The *X*-Ray Structure of 1,4-Dimethylhexahydro-*s*-tetrazine

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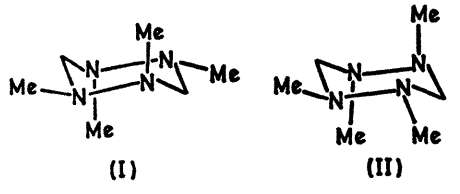
Summary The structure of 1,4-dimethylhexahydro-*s*-tetrazine is discussed on the basis of *X*-ray, n.m.r., and dipole-moment measurements.

ANDERSON AND ROBERTS[1] have reported that 1,2,4,5-tetramethylhexahydro-1,2,4,5-tetrazine exists in the (I) conformation. Katritzky *et al.*,[2] on the basis of dipole measurements feel that conformer(II) is more representative. We report the structure of the related molecule



1,4-dimethylhexahydro-*s*-tetrazine[3] which although having a similar variable-temperature n.m.r. spectrum to 1,2,4,5-tetramethylhexahydro-1,2,4,5-tetrazine has two major structural differences: (a) conformations (I) and (II) of the tetramethyl compound both have two axial N–Me groups whereas the corresponding conformers for the dimethyl compound have different numbers of axial and equatorial N–Me groups and (b) the dimethyl conformations also lack the *gauche*-butane interactions between adjacent N–Me groups which favour (II) relative to (I) for the tetramethyl compound.

The crystals are monoclinic with $a = 8{\cdot}996$, $b = 8{\cdot}905$, $c = 4{\cdot}086$ Å, $\beta = 95{\cdot}9°$; space group $P2_1/n$ from systematic absences $h0l$ $(h + l = 2n + l)$, $0k0$ $(k = 2n + 1)$; $Z = 2$.

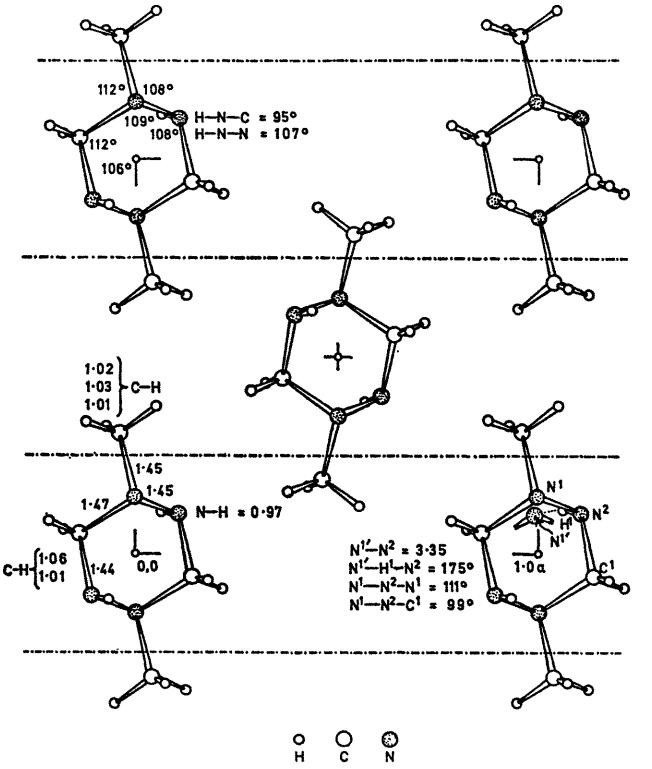


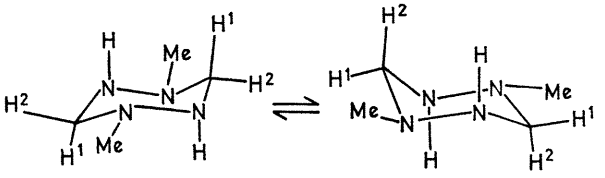
FIGURE. *Molecular packing as seen in projection down the* c*-axis.* (*σ for bonds not involving hydrogen* = 0·03 Å, *those with hydrogen* = 0·08 Å: *σ for angles* 1°.)

X-Ray data were collected on a diffractometer using Cu-K_α radiation and a scintillation counter. The structure was solved for C and N atoms by a three dimensional Patterson synthesis and packing considerations. Positional refinement for all atoms [anisotropic for C and N, isotropic ($B = 5{\cdot}0$ Å^2) for H] yielded an R factor of 0·043. Bond lengths and angles from this calculation are shown in the Figure. Refinement with the *N*-hydrogen removed gave an R value of 0·063. A difference-Fourier performed with the 0·063 data indicated a hydrogen atom only at 0·12 Å from the position indicated in the Figure.

The molecule is centrosymmetric and chair-shaped. All N–C, N–N, N–H, and C–H bonds and their corresponding angles agree closely with accepted values for tetrahedrally bonded carbon and nitrogen.[4] The two *N*-methyls are equatorial and the two *N*-hydrogens are axial. Bond lengths and angles shown in the Figure strongly indicate the two axial hydrogens of one molecule are hydrogen bonded to the nearest methyl carrying nitrogens in the molecules above and below when looking down the *c*-axis. This may well affect the configuration the molecule assumes in the crystalline form.

Preliminary n.m.r. investigation of the structure of 1,4-dimethylhexahydro-1,2,4,5-tetrazine in $CDCl_3$ solution has shown evidence of a slow ring inversion and simultaneous fast nitrogen inversion. The effect of these processes is to establish a conformational equilibrium between two forms which differ only by the interchange of methylene protons.

At room temperature both the methylene and NH spectra are broad single peaks. On cooling below 0° the spectrum becomes an ABC-type multiplet. Substitution of deuterium on the nitrogen simplifies this to an AB quartet ($J = 11{\cdot}2$ Hz, $\Delta\tau = 0{\cdot}57$) which coalesces on heating above 15°. From these values the activation energy for the conformational transition is calculated to be $11{\cdot}5 \pm 0{\cdot}5$ kcal.



These results are consistent with the observations of Anderson and Roberts[1] and Katritzky[2] that conformational equilibria are influenced not only by the preference for *N*-methyls to take equatorial positions but also by the tendency to assume orientations which minimize 1,3-interactions between lone pairs.

The dipole-moment measured in benzene at 20° is 1·06 ± 0·02D. This indicates the possibility of non-centrosymmetric conformers, similar to those described by Katritzky[2] for the tetramethyl compound existing in solution.

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[3] W. M. Tolles, W. R. McBride, and W. E. Thun, *J. Amer. Chem. Soc.*, 1969, **91**, 2443.
[4] International Tables for *X*-Ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England, 1969.