2007

7,8-Dichloro-1,2,3,4-tetrahydrophenazine

Cesar H. Zambrano

Robert D. Pike

Ricky J. Paul Gibson

Brittnay D. Barger

Eric E. Dueno

Follow this and additional works at: <https://scholarworks.wm.edu/aspubs>

Part of the [Chemistry Commons](#)

7,8-Dichloro-1,2,3,4-tetrahydro-phenazine

Cesar H. Zambrano,^a Robert D. Pike,^b Ricky Joseph Paul Gibson,^c Brittany D. Barger^c and Eric Efrain Dueno^{c*}^aDepartamento de Quimica, Universidad San Francisco de Quito, Pampite & Robles s/n, Cumbaya, Quito, Ecuador, ^bDepartment of Chemistry, College of William and Mary, PO Box 8795, Williamsburg, VA 23187-8795, USA, and ^cDepartment of Chemistry, Eastern Kentucky University, 521 Lancaster Avenue, Richmond, KY 40475, USA

Correspondence e-mail: eric.dueno@eku.edu

Received 22 January 2007; accepted 5 July 2007

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.089; data-to-parameter ratio = 10.1.In the structure of the title compound, $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2$, the cyclohexene ring adopts a half-chair conformation.

Related literature

For related literature, see: Brown *et al.* (2004); Farrugia (1997); Gibson *et al.* (2006); Page *et al.* (1998); Pascal & Ho (1993); Simpson & Gordon (1995); Willett *et al.* (2001); Wozniak *et al.* (1993); Wu *et al.* (2002).

Experimental

Crystal data

 $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2$
 $M_r = 253.12$
 Triclinic, $P\bar{1}$
 $a = 6.3442$ (3) Å
 $b = 7.3885$ (3) Å

 $c = 11.7831$ (5) Å
 $\alpha = 85.720$ (2)°
 $\beta = 82.122$ (2)°
 $\gamma = 83.572$ (2)°
 $V = 542.68$ (4) Å³
 $Z = 2$
 Cu $K\alpha$ radiation
 $\mu = 5.13$ mm⁻¹
 $T = 200$ (2) K
 $0.35 \times 0.21 \times 0.08$ mm

Data collection

 Bruker SMART APEXII CCD
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.267$, $T_{\max} = 0.685$

 9473 measured reflections
 1868 independent reflections
 1810 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.089$
 $S = 1.05$
 1868 reflections

 185 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

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: XSELL (Bruker, 2004); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

EED acknowledges the National Science Foundation for primary support of this research (EPSCOR grant No. 450901). RDP is indebted to 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: RT2001).

References

- Brown, D. J., Taylor, E. C. & Wipf, P. (2004). *The Chemistry of Heterocyclic Compounds*, Vol. 61, *Quinoxalines: Supplement II*, pp. 100–105. New York: Wiley.
- Bruker (2004). APEX2 (Version 2.0), SAINT-Plus (Version 7.12A) and XSELL (Version 6.3.1). Bruker AXS Inc., Madison Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gibson, R. J. P., Kass, J. P., Zambrano, C. H., Fronczek, F. R. & Dueno, E. E. (2006). *Acta Cryst.* **E62**, o2947–o2948.
- Page, S. E., Gordon, K. C. & Burrell, A. K. (1998). *Inorg. Chem.* **37**, 4452–4459.
- Pascal, R. A. Jr & Ho, D. M. (1993). *J. Am. Chem. Soc.* **115**, 8507–8508.
- Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
- Sheldrick, G. M. (2004). SADABS. University of Göttingen, Germany.
- Simpson, T. J. & Gordon, K. C. (1995). *Inorg. Chem.* **34**, 6323–6329.
- Willett, R. D., Jeitler, R. J. & Twamley, B. (2001). *Inorg. Chem.* **40**, 6502–6505.
- Wozniak, K., Krygowski, T. M., Grech, E., Kolodziejewski, W. & Klinowski, J. (1993). *J. Phys. Chem.* **97**, 1862–1867.
- Wu, C. D., Lu, C.-Z., Zhuang, H.-H. & Huang, J.-S. (2002). *Inorg. Chem.* **41**, 5636–5637.

supplementary materials

Acta Cryst. (2007). E63, o3841 [doi:10.1107/S1600536807032874]

7,8-Dichloro-1,2,3,4-tetrahydrophenazine

C. H. Zambrano, R. D. Pike, R. J. P. Gibson, B. D. Barger and E. E. Dueno

Comment

One of the primary interests of our lab is the synthesis and characterization of novel substituted quinoxalines and the closely related phenazines. Quinoxalines and their derivatives have received considerable attention in the past several years due to their electronic properties (Page *et al.*, 1998; Simpson & Gordon, 1995), H-bonding ability (Pascal & Ho, 1993; Wozniak *et al.*, 1993), and their capacity to coordinate to metals (Wu *et al.*, 2002; Willett *et al.*, 2001). During our investigations, we have prepared a number of substituted quinoxalines and phenazines, which readily coordinate to copper iodide forming novel structures. Our current work involves the synthesis of new nitrogen heterocycles (Gibson, *et al.*, 2006) which may lead to novel three-dimensional structures upon coordination to cuprous salts. Here, we report the crystal structure of 7,8-dichloro-1,2,3,4-tetrahydrophenazine (I), (Figure 1).

The structure of (I) exhibits bond distances and angles that are normal, for all fall within ranges established in the literature for similar nitrogen heterocycles (Brown *et al.*, 2004). There are two molecules per unit cell, related to each other by an inversion center. The chloride substituents are almost eclipsed with respect to each other, with a torsion angle C11—C10—C9—C12 of 0.36 (16)°. Both aromatic rings are essentially planar and almost co-planar with a dihedral angle of 1.20 (18)°, based on least-squares plane calculations on C12—C11—C10—C9—C8—C7 and C7—C12—N1—C1—C6—N2. The H-saturated fragment of the ring system adopts a twisted, cyclohexyl-like conformation as evidenced by the angles depicted by atoms C5 C4 C3 110.68 (12)°, C2 C3 C4 109.92 (12)°, and the C2—C3—C4—C5 torsion angle of 63.62 (17)°, which suggest the presence of some angle and torsional strain.

Experimental

A 20 ml test tube was charged with 4,5-Dichloro-*o*-phenylenediamine (177 mg, 1 mmol) and 1,2-Cyclohexanedione (112 mg, 1 mmol). This was heated in a boiling water bath for 1 h, until the reaction mixture was homogeneous. The residue was then dissolved in boiling ethanol (100% EtOH, 15 ml). Upon cooling to 0° C, light yellow crystals of (1) were obtained (215 mg, 85% yield) mp 215–216° C.

Refinement

H atoms were treated as riding, with C—H = 1.00 with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for all H atoms.

Figures

Fig. 1. ORTEP drawing of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres.

7,8-dichloro-1,2,3,4-tetrahydrophenazine

Crystal data

$C_{12}H_{10}Cl_2N_2$

$M_r = 253.12$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.3442$ (3) Å

$b = 7.3885$ (3) Å

$c = 11.7831$ (5) Å

$\alpha = 85.720$ (2)°

$\beta = 82.122$ (2)°

$\gamma = 83.572$ (2)°

$V = 542.68$ (4) Å³

$Z = 2$

$F_{000} = 260$

$D_x = 1.549$ Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 71 reflections

$\theta = 9.5\text{--}41.0^\circ$

$\mu = 5.13$ mm⁻¹

$T = 200$ (2) K

Block, yellow

$0.35 \times 0.21 \times 0.08$ mm

Data collection

Bruker SMART APEX II CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 200$ (2) K

ω and ψ scans

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

$T_{\min} = 0.267$, $T_{\max} = 0.685$

9473 measured reflections

1868 independent reflections

1810 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 67.0^\circ$

$\theta_{\min} = 3.8^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.089$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 0.0594P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.05$	$(\Delta/\sigma)_{\max} = 0.001$
1868 reflections	$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
185 parameters	$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.93385 (5)	0.65523 (4)	0.28885 (3)	0.04023 (16)
Cl2	0.50704 (6)	0.83977 (5)	0.20124 (3)	0.04102 (16)
N1	0.54783 (19)	0.67203 (16)	0.69452 (11)	0.0335 (3)
N2	0.16607 (18)	0.84040 (15)	0.61792 (10)	0.0314 (3)
C1	0.3736 (2)	0.71175 (17)	0.76619 (11)	0.0313 (3)
C2	0.3837 (3)	0.6595 (2)	0.89145 (13)	0.0402 (3)
C3	0.2006 (2)	0.7516 (2)	0.97160 (12)	0.0395 (3)
C4	−0.0116 (2)	0.7388 (2)	0.92727 (12)	0.0390 (3)
C5	−0.0180 (2)	0.8423 (2)	0.81112 (13)	0.0382 (3)
C6	0.1794 (2)	0.79711 (17)	0.72703 (11)	0.0307 (3)
C7	0.3461 (2)	0.79900 (16)	0.54201 (11)	0.0294 (3)
C8	0.3393 (2)	0.83969 (17)	0.42346 (12)	0.0322 (3)
C9	0.5173 (2)	0.79438 (17)	0.34757 (11)	0.0322 (3)
C10	0.7083 (2)	0.71125 (16)	0.38628 (11)	0.0316 (3)
C11	0.7188 (2)	0.67350 (18)	0.50048 (12)	0.0340 (3)
C12	0.5361 (2)	0.71473 (17)	0.58085 (11)	0.0298 (3)
H8	0.202 (3)	0.896 (2)	0.3985 (14)	0.039 (4)*
H11	0.855 (3)	0.616 (2)	0.5315 (13)	0.037 (4)*
H2A	0.376 (3)	0.524 (3)	0.9028 (15)	0.047 (4)*
H3A	0.205 (3)	0.698 (2)	1.0494 (15)	0.037 (4)*
H4A	−0.025 (3)	0.613 (2)	0.9204 (13)	0.036 (4)*
H5A	−0.142 (3)	0.818 (3)	0.7777 (16)	0.050 (5)*
H2B	0.523 (3)	0.682 (3)	0.9123 (17)	0.057 (5)*
H3B	0.218 (3)	0.880 (2)	0.9745 (14)	0.043 (4)*
H4B	−0.127 (3)	0.781 (2)	0.9851 (15)	0.043 (4)*
H5B	−0.032 (3)	0.976 (2)	0.8240 (15)	0.046 (4)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0375 (2)	0.0407 (2)	0.0404 (2)	−0.00292 (16)	0.00363 (15)	−0.00642 (15)
Cl2	0.0478 (2)	0.0431 (2)	0.0313 (2)	−0.00231 (17)	−0.00522 (15)	0.00027 (15)
N1	0.0326 (6)	0.0321 (6)	0.0357 (6)	−0.0007 (5)	−0.0071 (5)	−0.0007 (5)
N2	0.0302 (6)	0.0283 (6)	0.0354 (6)	−0.0037 (5)	−0.0041 (5)	0.0023 (4)
C1	0.0332 (7)	0.0272 (6)	0.0337 (7)	−0.0040 (5)	−0.0056 (5)	0.0001 (5)
C2	0.0387 (8)	0.0460 (8)	0.0348 (7)	−0.0002 (7)	−0.0069 (6)	0.0016 (6)
C3	0.0451 (8)	0.0406 (8)	0.0329 (7)	−0.0077 (6)	−0.0032 (6)	−0.0014 (6)
C4	0.0387 (7)	0.0392 (8)	0.0373 (7)	−0.0057 (6)	0.0011 (6)	0.0008 (6)
C5	0.0336 (7)	0.0381 (8)	0.0402 (8)	−0.0006 (6)	−0.0004 (6)	0.0025 (6)
C6	0.0325 (6)	0.0242 (6)	0.0354 (7)	−0.0051 (5)	−0.0048 (5)	0.0013 (5)
C7	0.0297 (6)	0.0231 (6)	0.0358 (7)	−0.0046 (5)	−0.0051 (5)	0.0001 (5)
C8	0.0337 (7)	0.0274 (6)	0.0363 (7)	−0.0043 (6)	−0.0077 (5)	0.0009 (5)
C9	0.0398 (7)	0.0261 (6)	0.0318 (6)	−0.0078 (5)	−0.0059 (5)	0.0003 (5)
C10	0.0328 (6)	0.0246 (6)	0.0372 (7)	−0.0044 (5)	−0.0013 (5)	−0.0041 (5)
C11	0.0318 (7)	0.0301 (6)	0.0399 (7)	−0.0012 (6)	−0.0059 (6)	−0.0024 (5)
C12	0.0320 (6)	0.0249 (6)	0.0331 (6)	−0.0039 (5)	−0.0066 (5)	−0.0002 (5)

Geometric parameters ($\text{\AA}$, $^\circ$)

Cl1—C10	1.7394 (13)	C4—C5	1.520 (2)
Cl2—C9	1.7405 (13)	C4—H4A	0.955 (17)
N1—C1	1.3151 (19)	C4—H4B	0.970 (18)
N1—C12	1.3632 (19)	C5—C6	1.5090 (19)
N2—C6	1.3132 (18)	C5—H5A	0.97 (2)
N2—C7	1.3716 (18)	C5—H5B	1.001 (18)
C1—C6	1.4378 (19)	C7—C12	1.4104 (19)
C1—C2	1.506 (2)	C7—C8	1.412 (2)
C2—C3	1.524 (2)	C8—C9	1.368 (2)
C2—H2A	1.006 (19)	C8—H8	0.995 (18)
C2—H2B	0.99 (2)	C9—C10	1.413 (2)
C3—C4	1.524 (2)	C10—C11	1.363 (2)
C3—H3A	0.974 (18)	C11—C12	1.4133 (19)
C3—H3B	0.969 (18)	C11—H11	1.019 (17)
C1—N1—C12	116.95 (11)	C4—C5—H5A	110.3 (11)
C6—N2—C7	116.96 (12)	C6—C5—H5B	108.7 (10)
N1—C1—C6	121.78 (13)	C4—C5—H5B	107.7 (10)
N1—C1—C2	117.16 (12)	H5A—C5—H5B	108.0 (16)
C6—C1—C2	121.04 (13)	N2—C6—C1	121.97 (13)
C1—C2—C3	113.99 (13)	N2—C6—C5	117.29 (12)
C1—C2—H2A	107.4 (10)	C1—C6—C5	120.73 (13)
C3—C2—H2A	107.6 (10)	N2—C7—C12	120.84 (12)
C1—C2—H2B	110.1 (12)	N2—C7—C8	119.23 (12)
C3—C2—H2B	111.0 (12)	C12—C7—C8	119.92 (12)
H2A—C2—H2B	106.4 (16)	C9—C8—C7	119.21 (12)

C4—C3—C2	109.92 (12)	C9—C8—H8	122.7 (9)
C4—C3—H3A	112.9 (10)	C7—C8—H8	118.0 (9)
C2—C3—H3A	109.4 (10)	C8—C9—C10	120.99 (12)
C4—C3—H3B	107.7 (10)	C8—C9—C12	119.22 (10)
C2—C3—H3B	110.3 (10)	C10—C9—C12	119.79 (10)
H3A—C3—H3B	106.5 (14)	C11—C10—C9	120.61 (12)
C5—C4—C3	110.68 (12)	C11—C10—C11	118.89 (11)
C5—C4—H4A	109.9 (9)	C9—C10—C11	120.50 (10)
C3—C4—H4A	107.9 (10)	C10—C11—C12	119.75 (13)
C5—C4—H4B	113.5 (11)	C10—C11—H11	122.7 (9)
C3—C4—H4B	108.5 (10)	C12—C11—H11	117.6 (9)
H4A—C4—H4B	106.2 (14)	N1—C12—C7	121.50 (12)
C6—C5—C4	113.28 (12)	N1—C12—C11	119.01 (12)
C6—C5—H5A	108.7 (11)	C7—C12—C11	119.49 (12)
C12—N1—C1—C6	−0.29 (19)	C12—C7—C8—C9	0.80 (19)
C12—N1—C1—C2	178.13 (12)	C7—C8—C9—C10	−1.3 (2)
N1—C1—C2—C3	164.89 (13)	C7—C8—C9—C12	178.55 (9)
C6—C1—C2—C3	−16.7 (2)	C8—C9—C10—C11	0.3 (2)
C1—C2—C3—C4	46.64 (17)	C12—C9—C10—C11	−179.53 (10)
C2—C3—C4—C5	−63.51 (17)	C8—C9—C10—C11	−179.73 (9)
C3—C4—C5—C6	48.59 (17)	C12—C9—C10—C11	0.43 (15)
C7—N2—C6—C1	0.57 (19)	C9—C10—C11—C12	1.2 (2)
C7—N2—C6—C5	179.97 (11)	C11—C10—C11—C12	−178.78 (9)
N1—C1—C6—N2	−0.3 (2)	C1—N1—C12—C7	0.49 (19)
C2—C1—C6—N2	−178.61 (11)	C1—N1—C12—C11	−179.57 (12)
N1—C1—C6—C5	−179.63 (11)	N2—C7—C12—N1	−0.18 (19)
C2—C1—C6—C5	2.0 (2)	C8—C7—C12—N1	−179.40 (11)
C4—C5—C6—N2	162.46 (13)	N2—C7—C12—C11	179.88 (11)
C4—C5—C6—C1	−18.14 (19)	C8—C7—C12—C11	0.66 (19)
C6—N2—C7—C12	−0.36 (18)	C10—C11—C12—N1	178.41 (12)
C6—N2—C7—C8	178.87 (11)	C10—C11—C12—C7	−1.6 (2)
N2—C7—C8—C9	−178.43 (11)		

Fig. 1

Copyright of *Acta Crystallographica*: Section E is the property of Blackwell Publishing Limited and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.