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1,2,3,4-Tetrahydroquinoxaline

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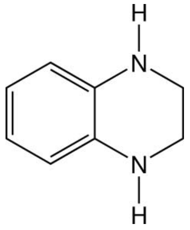
Key indicators: single-crystal X-ray study; *T* = 100 K; mean σ(C–C) = 0.001 Å; *R* factor = 0.030; *wR* factor = 0.087; data-to-parameter ratio = 9.6.

The title compound, $C_8H_{10}N_2$, was synthesized from the hydrogenation reaction of quinoxaline. The crystal structure reveals a puckered piperazine ring fused to a planar aromatic ring. A series of N—H···N hydrogen bonds produces an infinite zigzag chain.

Related literature

For related literature, see: Ammon *et al.* (1979); Beddoes *et al.* (1992); Bohlmann (1952); Brown *et al.* (1995); Bugle & Osteryoung (1979); Deprez-Poulain & Melnyk (2005); Eary & Clausen (2006); Epifani *et al.* (1987); Graham *et al.* (2000); Hamer & Holliday (1963); Maeyer *et al.* (2003); Maurer *et al.* (2004); McKinney *et al.* (2005); Murata *et al.* (1987); Nair *et al.* (2004); Nose & Kudo (1984); Pike *et al.* (2002); Pniewska & Anulewicz (1986); Ranu *et al.* (1998); Wiles & Pike (2006).



Experimental

Crystal data

$C_8H_{10}N_2$
M_r = 134.18
Orthorhombic, *Pbca*
a = 9.8609 (2) Å
b = 8.4986 (2) Å
c = 16.9639 (4) Å

V = 1421.64 (6) Å^3
Z = 8
Cu *Kα* radiation
μ = 0.60 mm^{-1}
T = 100 (2) K
0.34 × 0.22 × 0.22 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min}$ = 0.821, $T_{\max}$ = 0.879

14760 measured reflections
1262 independent reflections
1209 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.087
S = 1.06
1262 reflections

132 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 0.22 e Å^{-3}
$\Delta\rho_{\min}$ = −0.12 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···N1$^{\rm i}$	0.903 (15)	2.284 (15)	3.1740 (12)	168.4 (11)
N1—H1N···N2$^{\rm ii}$	0.913 (14)	2.192 (14)	3.0900 (12)	167.6 (11)

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *XSHELL* (Bruker, 2004); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Version 4.2.1; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

We acknowledge the Petroleum Research Fund of the American Chemical Society (44891-B3) and the Thomas F. and Kate Miller Jeffress Memorial Trust (J-678) for primary support of this research. We also acknowledge the NSF (CHE-0443345) and the College of William and Mary for the purchase of the X-ray equipment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2122).

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supplementary materials

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1,2,3,4-Tetrahydroquinoxaline

R. D. Pike and **E. C. Dugan**

Comment

Piperazines are an important class of compounds with antimalarial properties (Deprez-Poulain and Melnyk, 2005) and relevance to the problem of designer drugs (Maurer et al., 2004). We have recently been studying the coordination chemistry of diamines and diimines to copper(I) halides and pseudohalides (Graham et al., 2000; Pike et al., 2002; Maeyer et al., 2003; Wiles & Pike, 2006). In the course of this work, we have synthesized 1,2,3,4-tetrahydroquinoxaline (I). Several reduction strategies have been reported for the conversion of quinoxaline to I (Bohlmann, 1952; Hamer & Holliday, 1963; Bugle & Osteryoung, 1979; Nose & Kudo, 1984; Murata et al., 1987; Ranu et al., 1998; McKinney et al., 2005; Eary & Clausen, 2006). We prepared I by catalytic hydrogenation and are currently studying its network-forming coordination chemistry with copper(I) salts. Here we report the crystal structure of I (Figure 1).

Although 1,2,3,4-tetrahydroquinoxaline has been known for over 50 years, its structure has not yet been reported. Compound I crystallizes in the orthorhombic space group Pbca. The structure of I exhibits bond distances and angles that are unexceptional and are comparable to those of the relatively few previously reported tetrahydroquinoxaline structures (Ammon et al., 1979; Pniewska & Anulewicz, 1986; Epifani et al., 1987; Beddos et al., 1992; Brown et al., 1995; Nair et al., 2004).

The non-planar piperazine ring is fused to the planar aromatic ring with fairly minor deviations from the C3–C8 best plane: N1 = 0.1021 (14) Å, N2 = -0.1112 (14) Å, C1 = -0.4066 (17) Å, and C2 = 0.2353 (18) Å. A series of hydrogen bonds, N1···N2 = 3.0899 (12) and N2···N1 = 3.1740 (12), creates a zigzag chain between adjacent molecules that are nearly perpendicular (interplanar angle = 75.58 (2)°). The hydrogen-bonded chain propagates in a direction parallel to the b-axis (Figure 2).

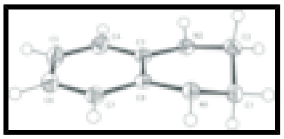
Experimental

Freshly sublimed quinoxaline (1.24 g, 9.51 mmol) and 5% rhodium on alumina catalyst (198 mg) were dissolved in 100% EtOH (20 ml). The mixture was placed in a glass Parr hydrogenation vessel and was pressurized to 3.4 atm with hydrogen gas. The mixture was shaken at room temp. for 18 h and then filtered and evaporated. The crude orange product was recrystallized by dissolving it in diethyl ether and then cooling, providing 792 mg of **1** as slightly orange crystals (62.0% yield); mp 88-90° C.

Refinement

All hydrogen atoms were located in the difference map and refined isotropically.

Figures



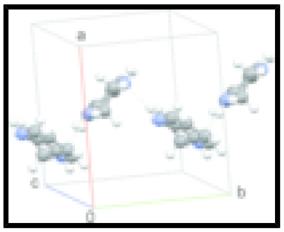


Figure 1. Ortep picture (Farrugia, 1997) of (1) Displacement ellipsoids have been drawn at the 50% probability level.

Figure 2. Ball and stick packing diagram of (1) showing hydrogen-bonding chains.

1,2,3,4-Tetrahydroquinoxaline

Crystal data

$C_8H_{10}N_2$

$M_r = 134.18$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 9.8609$ (2) Å

$b = 8.4986$ (2) Å

$c = 16.9639$ (4) Å

$V = 1421.64$ (6) Å^3

$Z = 8$

$F_{000} = 576$

$D_x = 1.254$ Mg m^{-3}

Cu *K*α radiation
λ = 1.54178 Å

μ = 0.60 mm^{-1}

$T = 100$ (2) K

Block, colorless

0.34 × 0.22 × 0.22 mm

Data collection

Bruker SMART APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100(2)$ K

ω and ψ scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

$T_{min} = 0.821$, $T_{max} = 0.879$

14760 measured reflections

1262 independent reflections

1209 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$

$\theta_{max} = 67.0$º

$\theta_{min} = 5.2$º

$h = -11 \rightarrow 11$

$k = -9 \rightarrow 10$

$l = -20 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.2875P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$wR(F^2) = 0.087$

$S = 1.06$

1262 reflections

132 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$\Delta\rho_{\max} = 0.22$ e Å^{-3}

$\Delta\rho_{\min} = -0.12$ e Å^{-3}

Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0017 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$
N1	0.54142 (8)	0.11160 (9)	0.25782 (4)	0.0213 (2)
N2	0.70309 (9)	0.38487 (10)	0.25085 (4)	0.0224 (2)
C1	0.55804 (10)	0.19734 (12)	0.18369 (5)	0.0228 (3)
C2	0.69619 (10)	0.27641 (12)	0.18412 (5)	0.0233 (3)
C3	0.65474 (9)	0.32959 (11)	0.32396 (5)	0.0205 (3)
C4	0.68628 (10)	0.40793 (12)	0.39369 (6)	0.0273 (3)
C5	0.63124 (11)	0.36107 (12)	0.46517 (6)	0.0306 (3)
C6	0.54215 (10)	0.23452 (12)	0.46790 (6)	0.0276 (3)
C7	0.51080 (9)	0.15467 (11)	0.39898 (5)	0.0222 (3)
C8	0.56618 (9)	0.19922 (10)	0.32676 (5)	0.0194 (2)
H1A	0.4851 (12)	0.2794 (13)	0.1754 (6)	0.024 (3)*
H1B	0.5532 (11)	0.1203 (14)	0.1400 (7)	0.029 (3)*
H1N	0.4626 (14)	0.0554 (15)	0.2602 (7)	0.035 (3)*
H2N	0.7827 (14)	0.4367 (16)	0.2546 (7)	0.035 (3)*
H2A	0.7695 (12)	0.1924 (14)	0.1874 (6)	0.028 (3)*
H2B	0.7108 (11)	0.3363 (14)	0.1342 (6)	0.028 (3)*
H4	0.7473 (13)	0.4979 (15)	0.3899 (6)	0.033 (3)*
H5	0.6535 (12)	0.4214 (15)	0.5133 (7)	0.040 (3)*
H6	0.5002 (13)	0.2045 (14)	0.5183 (7)	0.034 (3)*
H7	0.4479 (12)	0.0639 (14)	0.4000 (6)	0.028 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0211 (5)	0.0213 (4)	0.0215 (4)	−0.0022 (3)	0.0009 (3)	0.0002 (3)
N2	0.0200 (5)	0.0237 (5)	0.0234 (4)	−0.0030 (3)	0.0007 (3)	0.0037 (3)
C1	0.0250 (5)	0.0237 (5)	0.0198 (5)	0.0009 (4)	0.0006 (4)	−0.0002 (4)
C2	0.0231 (5)	0.0238 (5)	0.0231 (5)	0.0026 (4)	0.0035 (4)	0.0031 (4)
C3	0.0169 (5)	0.0213 (5)	0.0233 (5)	0.0016 (4)	−0.0008 (3)	0.0041 (3)
C4	0.0266 (5)	0.0272 (5)	0.0280 (5)	−0.0064 (4)	−0.0030 (4)	0.0013 (4)
C5	0.0356 (6)	0.0345 (6)	0.0217 (5)	−0.0056 (5)	−0.0030 (4)	−0.0021 (4)
C6	0.0279 (5)	0.0331 (6)	0.0216 (5)	−0.0012 (4)	0.0011 (4)	0.0040 (4)
C7	0.0195 (5)	0.0225 (5)	0.0247 (5)	−0.0006 (4)	−0.0002 (4)	0.0037 (4)
C8	0.0162 (5)	0.0192 (5)	0.0227 (5)	0.0029 (3)	−0.0018 (3)	0.0014 (3)

Geometric parameters (Å, °)

N1—C8	1.4078 (11)	C3—C4	1.3925 (13)
N1—C1	1.4626 (12)	C3—C8	1.4115 (14)
N1—H1N	0.913 (14)	C4—C5	1.3869 (14)
N2—C3	1.4094 (11)	C4—H4	0.975 (13)
N2—C2	1.4613 (12)	C5—C6	1.3895 (14)
N2—H2N	0.903 (15)	C5—H5	0.989 (13)
C1—C2	1.5191 (14)	C6—C7	1.3867 (13)
C1—H1A	1.011 (11)	C6—H6	0.984 (12)
C1—H1B	0.990 (12)	C7—C8	1.3938 (12)
C2—H2A	1.017 (12)	C7—H7	0.990 (12)
C2—H2B	0.998 (11)		
C8—N1—C1	115.56 (7)	C4—C3—C8	119.00 (8)
C8—N1—H1N	112.8 (7)	C4—C3—N2	120.83 (8)
C1—N1—H1N	113.2 (8)	C8—C3—N2	120.04 (8)
C3—N2—C2	117.10 (8)	C5—C4—C3	121.20 (9)
C3—N2—H2N	113.3 (7)	C5—C4—H4	121.7 (6)
C2—N2—H2N	113.7 (8)	C3—C4—H4	117.1 (6)
N1—C1—C2	108.46 (7)	C4—C5—C6	119.92 (9)
N1—C1—H1A	112.5 (6)	C4—C5—H5	119.1 (7)
C2—C1—H1A	109.5 (6)	C6—C5—H5	120.9 (7)
N1—C1—H1B	108.0 (6)	C7—C6—C5	119.45 (9)
C2—C1—H1B	109.9 (6)	C7—C6—H6	120.8 (7)
H1A—C1—H1B	108.5 (9)	C5—C6—H6	119.7 (7)
N2—C2—C1	108.94 (8)	C6—C7—C8	121.39 (9)
N2—C2—H2A	111.5 (6)	C6—C7—H7	120.5 (6)
C1—C2—H2A	109.1 (7)	C8—C7—H7	118.2 (6)
N2—C2—H2B	109.2 (6)	C7—C8—N1	121.24 (8)
C1—C2—H2B	110.5 (6)	C7—C8—C3	119.03 (8)
H2A—C2—H2B	107.5 (9)	N1—C8—C3	119.64 (8)
C8—N1—C1—C2	51.72 (11)	C5—C6—C7—C8	−0.38 (15)
C3—N2—C2—C1	45.09 (11)	C6—C7—C8—N1	175.67 (9)

N1—C1—C2—N2	−59.95 (10)	C6—C7—C8—C3	−0.75 (14)
C2—N2—C3—C4	164.45 (9)	C1—N1—C8—C7	157.24 (8)
C2—N2—C3—C8	−19.61 (12)	C1—N1—C8—C3	−26.36 (12)
C8—C3—C4—C5	−0.67 (15)	C4—C3—C8—C7	1.26 (13)
N2—C3—C4—C5	175.30 (9)	N2—C3—C8—C7	−174.74 (8)
C3—C4—C5—C6	−0.47 (16)	C4—C3—C8—N1	−175.22 (8)
C4—C5—C6—C7	0.99 (16)	N2—C3—C8—N1	8.78 (13)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···N1^{i}	0.903 (15)	2.284 (15)	3.1740 (12)	168.4 (11)
N1—H1N···N2^{ii}	0.913 (14)	2.192 (14)	3.0900 (12)	167.6 (11)

Symmetry codes: (i) −*x*+3/2, *y*+1/2, *z*; (ii) −*x*+1, *y*−1/2, −*z*+1/2.

Fig. 1

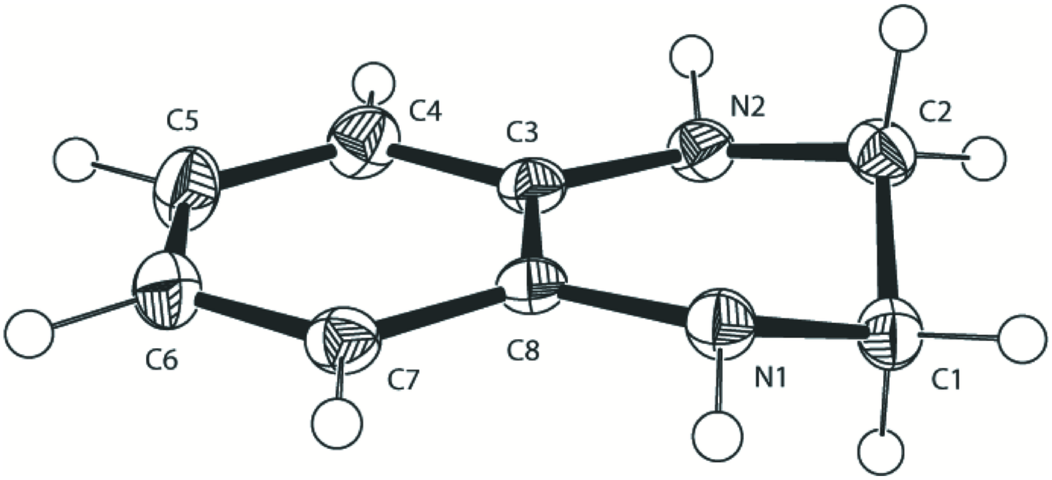


Fig. 2