}824Z = 2{\cdot}871$
Plane 2 $7{\cdot}294X + 2{\cdot}236Y + 2{\cdot}568Z = 2{\cdot}914$
Plane 3 $6{\cdot}927X + 2{\cdot}202Y + 2{\cdot}907Z = 2{\cdot}890$
Plane 4 $7{\cdot}281X + 1{\cdot}849Y + 2{\cdot}721Z = 2{\cdot}612$

Plane 1		Plane 2		Plane 3	
C(1)	−0·015	C(1)	−0·001	C(2)	−0·003
C(2)	−0·005	N(4)	0·000	N(5)	0·001
C(3)	0·015	N(8)	0·000	N(7)	0·001
N(4)*	−0·065	N(9)	0·000	N(9)	0·001
N(5)*	−0·007	H(1)*	0·246	H(3)*	−0·074
N(6)*	0·095	H(2)*	0·048	H(4)*	−0·172
N(7)	−0·011				
N(8)	−0·001	Plane 4			
N(9)	0·017				
H(1)*	0·157	C(3)	−0·008		
H(2)*	−0·028	N(6)	0·002		
H(3)*	−0·074	N(7)	0·003		
H(4)*	−0·193	N(8)	0·003		
H(5)*	−0·199	H(5)*	−0·310		
H(6)*	−0·241	H(6)*	−0·360		

Acute angle (°) between planes

	1	2	3	4
1	0·0			
2	2·17	0·0		
3	0·74	2·87	0·0	
4	2·95	3·22	3·40	0·0

* Not included in the plane calculations.

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† See previous footnote.

similar, while the distance to the pyrimidal group N(6) is 0·02 Å longer. Within the ring the two C—N bonds adjacent to C(3) are shorter than the other four ring bonds for the X-ray structure. This is consistent with larger contributions from valence structures having the double bond to the amine group N(6).

The hydrogen-bonding system proposed by Hughes has been confirmed by the location of the H atom positions. The relevant distances and angles associated with hydrogen bonding are shown in Table 6 for the NR structure. A schematic representation of the hydrogen-bonding configuration is indicated in Fig. 4. The four N · · · N distances vary from 3·02 to 3·12 Å, and the H · · · N distances from 2·05 to 2·11 Å. None of the angles at the H atoms differ from linearity by more than 14°. The angles of the acceptor N atoms (C—N · · · H) vary from 117 to 138° and have a mean value of 123°, which matches the trigonal position of the N lone-pair electrons relative to the ring C—N bonds.

Five other intermolecular contacts of 3·40 Å or less involving the C and N atoms are listed in Table 7. The amine N(6) is involved in four of these contacts, the shortest being 3·24 Å between N(6) and N(4). This accounts for the large deviation of N(6) from the ring plane and the overcrowding is responsible for the pyrimidal configuration of the H atoms.

The thermal ellipsoids (50% probability surfaces) indicating the magnitudes and directions, relative to the cell axes, of the vibration ellipsoids are included in Fig. 1. The major direction of vibration is approximately perpendicular to the plane of the ring in each case. However, the molecule does not vibrate simply as a rigid body, since the out-of-plane mean-square am-

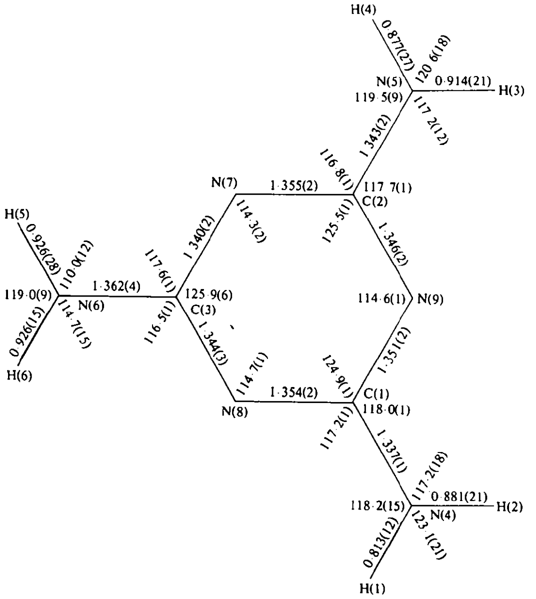

Fig. 2. X-ray bond lengths (Å) and angles (°).

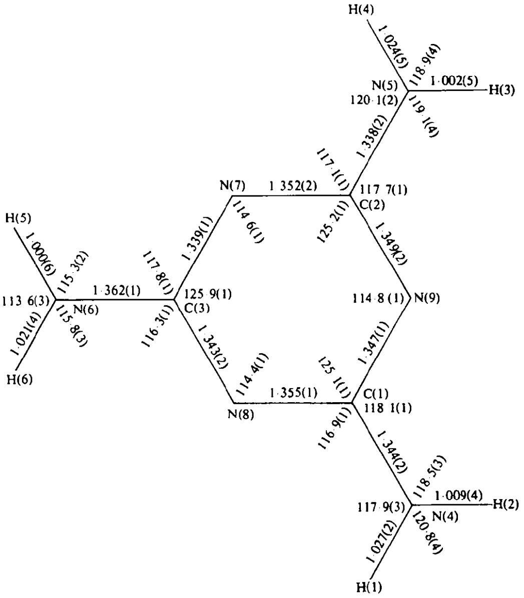

Fig. 3. Neutron bond lengths (Å) and angles (°).

Table 6. *Hydrogen-bond distances and angles, with e.s.d.'s in parentheses*

	N—H	N · · · N	H · · · N	N—H · · · N
$N(4)—H(1) \cdots N(9^{i})$	1·027 (2) Å	3·060 (1) Å	2·052 (4) Å	166·5°
$N(4)—H(2) \cdots N(8^{ii})$	1·009 (4)	3·116 (1)	2·110 (4)	174·6
$N(5)—H(4) \cdots N(7^{iii})$	1·024 (5)	3·021 (2)	2·000 (5)	174·6
$N(6)—H(6) \cdots N(8^{iv})$	1·021 (4)	3·082 (2)	2·080 (3)	166·1

The atoms of the different asymmetric units are related to the atoms of the fundamental unit by the following superscripts:

None x,y,z
(i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$
(ii) $\frac{1}{2}-x, -\frac{1}{2}+y, -z$
(iii) $-x, 1-y, 1-z$
(iv) $-x, 2-y, -z$
(v) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
(vi) $\frac{1}{2}+x, \frac{3}{2}-y, z$
(vii) $x, -1+y, z$
(viii) $-x, 2-y, 1-z$
(ix) $-\frac{1}{2}+x, \frac{3}{2}-y, z$

plitudes of the ring N atoms are about 12% larger than those of the C atoms. This corresponds to an internal buckling mode around the ring with the N atoms corresponding to antinodes and the C atoms to the nodes. Similar results were obtained by Coppens (1967) in analyses of *s*-triazine and cyanuric acid. For the amine groups the out-of-plane vibration of N(6) is 10% less than for N(4) and N(5), presumably as a result of rather tight intermolecular packing associated with N(6).

An analysis of the thermal parameters for the H atoms represented as the difference between their thermal ellipsoids and those of the amine N atoms to which they are bonded is shown in Table 8. The longest of these principal axes for these difference ellipsoids are nearly parallel to the normal of the plane formed by the amine N and H atoms, and the shortest parallel to the N–H bond. The mean-square amplitudes in these directions were estimated by projecting the difference ellipsoids onto the mutually orthogonal N–H bond direction, the plane normal and the plane perpendicular. These estimates, shown in Table 8, are clearly related to the hydrogen-bond environment of these atoms.

H(3) and H(5), which are not involved in hydrogen bonds, have large amplitudes perpendicular to the N–H bonds, but low amplitudes along the bonds. Tight packing in the vicinity of H(6) limits its motion generally. H(1), H(2) and H(4) are restricted to their motion normal to the ring plane by the hydrogen-bond system, but have a relatively high amplitude along the N–H bond, consistent with a lowering of the potential energy for displacement in the direction of the strong N–H · · · N hydrogen bonds.

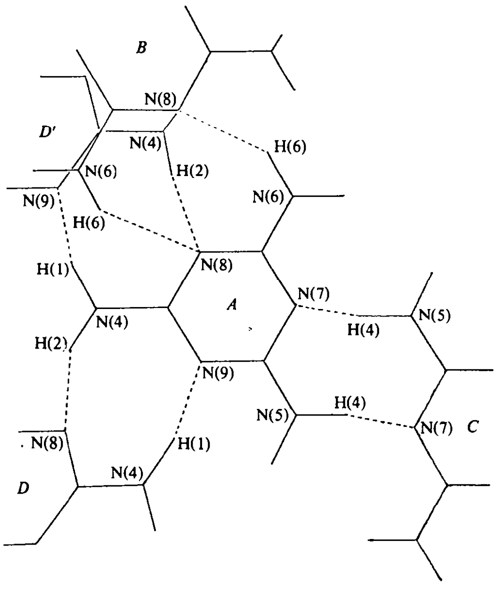

Fig. 4. An oblique projection of a portion of structure [adapted from Hughes (1941)] indicating the hydrogen bonding around molecule *A*. The normal to the plane of molecule *A* is the oblique axis. Molecules *A*, *B*, and *C* are parallel to the plane of projection, and molecules *D* and *D'* are inclined to it at 33°.

In comparing the X-ray and neutron structure refinements the differences in coordinates for the C and N atoms are rather small, and are certainly less than those observed with more restricted sets of X-ray data. There is some evidence for a shift of the amine N atoms along the C–N bonds, and for a displacement of the ring N atoms towards the lone pairs. These shifts, which are expected as a result of the redistribution of electron density due to bonding, are of the same order as the standard deviations. There are systematic differences in the thermal parameters for these atoms, which are generally larger in the X-ray structure.

The behaviour of the N–H bond lengths in the two analyses is of particular interest. The neutron N–H bond lengths involving the hydrogen-bonded atoms H(1), H(2), H(4) and H(6) are longer than those for H(3) and H(5), but the foreshortening of these bonds is larger for the longer bonds, so that the lengths in the two analyses are inversely correlated. This is not due directly to a redistribution of density associated with the hydrogen bonding since that would have an effect opposite to that observed.

The explanation of this effect is implicit in the observations of Coulson & Thomas (1971). These authors have shown that the motion of the H nucleus in an *X*–H bond produces a foreshortening of the bond, additional to that arising from the distribution of the electrons relative to the instantaneous position of the nucleus, when isotropic scattering factors are used to represent the H scattering. This additional foreshorten-

Table 7. *Non-bonded intermolecular contacts* (Å), *with e.s.d.'s in parentheses*

For symmetry code see Table 6.

C(3) · · · N(5^{v})	3·342 (1)	N(6) · · · N(6^{viii})	3·413 (2)
N(4) · · · N(6^{vi})	3·240 (1)	N(6) · · · N(9^{ix})	3·314 (1)
N(5) · · · N(6^{vii})	3·309 (1)		

Table 8. *Effect of hydrogen bonding on hydrogen thermal motion*

Excess thermal vibration in the direction of the orthogonal axes parallel to the bond, coplanar with the bond and ring normal, and the mutually perpendicular directions, are referred to as Bond, ⊥ and ∥ respectively, with e.s.d.'s in parentheses.

	Bond	⊥	∥
H(3)*	0·057 (14) Å	0·272 (11) Å	0·162 (6) Å
H(5)	0·062 (12)	0·210 (9)	0·166 (6)
H(2)	0·092 (8)	0·136 (14)	0·152 (6)
H(6)	0·086 (10)	0·177 (9)	0·133 (6)
H(1)	0·071 (10)	0·152 (12)	0·126 (6)
H(4)	0·092 (8)	0·119 (15)	0·137 (6)

* Atoms in order of increasing hydrogen-bond strength.

ing will be larger for the hydrogen-bonded H atoms in view of the larger motion of these atoms in the direction of the N—H bonds.

The X-ray data were collected with the assistance of the Crystallography Group of the University of Göteborg in Sweden. The neutron data were collected with the assistance of Dr F. H. Moore of the Australian Institute of Nuclear Science and Engineering at Lucas Heights in Sydney.

While most of the calculations were carried out on the University of Western Australia's PDP-6 and Cyber 72 computers with programs written by the authors, access to the XRAY system (1972) and the *ORTEP* plotting program of Johnson (1965) is gratefully acknowledged.

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Neutron Diffraction Refinement of Paraelectric $NaH_3(SeO_3)_2$

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A three-dimensional single-crystal neutron diffraction refinement of paraelectric sodium trihydrogen selenite has been made. The crystals are monoclinic, space group $P2_1/n$, with two formula units in a cell of dimensions $a = 10{\cdot}3428\,(8)$, $b = 4{\cdot}8372\,(3)$, $c = 5{\cdot}7876\,(3)$ Å, $\beta = 91{\cdot}162\,(5)°$. A full-matrix least-squares refinement based on F gave a final R value of 0·040. The structure consists of hydrogen-bonded chains of H_2SeO_3 molecules and $HSeO_3^-$ ions. The H atoms are disordered as a result of a statistical superposition of chains running in opposite directions.

Introduction

Sodium trihydrogen selenite has been the subject of a number of NMR and diffraction studies. One previous neutron diffraction study has been reported (Kaplan, Kay & Morosin, 1970; this paper should be consulted for further references). There has been some uncertainty as to whether the H atoms are disordered in double-minimum potential wells or are located in a single-minimum potential. Both types of interpretation of NMR results have been presented (Gavrilova-Podol'skaya, Gabuda & Lundin, 1967; Soda & Chiba, 1969; Blinc & Pirš, 1971; Silvidi & Workman, 1971). Kaplan *et al.* (1970), in their neutron diffraction study, came to the conclusion that one of the H atoms was probably disordered, whereas the other was situated in a shallow skew potential well. In this situation, the

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