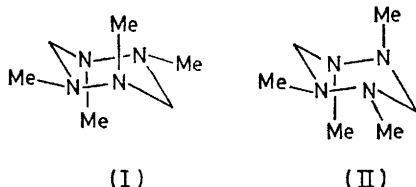


X-Ray Crystal Structure of Hexahydro-1,4-dimethyl-s-tetrazine

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The structure of the title compound has been established by X-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, $Z = 2$ and cell dimensions $a = 8.996 \pm 0.005$, $b = 8.905 \pm 0.005$, $c = 4.086 \pm 0.002$ Å, $\beta = 95.9(\pm 0.1)^\circ$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to $R = 0.044$ for 315 observed reflections. The molecule is centrosymmetric and chair-shaped. *N*-Methyl groups are equatorial and *N*-hydrogen atoms axial. All bond lengths agree with previously found values. Each molecule is $\text{NH} \cdots \text{N}$ bonded to two others forming strings running parallel to the c axis.

THE title compound was studied because of its similarity to hexahydro-1,2,4,5-tetramethyl-s-tetrazine for which two conformers (I)¹ and (II)² have been suggested. The preparation, ¹H n.m.r. spectra, dipole moment, and preliminary X-ray structure have been discussed previously.^{3,4}



EXPERIMENTAL

All dimensions and intensity data were measured on a General Electric single-crystal orienter by use of $\text{Cu-K}\alpha_1$ and $-\text{K}\alpha_2$ radiation [$\lambda = 1.54050$ and 1.54434 Å]. The errors were estimated from the observed deviations of individual values from their mean.

Crystal Data.— $\text{C}_4\text{N}_4\text{H}_{12}$, $M = 116$. Monoclinic, $a = 8.996 \pm 0.005$, $b = 8.905 \pm 0.005$, $c = 4.086 \pm 0.002$, $\beta = 95.9(\pm 0.1)^\circ$, $D_m = 1.18$, $Z = 2$, $D_o = 1.18$. Space group $P2_1/n$ from systematic absences: $h0l$ when $h + l = 2n + 1$, $0k0$ when $k = 2n + 1$. $\mu(\text{Cu-K}\alpha) = 7.5 \text{ cm}^{-1}$.

All intensity data below $2\theta 120^\circ$ were measured by use of a block-shaped crystal, of dimensions $0.01 \times 0.01 \times 0.01$ cm, mounted along the c axis. To prevent sublimation the crystal was enclosed in a capillary. Total intensities (T_o) were measured by use of an automated General Electric diffractometer, equipped with a scintillation counter and pulse-height selector, by the moving-crystal moving-counter technique (3.66° at 2° min^{-1}). Background counts (B_1 and B_2) of 40 s were measured at the beginning and end of each scan. The integrated intensity I was calculated as $I = T_o - 1.376(B_1 + B_2)$. Structure factors were obtained by application of the usual Lorentz and polarization corrections. Equivalent hkl and $\bar{h}\bar{k}l$ reflections were averaged. Of the 477 reflections measured, 315, having $I > 1.5\sigma$ [where $\sigma^2 = T_o + 1.376(B_1 + B_2)$], were considered statistically significant, and were used in the subsequent structure determination. No absorption correction was made.

Solution and Refinement.—Nitrogen and carbon atoms were located from a three-dimensional Patterson synthesis and from packing considerations. Full-matrix isotropic refinement⁵ yielded $R = 0.18$. A difference-Fourier syn-

† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

¹ J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 4186.

² R. A. Y. Jones, A. R. Katritzky, and A. C. Richards, *Chem. Comm.*, 1969, 708.

thesis then enabled location of all hydrogen atoms. For the remaining cycles of least-squares, carbon and nitrogen were refined anisotropically and the hydrogen isotropically (B fixed at 5.0 Å^{-2}). At $R = 0.004$ and $R' = 0.046$ the shifts were $\leq \frac{1}{3}\sigma$ and refinement was considered complete.⁵ A weighting scheme giving reasonably similar mean values of $w\Delta^2$ for ranges of F was chosen such that for reflections with $F_o > 15$, $\sqrt{w} = 15/F_o$; $F_o < 1.5$, $\sqrt{w} = F_o/1.5$; and $1.5 < F_o < 15$, $\sqrt{w} = 1$. A difference-Fourier computed with this data was entirely featureless. All 159

TABLE I
Atomic fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x	y	z
C(1)	-417(5)	3053(4)	621(10)
C(2)	-1404(3)	525(4)	291(9)
N(1)	-84(3)	1463(3)	1182(6)
N(2)	1083(3)	1050(3)	-838(7)
H(1)	485(40)	3728(47)	1054(90)
H(2)	-782(41)	3242(45)	-1780(96)
H(3)	-1250(43)	3347(45)	1878(94)
H(4)	669(39)	1140(44)	-3169(105)
H(5)	-1805(39)	640(41)	2279(101)
H(6)	-2145(39)	815(42)	1868(95)

TABLE 2
Bond lengths and angles, with estimated errors in parentheses. The estimated errors were calculated from the formula given by G. A. Jeffrey and D. W. J. Cruickshank (*Quart. Rev.*, **7**, 335, 1953)

(a) Bond lengths (Å)			
N(2)-N(1)	1.447(3)	C(1)-H(2)	1.02(4)
N(1)-C(1)	1.460(4)	C(1)-H(3)	0.99(4)
C(2)-N(1)	1.467(4)	C(2)-H(5)	1.08(4)
C(2)-N(2)	1.445(4)	C(2)-H(6)	1.01(4)
C(1)-H(1)	1.01(4)	N(2)-H(4)	0.99(4)
(b) Bond angles (deg.)			
N(2)-N(1)-C(1)	107.8(2)	H(2)-C(1)-H(3)	105.7(32)
C(2)-N(1)-N(2)	109.3(2)	N(1)-C(2)-H(5)	111.6(35)
N(2)-C(2)-N(1)	111.8(3)	N(1)-C(2)-H(6)	105.6(21)
N(1)-N(2)-C(2)	107.7(2)	N(2)-C(2)-H(5)	106.5(20)
C(2)-N(1)-C(1)	111.4(3)	N(2)-C(2)-H(6)	106.6(21)
N(1)-C(1)-H(1)	113.7(22)	H(5)-C(2)-H(6)	114.9(29)
N(1)-C(1)-H(3)	109.3(23)	N(1)-N(2)-H(4)	107.7(23)
H(1)-C(1)-H(2)	104.2(31)	C(2)-N(2)-H(4)	106.1(23)
H(1)-C(1)-H(3)	112.9(32)		

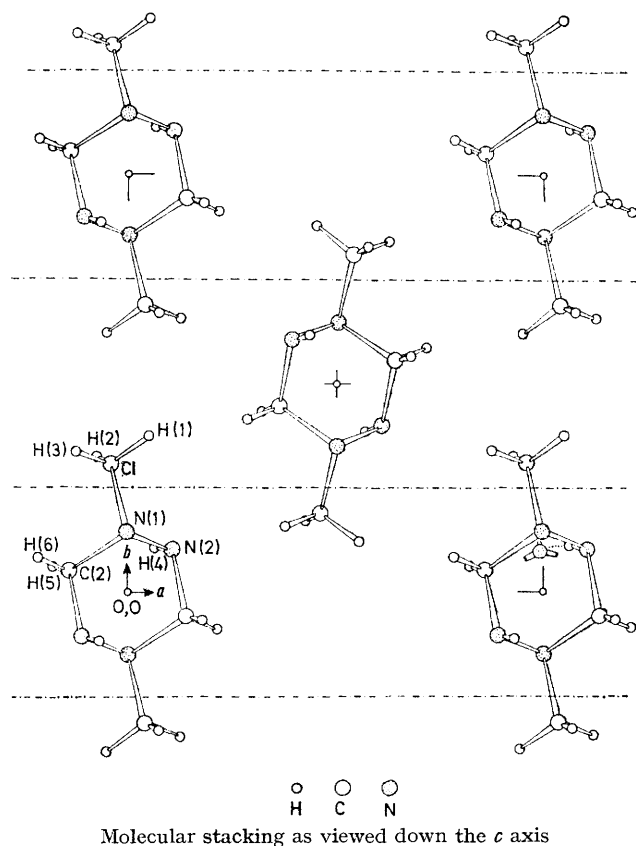
reflections with intensities $< 1.5\sigma$ gave small F_o values. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21167 (4 pp.).[†] Atomic fractional co-ordinates are listed in Table I, bond

³ W. M. Tolles, W. R. McBride, and W. E. Thun, *J. Amer. Chem. Soc.*, 1969, **91**, 2443.

⁴ G. B. Ansell, J. L. Erickson, and D. W. Moore, *Chem. Comm.*, 1970, 446.

⁵ W. R. Busing, K. O. Martin, and H. A. Levy, Fortran Crystallographic Least-squares Program, Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee, 1962 (modified for the effects of anomalous dispersion by W. C. Hamilton).

lengths and angles in Table 2, and thermal parameters in Table 3. Atomic labelling and molecular packing are shown in the Figure. Reflections 101, $\bar{1}01$, and



200 having $F_o \ll F_c$, also have low 2θ values, and probably suffer from extinction. They were not included in the final cycles of least-squares. Scattering factor tables for all atoms were taken from ref. 6.

⁶ 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1965.

TABLE 3

Anisotropic * thermal parameters ($\times 10^4$), with their estimated standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	198(6)	133(7)	893(30)	21(5)	40(11)	8(10)
C(2)	109(4)	150(6)	702(26)	4(4)	58(8)	-5(9)
N(1)	122(3)	131(4)	657(17)	5(3)	60(6)	1(7)
N(2)	115(3)	150(5)	670(19)	-5(3)	64(7)	10(7)

* In the form $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2(\beta_{12}hk + \beta_{13}hl + \beta_{23}kl))$. All hydrogen atoms isotropic, B 5.0 \AA^{-2} .

DISCUSSION

The molecule is centrosymmetric and chair-shaped with the two N -methyl groups equatorial and the two N -hydrogen atoms axial. The N - N value (1.447 \AA) is in close agreement with the accepted single-bond value 1.44(4) \AA . The C - N values (1.460 and 1.467 \AA) are similar and again are in close agreement with accepted values for carbon bonded to three-covalent nitrogen [1.472(5)]. C - H and N - H values (0.99–1.08 \AA) are as expected. Bond angles at C(1), C(2), N(1), and N(2) show they all have tetrahedral configuration with lone pairs on N(1) and N(2) and occupy the axial and equatorial positions respectively. The bond distance between N(2) and N(1^{II}) in the adjacent molecule, one unit cell along c , is short (3.337 \AA). Bond angles [$N(1)$ - $N(2) \cdots N(1^{II})$ 110.7°, $C(2)$ - $N(2) \cdots N(1^{II})$ 107.2°, $N(2^{II})$ - $H(4) \cdots N(1^{II})$ 174.2°] indicate quite clearly that there are strong hydrogen bonds between the axial hydrogens on N(2) and N(2^I) and the methyl group carrying nitrogens N(1), N(1^I) (*via* the axial lone-pair) in the molecules above and below, when viewed down the c axis. Undoubtedly this rigid hydrogen bonding and the absence of axial interaction between the lone pairs and methyl groups accounts for the symmetrical chair configuration of this molecule in the solid state. As previously reported^{3,4} however, there is evidence for unsymmetrical conformers in solution.

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