Le réseau des liaisons hydrogène

Le Tableau 8 et la Fig. 2 présentent le réseau des liaisons hydrogène qui relient une molécule à ses voisines. Chaque molécule est associée à quatre autres par l'intermédiaire de huit liaisons hydrogène. Parmi celles-ci, les atomes d'oxygène O(1) et O(4) interviennent une fois, l'atome O(2) deux fois, l'atome O(3) trois fois. Les liaisons entre atomes de carbone et d'oxygène correspondantes croissent en longueur dans cet ordre. L'atome O(5) accepte une liaison hydrogène. Cet ensemble de liaisons assure une bonne cohésion des molécules au sein du réseau cristallin.

Tableau 8. *Liaisons hydrogène* (Å)

O(1)–HO(1) · · · O(5)	1,89 (3)	2,804 (2)	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$
O(2)–HO(2) · · · O(3)	2,01 (3)	2,761 (2)	$1-x, 2-y, -z$
O(2) · · · HO(3)–O(3)	2,14 (3)	2,755 (2)	$1-x, 1-y, -z$
O(3)–HO(3) · · · O(2)			$1-x, 1-y, -z$
O(3) · · · HO(2)–O(2)			$1-x, 2-y, -z$
O(3) · · · HO(4)–O(4)	2,19 (3)	2,948 (2)	$-x, 2-y, -z$
O(4)–HO(4) · · · O(3)			$-x, 2-y, -z$
O(5) · · · HO(1)–O(1)			$1-x, \frac{1}{2}+y, \frac{1}{2}-z$

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Stacking Patterns of Halogenated Purines: Crystal Structure of 8-Bromoinosine

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$C_{10}H_{11}N_4O_5Br$, orthorhombic, $P2_12_12_1$, $a = 39{\cdot}184\ (2)$, $b = 7{\cdot}9873\ (2)$, $c = 7{\cdot}6271\ (3)$ Å, $Z = 8$, $M_r = 347{\cdot}14$, $D_c = 1{\cdot}931$, $D_m = 1{\cdot}94$ g cm^{-3}, $\mu = 55{\cdot}4$ cm^{-1}. The structure was solved by use of 2321 independent reflections measured on an automated diffractometer, and was refined by least squares to $R = 0{\cdot}034$. The crystallographically independent purine moieties are stacked in a pattern that is mainly characterized by Br—purine contacts.

Introduction

Recent analyses of the base-stacking patterns in crystals of halogenated purines and pyrimidines have suggested that these systems generally display stacking patterns that involve intimate halogen–base interactions. These results have led to suggestions that similar stacking interactions may partially account for the unusual physical (Katritzky & Waring, 1962; Berens & Shugar, 1963) and biological (Brockman & Anderson, 1963) properties of polynucleotides that contain halogenated bases. We determined the crystal structure of 8-bromoinosine to obtain additional information about the base-stacking patterns of halogenated purines.

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Clear, needle-shaped crystals of 8-bromoinosine were obtained by slow cooling of a hot, aqueous solution. Oscillation and Weissenberg photographs showed the crystals to be orthorhombic, space group $P2_12_12_1$, as indicated by the systematic absence of reflections *h*00 with *h* odd, 0*k*0 with *k* odd and 00*l* with *l* odd. A crystal, with approximate dimensions 0·11 × 0·10 × 0·07 mm, was mounted on a Picker FACS-1 diffractometer with the needle axis, *c*, slightly inclined to the φ axis of the goniostat. Cell parameters were measured before and after intensity data were collected. Approximate cell parameters for use in collecting intensity data were calculated by a least-squares analysis of the angular settings for seven high-angle reflections. Accurate values for cell parameters were determined immediately after data collection by a least-squares analysis of 2θ values for 15 high-angle reflections (Cu $K\alpha_1$, $\lambda = 1{\cdot}5405$ Å and Cu $K\alpha_2$, $\lambda = 1{\cdot}5443$ Å). These cell parameters were not significantly different from those obtained prior to the collection of intensity data.

Intensity data were measured by use of a scintillation counter, Ni-filtered Cu radiation, and a θ–2θ scanning technique. The scanning speed was 1° min^{-1}, and the background was counted for 20 s at each terminus of the scans. Measurements were made for 2321 unique reflections with $2\theta \le 128°$. Those reflections with scan counts below background levels were given their calculated negative intensity values and were retained in all subsequent calculations. Intensities were assigned variances, $\sigma^2(I)$, according to counting statistics plus a correctional term $(0{\cdot}03S)^2$, S being the scan count. The intensities and their variances were corrected for Lorentz and polarization effects, absorption corrections were applied with the program *ORABS* (Wehe, Busing & Levy, 1962), and the data were scaled by a Wilson (1942) plot.

We arrived at a suitable trial structure by the heavy-atom method: coordinates for the first Br atom were found from a sharpened, three-dimensional Patterson map; coordinates for the second Br atom were deter-

Table 1. *Nonhydrogen-atom positional parameters and their estimated standard deviations*

The values for Br have been multiplied by 10^5, all other values by 10^4. The final value of the isotropic extinction parameter is $g = 0{\cdot}020$ (2).

	x	*y*	*z*
Molecule *A*			
Br	15005 (1)	18717 (6)	−833 (8)
N(1)	949 (1)	8716 (4)	2509 (5)
C(2)	643 (1)	8045 (6)	2024 (7)
N(3)	603 (1)	6555 (5)	1349 (6)
C(4)	904 (1)	5726 (5)	1142 (6)
C(5)	1223 (1)	6314 (6)	1533 (6)
C(6)	1260 (1)	7916 (6)	2326 (6)
O(6)	1527 (1)	8569 (4)	2876 (5)
N(7)	1476 (1)	5140 (5)	1181 (5)
C(8)	1303 (1)	3883 (6)	599 (6)
N(9)	953 (1)	4101 (4)	533 (5)
O(1′)	676 (1)	2713 (4)	−1784 (4)
C(1′)	705 (1)	2792 (5)	79 (7)
C(2′)	344 (1)	3044 (7)	846 (7)
O(2′)	234 (1)	1418 (5)	1350 (5)
C(3′)	148 (1)	3648 (7)	−775 (7)
O(3′)	−207 (1)	3452 (5)	−685 (6)
C(4′)	320 (1)	2687 (6)	−2266 (8)
C(5′)	275 (1)	3345 (8)	−4078 (8)
O(5′)	377 (1)	5067 (5)	−4278 (6)
Molecule *B*			
Br	60644 (1)	63634 (6)	27459 (7)
N(1)	6575 (1)	13324 (4)	5281 (5)
C(2)	6872 (1)	12761 (6)	4567 (6)
N(3)	6917 (1)	11335 (5)	3786 (5)
C(4)	6628 (1)	10409 (5)	3793 (6)
C(5)	6314 (1)	10847 (6)	4474 (6)
C(6)	6271 (1)	12418 (6)	5296 (7)
O(6)	6014 (1)	13013 (4)	6002 (4)
N(7)	6080 (1)	9557 (5)	4219 (5)
C(8)	6253 (1)	8398 (6)	3410 (6)
N(9)	6589 (1)	8810 (4)	3088 (5)
O(1′)	6956 (1)	6552 (4)	3723 (4)
C(1′)	6850 (1)	7641 (5)	2391 (6)
C(2′)	7176 (1)	8443 (6)	1621 (6)
O(2′)	7302 (1)	7310 (5)	345 (4)
C(3′)	7412 (1)	8438 (5)	3206 (6)
O(3′)	7767 (1)	8358 (4)	2814 (5)
C(4′)	7314 (1)	6820 (7)	4137 (6)
C(5′)	7345 (1)	6866 (8)	6092 (7)
O(5′)	7140 (1)	8106 (4)	6920 (4)

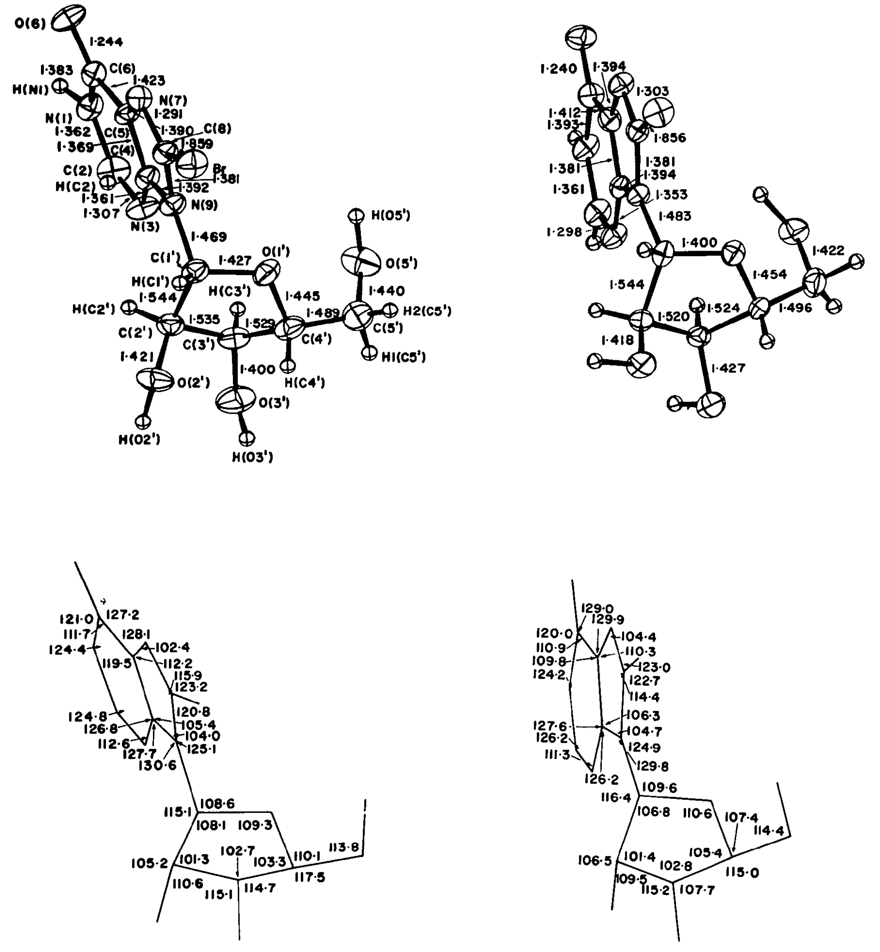
Table 2. *Hydrogen-atom parameters*

All values have been multiplied by 10^3. The isotropic temperature parameter is the coefficient in the expression

$$T = \exp(-8\pi^2 U \sin^2\theta/\lambda^2).$$

	x	*y*	*z*	*U*
Molecule *A*				
H(N1)	96	965	325	19
H(C2)	46	885	221	34
H(C1′)	78	175	50	30
H(C2′)	35	395	190	22
H(O2′)	2	112	175	38
H(C3′)	20	460	−93	38
H(O3′)	−30	235	−90	43
H(C4′)	24	156	−214	37
H1(C5′)	4	331	−430	41
H2(C5′)	39	267	−495	41
H(O5)	66	510	−425	48
Molecule *B*				
H(N1)	658	1434	580	25
H(C2)	706	1345	465	28
H(C1′)	673	700	140	19
H(C2′)	708	945	110	19
H(O2′)	717	750	−90	41
H(C3′)	733	940	418	29
H(O3′)	775	950	258	29
H(C4′)	744	610	350	20
H1(C5′)	752	695	650	32
H2(C5′)	726	560	665	32
H(O5′)	688	820	635	32

mined from a sum-function superposition of sharpened Patterson maps translated to the first Br atom position; and the remaining nonhydrogen atoms were located in a Fourier map phased with the two Br atoms. A modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962; Busing, 1971) was used to refine the trial structure. The quantity minimized was $\Sigma\ w(F_o^2 - F_c^2/k^2)^2$, with k as a scale factor and the weight, w, equal to $1/\sigma^2(F_o^2)$. Scattering factors for the nonhydrogen atoms were from *International Tables for X-ray Crystallography* (1962), and anomalous dispersion correction factors for these atoms were from Cromer & Liberman (1970). H atom scattering factors were from Stewart, Davidson & Simpson (1965). All H atoms were located in a difference Fourier map that was computed during the latter stages of refinement. Final cycles of refinement included the scale factor, k; positional and anisotropic temperature parameters for the nonhydrogen atoms; and Zachariasen's (1963) isotropic extinction parameter, g [as formulated by Coppens & Hamilton (1970)]. H atoms, which were assigned the approximate isotropic temperature factors of the atoms to which they are bonded, were included in structure-factor calculations but not in the least-squares refinement. Since limited core storage prevented simultaneous variation of all parameters, blocks of 12, 12, and 16 nonhydrogen atoms were refined in successive cycles. The structure refined to an R index, $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$, of 0·034 and a goodness-of-fit, $\{[\Sigma\ w(F_o^2 -$



(a) (b)

Fig. 1. Conformation of 8-bromoinosine (*a*) molecule *A*, (*b*) molecule *B*. Nonhydrogen atoms are represented by thermal ellipsoids defined by the principal axes of thermal vibration and scaled to include 50% probability. Hydrogen atoms are represented by spheres of 0·1 Å radius. Estimated standard deviations are about 0·006 Å and 0·3° for (top) bond lengths and (bottom) bond angles, respectively (*ORTEP*: Johnson, 1965).

$F_c^2)^2/(m - s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined} of 1·09. During the last cycle of refinement no parameter shifted more than one-fifth of its standard deviation and the average shift was less than one-tenth of the estimated standard deviation. A final three-dimensional difference Fourier map showed no peaks or troughs that exceeded 0·33 e Å^{-3} in magnitude. The atomic parameters are given in Tables 1 and 2.*

Discussion

Estimated errors in positional parameters are about 0·0005 Å for Br, and 0·004 Å for other nonhydrogen atoms. Errors in the unrefined positional parameters of the H atoms are probably 0·1–0·3 Å.

The conformations of the two nucleoside molecules, together with bond lengths and angles involving only nonhydrogen atoms, are shown in Fig. 1. The C–H lengths range from 0·76 to 1·15 Å, with an average value of 0·96 Å; the O–H bond lengths range from 0·92 to 1·11 Å with an average value of 1·02 Å; and the length of the N(1)–H bond is 0·94 Å for molecule *A* and 0·90 Å for molecule *B*. As in other crystal structures of 8-substituted purine nucleosides (Bugg & Sternglanz, 1974; and references therein) the nucleosides are in the *syn* conformation (Donohue & Trueblood, 1960; χ_{CN}, the torsion angle defined by atoms O(1′)–C(1′)–N(9)–C(8) (Sundaralingam, 1969), is −84·6° and −76·1° for molecules *A* and *B* respectively. The torsion angles of the ribose, τ_0, τ_1, τ_2, τ_3, and τ_4 (Sundaralingam, 1971; Sundaralingam & Abola, 1972) are −7·0, −17·5, 33·9, −39·1 and 28·9° for molecule *A* and 11·7, −29·7, 35·3, −29·7 and 11·4° for molecule *B*. According to the notation of pseudorotation, this corresponds to a phase angle, *P*, of 28·9° for molecule *A* and $P = 0°$ for molecule *B*, with an amplitude of pucker, τ_m, equal to 38·7° for molecule *A* and $\tau_m = 35{\cdot}3°$ for molecule *B* (Altona & Sundaralingam, 1972). Thus the conformation of the ribose for molecule *A* can be described as C(3′)-*endo* and that for molecule *B* as C(3′)-*endo*–C(2′)-*exo*. The torsion angles O(5′)–C(5′)–C(4′)–O(1′) and O(5′)–C(5′)–C(4′)–C(3′) are −62·8 and 55·1° for molecule *A* and −57·3 and 59·6° for molecule *B*. This corresponds to

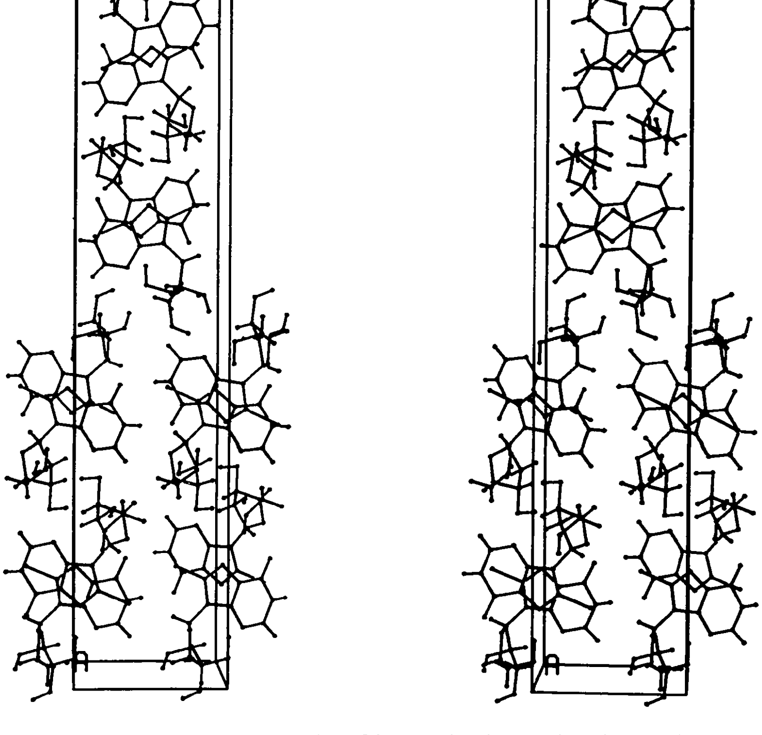


Fig. 2. Stereo drawing of the crystal packing of 8-bromoinosine, as viewed approximately down **c**.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32469 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

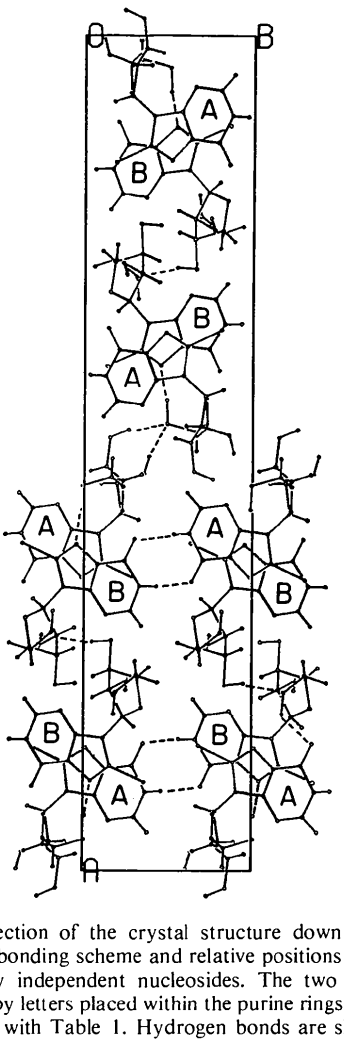

Fig. 3. Projection of the crystal structure down **c**, showing the hydrogen-bonding scheme and relative positions of the crystallographically independent nucleosides. The two nucleosides are identified by letters placed within the purine rings; these labels are consistent with Table 1. Hydrogen bonds are shown as dashed lines.

Table 3. *Hydrogen-bond distances and angles*

Donor atom X	Hydrogen atom H	Acceptor atom Y	Symmetry code	Distances (Å) $X-Y$	Distances (Å) $Y-$H	Angles (°) $X-$H$-Y$
N(1)*A*	H(N1)*A*	O(6)*B*	i	2·860	2·0	160
O(2′)*A*	H(O2′)*A*	O(5′)*A*	ii	3·065	2·6	113
O(3′)*A*	H(O3′)*A*	O(5′)*A*	ii	2·785	1·9	161
O(5′)*A*	H(O5′)*A*	N(7)*B*	iii	2·770	1·7	172
N(1)*B*	H(N1)*B*	O(6)*A*	iv	2·859	2·0	171
O(2′)*B*	H(O2′)*B*	O(5′)*B*	v	2·762	1·7	155
O(3′)*B*	H(O3′)*B*	O(5′)*B*	vi	2·928	2·0	163
O(5′)*B*	H(O5′)*B*	O(6)*A*	vii	2·754	2·1	117

Symmetry codes

(i) $x-\frac{1}{2}, \frac{5}{2}-y, 1-z$
(ii) $-x, y-\frac{1}{2}, -z-\frac{1}{2}$
(iii) $\frac{1}{2}+x, \frac{3}{2}-y, -z$
(iv) $\frac{1}{2}+x, \frac{5}{2}-y, 1-z$
(v) $x, y, z-1$
(vi) $\frac{3}{2}-x, 2-y, z-\frac{1}{2}$
(vii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$

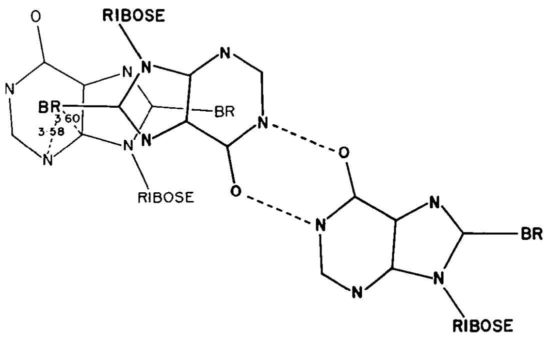

Fig. 4. Hydrogen-bonding and base-stacking interactions between the crystallographically independent purine moieties, as viewed perpendicular to the central base. Hydrogen atoms are omitted. All halogen–purine stacking contacts below 3·6 Å are shown. The purine moieties at the far left and the far right are from symmetry-related *B* nucleosides; the third is from nucleoside *A*.

the *gauche–gauche* conformation about the C(5′)–C(4′) bond for both molecules (Shefter & Trueblood, 1965). The nine-atom purine rings are planar to within 0·03–0·04 Å for molecule *A* and to within 0·01 Å for molecule *B*. The Br atom and C(1′) deviate by 0·199 and 0·075 Å, respectively, from the least-squares plane of purine ring *A*. For molecule *B* these values are 0·025 and 0·176 Å.

The crystal-packing and hydrogen-bonding schemes are shown in Figs. 2 and 3. Distances and angles of possible hydrogen bonds are listed in Table 3. The hydrogen-bonding scheme appears to utilize all H atoms that are bonded to O or N atoms. The base-stacking and hydrogen-bonding interactions between the purine moieties of crystallographically independent nucleosides are depicted in Fig. 4. The purines are joined by a pair of N(1)–H···O(6) hydrogen bonds across a pseudo twofold axis that runs approximately in the **c** direction. No hydrogen bonding exists between purine moieties of symmetry-related nucleosides. The stacked bases are related by a pseudo twofold screw axis.

The base-stacking pattern can also be seen in Fig. 2. The purines are stacked in the **c** direction, forming continuous stacked columns wherein the crystallographically independent purine moieties alternate. Neighboring bases are tilted about 3 ° toward each other and are separated by an interplanar spacing of about 3·2–3·5 Å. As in most other crystal structures of halogenated purines and pyrimidines (Bugg & Sternglanz, 1974; and references therein), the base-stacking pattern involves interactions of the halogen substituents with the ring systems of adjacent bases. The halogen substituents are sandwiched between the stacked purine rings, and form several Br–purine contacts that are in the range expected for van der Waals contacts. The shortest halogen contacts are shown in Fig. 4. A more detailed discussion of the stacking pattern has been published, along with a detailed comparison 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 ($\sin\theta/\lambda < 0{\cdot}91$) and neutron ($\sin\theta/\lambda < 0{\cdot}84$ 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