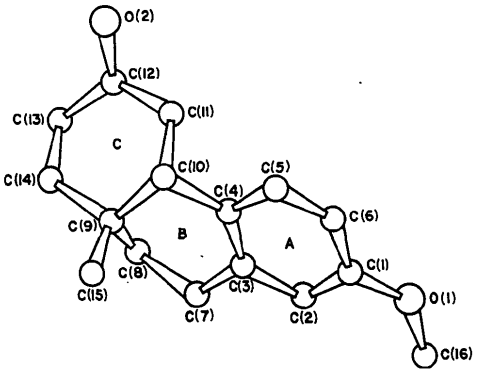

Fig. 1. The view of the molecule projected along the *c* axis.

stereospecificity of the reduction process, *i.e.* the formation of a *cis* ketone (Bucourt, 1974). The ring-fusion methyl group is axial to the *B* ring and equatorial to the ketone-containing *C* ring of the molecule and the ring-fusion hydrogen atom is equatorial to the *B* ring and axial to ring *C*. The calculated distance of 2·67 Å between the H atom attached to aromatic C(5) and that attached to C(1) of the *A* ring coincides with the computed distance (from a Dreiding model) of 2·7 Å between these hydrogen atoms in one of the *cis* models (Nagata, Terasawa & Tori, 1964) that is in the ground state. The crystal structure consists of discrete molecules with no intermolecular distance shorter than van der Waals radii (Pauling, 1960).

The authors sincerely acknowledge the kind help of Professor G. Germain, Department of Quantum Chemistry, Catholic University of Louvain, Belgium, who collected the diffraction data for us. The authors also offer sincere thanks to Professor A. Chatterjee, Jadavpur University, Calcutta, for his helpful discussion on the conformation of the title compound which was synthesized in his laboratory and to Dr S. Roy of IACS, Calcutta, for his help in solving some of the computational problems.

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3,6-Diamino-1,2,4,5-tetrazine: An Example of Strong Intermolecular Hydrogen Bonding

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Abstract. $C_2H_4N_6$, $M_r = 112·1$, orthorhombic, *Amam*, $a = 6·257$ (1), $b = 7·839$ (1), $c = 9·424$ (1) Å, $V = 462·2$ (2) Å^3, $Z = 4$, $D_x = 1·611$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0·71069$ Å, $\mu = 0·1160$ mm^{-1}, $F(000) = 232$, room temperature, final conventional $R = 0·038$ for 260 unique observed reflections. The crystal-structure analysis confirms the 3,6-diamino-1,2,4,5-tetrazine structure. The amino groups act as proton donors forming intermolecular hydrogen bonds with adjacent N atoms of neighbouring 1,2,4,5-tetrazine rings. The intermolecular hydrogen-bonding network leads to planar molecular layers separated from each other by $\frac{1}{2}a$ [3·129 (1) Å].

Introduction. In the context of detailed studies of 3,6-disubstituted 1,2,4,5-tetrazines some unusual properties of the title compound (1*a*) (Lin, Lieber & Horowitz, 1954) attracted attention, *e.g.* the unexpectedly high first ionization potential in the photoelectron spectrum (Gleiter, Spanget-Larsen, Fischer &

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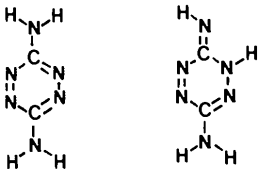
Neugebauer, 1987). In order to exclude the possible tautomeric form (1*b*) a direct structure confirmation was indicated. Furthermore, the extreme insolubility of the compound pointed to strong intermolecular hydrogen bonding. A molecular-packing analysis should give information on the arrangement of hydrogen bridges.



(1*a*) (1*b*)

Experimental. From a slowly evaporating aqueous solution brown needle-shaped crystals of approximate size 0·4 × 0·1 × 0·1 mm were obtained. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; $\theta/2\theta$ scanning technique. Lattice parameters from least-squares fit with 30 reflections (θ range 14–18°); 350 unique reflections measured in the range $1{\cdot}5 \le \theta \le 29°$, $0 \le h \le 8$, $0 \le k \le 10$, $0 \le l \le 12$; 260 $[I \ge 1{\cdot}98\sigma(I)]$ used for structure solution and refinement. Lorentz and polarization corrections were applied. On the assumption of C_{2v} symmetry the structure was solved by analysis of a Patterson map. H-atom positions were obtained from difference Fourier map at intermediate stage of refinement. Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms refined with isotropic temperature factors, all other atoms refined anisotropically; 31 variables. $R = 0{\cdot}038$, $wR = 0{\cdot}042$, $w = [\sigma^2(F) + 0{\cdot}003\sigma(F^2)]^{-1}$, max. $\Delta/\sigma = 0{\cdot}04$. Residual electron density in final difference map $-0{\cdot}09 \le \rho \le 0{\cdot}06$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Programs used were those of B. A. Frenz & Associates Inc. (1982).

Discussion. Atomic coordinates and temperature factors are listed in Table 1.* The atomic numbering scheme as well as bond distances and angles are shown in Fig. 1. The crystal-structure determination confirms the 3,6-diamino-1,2,4,5-tetrazine structure (1*a*). The planar molecule has C_{2v} symmetry with one mirror plane bisecting the N(1)–N(1^i) and N(2)–N(2^i) bonds, the second being the plane of the molecule [symmetry code: (i) $x, y, -z$]. In addition, one could expect a third mirror plane bisecting the molecule along the exocyclic N(4)–C(3) bonds corresponding to D_{2h} symmetry.

* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43783 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic or isotropic (for* H *atoms) thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	y	B_{eq}/B_{iso}
N(1)	0·250	−0·0330 (2)	0·0704 (1)	2·37 (5)
N(2)	0·250	0·2701 (2)	0·0697 (2)	2·61 (5)
C(3)	0·250	0·1189 (2)	0·1376 (2)	2·33 (5)
N(4)	0·250	0·1197 (2)	0·2789 (2)	3·81 (6)
H(4*A*)	0·250	0·018 (3)	0·331 (2)	4·4 (6)
H(4*B*)	0·250	0·213 (2)	0·330 (2)	4·0 (6)

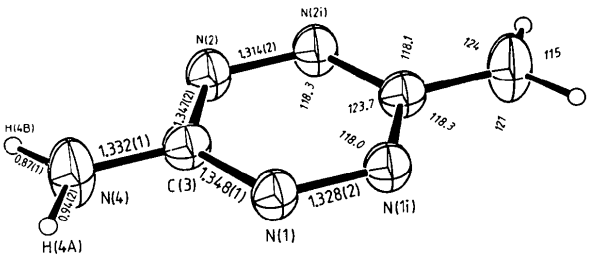


Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound showing labelling scheme, bond distances and bond angles (e.s.d.'s 0·1°). E.s.d.'s for angles involving H atoms are *ca* 1°. Thermal ellipsoids to 50% probability.

However, there are small differences in the N–N bonds which may be the result of packing effects.

Bond distances and bond angles of the 1,2,4,5-tetrazine ring found in this structure are similar to those reported for the unsubstituted 1,2,4,5-tetrazine (Bertinotti, Giacomello & Liquori, 1956) and the 3,6-dimethyl derivative (Huffman, 1981). The exocyclic C(3)–N(4) bond is remarkably short, 1·332 (1) Å. This indicates substantial double-bond character as observed, for example, in amide groups. We interpret this finding as a result of the strong electron-accepting property of the 1,2,4,5-tetrazine ring. The amino groups of (1*a*) act as π-electron donors. The lone pair of electrons at N(4) is partly included in the π-electron system of the molecule.

The crystal structure of (1*a*) consists of planar molecular layers in which each molecule is surrounded by four neighbouring molecules. Each H atom of the amine functions forms an intermolecular hydrogen bridge to an adjacent N atom of a neighbouring 1,2,4,5-tetrazine ring. These hydrogen bridges are nearly linear; N(4)···N(1) ($x, \frac{1}{2}+y, \frac{1}{2}-z$) 3·071 (2), N(4)···N(2) ($x, -\frac{1}{2}+y, \frac{1}{2}-z$) 3·089 (2), N(4)–H(4*A*) 0·94 (2), N(4)–H(4*B*) 0·87 (1), H(4*A*)···N(2) 2·16 (2), H(4*B*)···N(1) 2·20 (2) Å; N(4)–H(4*B*)···N(1) 172 (1), N(4)–H(4*A*)···N(2) 174 (1)°. The intermolecular hydrogen-bonding network (Fig. 2) leads to the formation of planar molecular layers which are separated from each other by 3·129 (1) Å. The shortest interlayer contact is 3·171 (2) Å between N(1) and N(1) ($-x, -y, z$). The packing arrangement of the

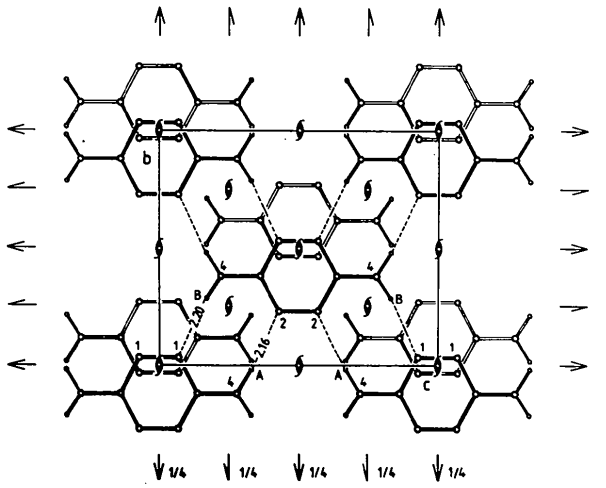


Fig. 2. Projection of the structure along [100]. Dashed lines indicate intermolecular H···N interactions within the layer.

layers is illustrated in Fig. 2. According to the results obtained, the insolubility of (1*a*) and its remarkably high density have to be attributed to strong intermolecular hydrogen bonding in the crystal.

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Two Diastereomers of 1-Acetylperhydrocyclopenta[*b*]pyrrole-2-carbonitrile

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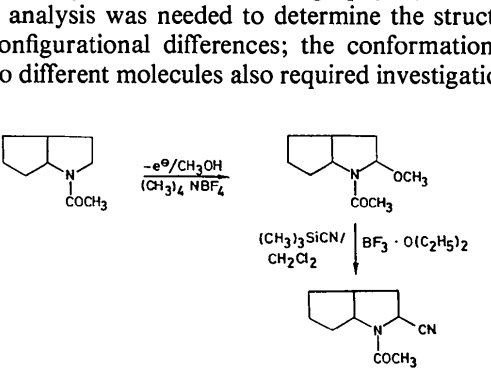
Abstract. $C_{10}H_{14}N_2O$. The steric difference between the two diastereomers (2*SR*,3a*RS*,6a*RS*) (I) and (2*RS*, 3a*RS*,6a*RS*) (II) is that the carbonitrile group in compound (I) is in an *exo* and in compound (II) an *endo* position. $M_r = 178{\cdot}24$, both compounds are monoclinic, $P2_1/c$, $a = 12{\cdot}137\ (2)$, $b = 10{\cdot}329\ (1)$, $c = 7{\cdot}783\ (1)$ Å, $\beta = 98{\cdot}58\ (1)°$ [$a = 13{\cdot}257\ (3)$, $b = 6{\cdot}010\ (1)$, $c = 13{\cdot}333\ (5)$ Å, $\beta = 115{\cdot}46\ (5)°$] [square brackets denote values for (II) differing from those for (I)], $U = 964{\cdot}77$ [959·14] Å^3, $Z = 4$, $F(000) = 384$, $D_m = 1{\cdot}23$ [1·20] (flotation in CCl_4/*n*-heptane mixture), $D_x = 1{\cdot}227$ [1·234] Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}076$ mm^{-1}. The intensities of (I) were measured at 295 K, the intensities of (II) at 140 K and 295 K [at the latter temperature $a = 13{\cdot}309\ (3)$, $b = 6{\cdot}121\ (1)$, $c = 13{\cdot}409\ (5)$ Å, $\beta = 115{\cdot}13\ (5)°$, $U = 988{\cdot}74$ Å^3, $D_x = 1{\cdot}197$ Mg m^{-3}]. $wR = 0{\cdot}034$ [0·055] for 1879 [2074] unique reflections [$F^2 > \sigma(F^2)$]. The respective values for compound (II) at room temperature are 0·056 and 1864 unique reflections. In both compounds the pyrrolidine ring has the envelope conformation; the five-membered rings are *cis*-fused. The tendency for the *endo* conformation of the methylene group at C6 is so large in (II) that at low temperature the *endo* and *exo* conformations have almost equal weight, although the carbonitrile group is in the *endo* position and is causing steric hindrance.

Introduction. The anodic oxidation of racemic 2-acetyl-*cis*-2-azabicyclo[3.3.0]octane in methanol in the presence of $(CH_3)_4NBF_4$ and subsequent reaction with trimethylsilylcyanide at low temperature results in a product mixture containing (I) and (II), which can be separated by column chromatography (silica gel). X-ray analysis was needed to determine the structural and configurational differences; the conformations of the two different molecules also required investigation.



(I)/(II)

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