organic compounds

2-Chloro-3-methylquinoxaline

A. Thiruvalluvar,^{a}* M. Subramanyam,^{a} R. J. Butcher,^{b} A. V. Adhikari^{c} and S. Wagle^{c}

^{a}PG Research Department of Physics, Rajah Serfoji Government College (Autonomous), Thanjavur 613 005, Tamil Nadu, India, ^{b}Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and ^{c}Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India
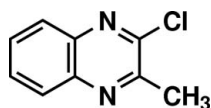
Correspondence e-mail: athiru@vsnl.net

The title molecule, $C_9H_7ClN_2$, is essentially planar, except for two methyl H atoms. The dihedral angle between the benzene ring and the pyrazine ring is 0.48 (7)°. A weak C—H⋯π interaction is found in the crystal structure and there are no classical hydrogen bonds.

Related literature

For the uses of quinoxalines, see Craig & Akinpelu (2005); Michaus & Belen (2005); Vyas et al. (2005).

Experimental

Crystal data

$C_9H_7ClN_2$
M_r = 178.62
Triclinic, $P\bar{1}$
a = 6.8876 (4) Å
b = 7.4022 (4) Å
c = 9.4124 (5) Å
α = 70.654 (4)°
β = 72.438 (5)°

γ = 65.019 (5)°
V = 403.01 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 200 (2) K
0.51 × 0.49 × 0.22 mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)

T_{min} = 0.723, T_{max} = 1.000
(expected range = 0.661–0.914)
5962 measured reflections
2645 independent reflections
2094 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.135
S = 1.08
2645 reflections

110 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

Cg is the centroid of the benzene ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C31—H31B⋯Cg^{i}	0.98	2.71	3.461 (2)	133.00

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2458).

References

Craig, O. & Akinpelu, D. (2005). *Phosphorus Sulfur*, **180**, 1795–1807.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Michaus, Z. & Belen, M. (2005). *Diss. Abstr. Int.* C 66, 148. Universidad de Navarra, Pamplona, Spain.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Vyas, D. A., Chauhan, N. A. & Parik, A. R. (2005). *J. Indian Chem. Soc.* **82**, 972–974.

supplementary materials

2-Chloro-3-methylquinoxaline

A. Thiruvalluvar, M. Subramanyam, R. J. Butcher, A. V. Adhikari and S. Wagle

Comment

Various quinoxaline derivatives have aroused considerable interest of chemistry due to their versatile practical applications as well as their wide range of biological properties. Literature survey reveals that a large number of quinoxaline derivatives have been shown to possess a variety of pharmacological properties like antibacterial, antifungal, antiturberculosis, analgesic and anti-inflammatory activities and hence it is found to be an important structural feature in some synthetic drugs (Craig & Akinpelu, 2005; Michaus & Belen, 2005; and Vyas *et al.* 2005). Certain quinoxaline derivatives have been reported to possess antiallergic properties. Some natural compounds (echinomicine, triostine) contains quinoxaline skeleton. Thus quinoxaline derivatives continue to attract much attention as potential biological interest.

In the title molecule, $C_9H_7ClN_2$, (Fig.1), the quinoxaline unit is planar. The benzene ring makes a dihedral angle of 0.48 (7)° with the pyrazine ring. A weak C31—H31B···π interaction involving a methyl hydrogen and the benzene ring is found in the crystal structure and there are no classical hydrogen bonds.

Experimental

3-methylquinoxalin-2(1*H*)-one (5.0 g, 0.0312 mol) was added to cold phosphorus oxychloride (41.0 g, 0.26 mol) in portions to get a slurry. To the resulting slurry *N,N*-Dimethyl aniline (0.95 g, 0.0078 mol) was added drop wise below 288 K. The brick red mixture was refluxed (at approx. 378 K) for 15 min and the resulting dark brown clear solution was then cooled to ambient temperature. It was added to ice cold water (250 ml) and basified slowly under cooling with 40% aq. NaOH to pH 8. The brick red solid, thus separated was filtered, washed with water (2x50 ml) and dried to obtain crude 2-chloro-3-methylquinoxaline. The crude product was dissolved in hot hexane (75 ml), treated with activated charcoal and filtered. The filtrate on concentration to a small volume (5 ml) gave pure 2-chloro-3-methylquinoxaline, as brick red crystals, which was further recrystalized from acetone to get colourless crystals, 4.0 g (72%).

Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95 or 0.98Å and U_{iso}=1.2 or1.5 times U_{eq}(C).
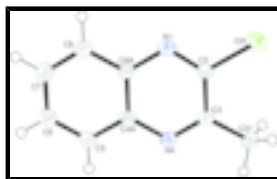
Figures

Fig. 1. The molecular structure of the title compound with the atomic numbering and 50% probability displacement ellipsoids. H atoms are shown shown as small spheres of arbitrary radius.

2-Chloro-3-methylquinoxaline

Crystal data

$C_9H_7ClN_2$	$Z = 2$
$M_r = 178.62$	$F_{000} = 184$
Triclinic, $P\bar{1}$	$D_x = 1.472$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 352(1) K
$a = 6.8876 (4)$ Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 7.4022 (4)$ Å	Cell parameters from 3999 reflections
$c = 9.4124 (5)$ Å	$\theta = 4.7–32.3°$
$\alpha = 70.654 (4)°$	$\mu = 0.41$ mm^{-1}
$\beta = 72.438 (5)°$	$T = 200 (2)$ K
$\gamma = 65.019 (5)°$	Square-plate, pale-pink
$V = 403.01 (4)$ Å^3	$0.51 \times 0.49 \times 0.22$ mm

Data collection

Oxford Diffraction Gemini diffractometer	2645 independent reflections
Radiation source: fine-focus sealed tube	2094 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 200(2)$ K	$\theta_{max} = 32.4°$
φ and ω scans	$\theta_{min} = 4.7°$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)	$h = -9 \rightarrow 10$
$T_{min} = 0.723$, $T_{max} = 1.000$	$k = -10 \rightarrow 11$
5962 measured reflections	$l = -8 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.135$	$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.0905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = <0.001$
2645 reflections	$\Delta\rho_{max} = 0.51$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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*	$U_{iso}*/U_{eq}$
Cl2	0.00177 (6)	0.70740 (7)	0.80205 (4)	0.0376 (1)
N1	0.21428 (18)	0.72294 (18)	0.52218 (14)	0.0255 (3)
N4	−0.14312 (18)	0.76886 (17)	0.40874 (13)	0.0247 (3)
C2	0.0251 (2)	0.7312 (2)	0.60775 (15)	0.0241 (3)
C3	−0.1618 (2)	0.7568 (2)	0.55461 (15)	0.0231 (3)
C4A	0.0544 (2)	0.7597 (2)	0.31326 (15)	0.0235 (3)
C5	0.0785 (2)	0.7733 (2)	0.15555 (16)	0.0296 (4)
C6	0.2739 (3)	0.7667 (3)	0.05928 (17)	0.0350 (5)
C7	0.4533 (3)	0.7452 (3)	0.11537 (18)	0.0352 (4)
C8	0.4348 (2)	0.7302 (2)	0.26786 (18)	0.0304 (4)
C8A	0.2340 (2)	0.7380 (2)	0.36893 (15)	0.0237 (3)
C31	−0.3786 (2)	0.7725 (2)	0.66060 (17)	0.0281 (4)
H5	−0.04064	0.78701	0.11676	0.0355*
H6	0.28933	0.77665	−0.04652	0.0420*
H7	0.58771	0.74115	0.04689	0.0422*
H8	0.55602	0.71478	0.30513	0.0364*
H31A	−0.47923	0.77223	0.60606	0.0422*
H31B	−0.35850	0.65528	0.74960	0.0422*
H31C	−0.43902	0.90007	0.69508	0.0422*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0392 (2)	0.0539 (3)	0.0267 (2)	−0.0194 (2)	−0.0076 (1)	−0.0133 (2)
N1	0.0232 (5)	0.0307 (6)	0.0270 (5)	−0.0123 (4)	−0.0069 (4)	−0.0068 (4)
N4	0.0210 (5)	0.0291 (6)	0.0268 (5)	−0.0097 (4)	−0.0064 (4)	−0.0074 (4)
C2	0.0248 (6)	0.0269 (6)	0.0246 (6)	−0.0102 (5)	−0.0071 (5)	−0.0076 (5)
C3	0.0211 (5)	0.0230 (6)	0.0273 (6)	−0.0085 (4)	−0.0062 (4)	−0.0063 (5)
C4A	0.0220 (5)	0.0259 (6)	0.0246 (6)	−0.0094 (5)	−0.0068 (4)	−0.0053 (5)
C5	0.0297 (6)	0.0371 (8)	0.0253 (6)	−0.0131 (6)	−0.0086 (5)	−0.0069 (5)
C6	0.0367 (8)	0.0445 (9)	0.0240 (7)	−0.0160 (7)	−0.0042 (5)	−0.0077 (6)
C7	0.0286 (7)	0.0442 (9)	0.0308 (7)	−0.0163 (6)	0.0007 (5)	−0.0077 (6)
C8	0.0229 (6)	0.0355 (8)	0.0345 (7)	−0.0132 (5)	−0.0044 (5)	−0.0078 (6)

C8A	0.0215 (5)	0.0263 (6)	0.0259 (6)	−0.0099 (5)	−0.0068 (4)	−0.0057 (5)
C31	0.0213 (5)	0.0339 (7)	0.0298 (7)	−0.0105 (5)	−0.0013 (5)	−0.0107 (5)

Geometric parameters (Å, °)

Cl2—C2	1.7420 (14)	C6—C7	1.415 (3)
N1—C2	1.297 (2)	C7—C8	1.373 (2)
N1—C8A	1.3782 (18)	C8—C8A	1.413 (2)
N4—C3	1.3159 (17)	C5—H5	0.9500
N4—C4A	1.374 (2)	C6—H6	0.9500
C2—C3	1.436 (2)	C7—H7	0.9500
C3—C31	1.507 (2)	C8—H8	0.9500
C4A—C5	1.4169 (19)	C31—H31A	0.9800
C4A—C8A	1.414 (2)	C31—H31B	0.9800
C5—C6	1.368 (3)	C31—H31C	0.9800
Cl2···C4A^i	3.6077 (15)	C5···H31B^{vi}	2.9300
Cl2···H5^{ii}	3.1100	C6···H31B^{vi}	2.9500
Cl2···H6^{ii}	3.0400	C7···H31B^{vi}	3.0800
Cl2···H31B	2.8700	C8···H31C^i	2.8800
Cl2···H31C	3.0800	C31···H6^{iii}	3.0000
Cl2···H7^{iii}	3.0500	H5···Cl2^{vii}	3.1100
N1···N4	2.820 (2)	H6···Cl2^{vii}	3.0400
N4···N1	2.820 (2)	H6···C31^{viii}	3.0000
N1···H31A^{iv}	2.6600	H7···Cl2^{viii}	3.0500
N4···H8^v	2.7500	H8···N4^{iv}	2.7500
C3···C4A^{vi}	3.425 (2)	H31A···N1^v	2.6600
C4A···Cl2^i	3.6077 (15)	H31B···Cl2	2.8700
C4A···C3^{vi}	3.425 (2)	H31B···C4A^{vi}	3.0300
C4A···C31^{vi}	3.581 (2)	H31B···C5^{vi}	2.9300
C8A···C31^{vi}	3.564 (2)	H31B···C6^{vi}	2.9500
C31···C4A^{vi}	3.581 (2)	H31B···C7^{vi}	3.0800
C31···C8A^{vi}	3.564 (2)	H31C···Cl2	3.0800
C4A···H31B^{vi}	3.0300	H31C···C8^i	2.8800
C2—N1—C8A	116.20 (14)	N1—C8A—C8	119.77 (14)
C3—N4—C4A	118.27 (13)	C4A—C8A—C8	120.11 (13)
Cl2—C2—N1	116.17 (12)	C4A—C5—H5	120.00
Cl2—C2—C3	118.67 (11)	C6—C5—H5	120.00
N1—C2—C3	125.16 (13)	C5—C6—H6	120.00
N4—C3—C2	118.88 (13)	C7—C6—H6	120.00
N4—C3—C31	119.21 (14)	C6—C7—H7	120.00
C2—C3—C31	121.91 (12)	C8—C7—H7	120.00
N4—C4A—C5	119.38 (14)	C7—C8—H8	120.00
N4—C4A—C8A	121.37 (12)	C8A—C8—H8	120.00
C5—C4A—C8A	119.25 (13)	C3—C31—H31A	109.00
C4A—C5—C6	119.78 (15)	C3—C31—H31B	109.00

C5—C6—C7	120.82 (14)	C3—C31—H31C	109.00
C6—C7—C8	120.58 (17)	H31A—C31—H31B	109.00
C7—C8—C8A	119.46 (16)	H31A—C31—H31C	109.00
N1—C8A—C4A	120.12 (13)	H31B—C31—H31C	109.00
C8A—N1—C2—Cl2	178.86 (10)	N4—C4A—C5—C6	179.25 (15)
C8A—N1—C2—C3	−0.8 (2)	C8A—C4A—C5—C6	−0.4 (2)
C2—N1—C8A—C4A	−0.4 (2)	N4—C4A—C8A—N1	0.8 (2)
C2—N1—C8A—C8	−179.95 (12)	N4—C4A—C8A—C8	−179.64 (13)
C4A—N4—C3—C2	−1.05 (19)	C5—C4A—C8A—N1	−179.50 (13)
C4A—N4—C3—C31	178.28 (12)	C5—C4A—C8A—C8	0.0 (2)
C3—N4—C4A—C5	−179.71 (13)	C4A—C5—C6—C7	0.4 (3)
C3—N4—C4A—C8A	0.0 (2)	C5—C6—C7—C8	0.1 (3)
Cl2—C2—C3—N4	−178.05 (11)	C6—C7—C8—C8A	−0.5 (3)
Cl2—C2—C3—C31	2.63 (18)	C7—C8—C8A—N1	179.97 (15)
N1—C2—C3—N4	1.6 (2)	C7—C8—C8A—C4A	0.4 (2)
N1—C2—C3—C31	−177.76 (13)		

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $x, y, z+1$; (iii) $x-1, y, z+1$; (iv) $x+1, y, z$; (v) $x-1, y, z$; (vi) $-x, -y+1, -z+1$; (vii) $x, y, z-1$; (viii) $x+1, y, z-1$.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C31—H31B⋯Cg[vi]	0.98	2.71	3.461 (2)	133.00

Symmetry codes: (vi) $-x, -y+1, -z+1$.

Fig. 1