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6,8-Dichloro-3-(pyridin-2-yl)-2-[1-(pyridin-2-yl)ethyl]-1,2-dihydroquinoxaline

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Keywords: crystal structure; quinoxaline derivative; chiral compound.

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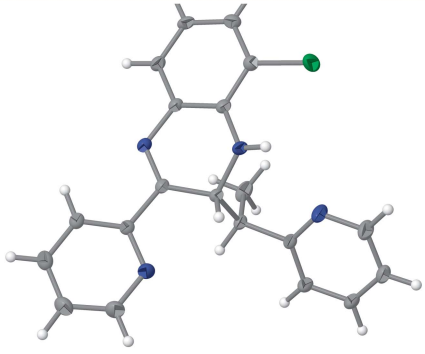
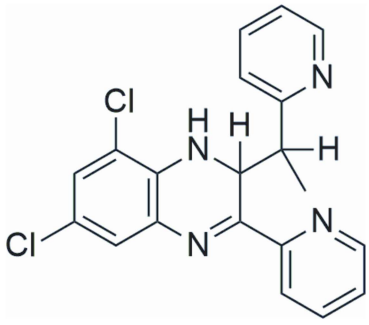
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the racemic title compound, $C_{20}H_{16}C_{l2}N_4$ is described, where the formation of a di-substituted 6,8-dichloro quinoxaline, containing two stereogenic centres, is confirmed.

3D view



Chemical scheme



Structure description

The family of functionalized quinoxaline compounds is an important class of heterocyclic compounds because of their synthetic utility and electroluminescent properties, as well as the different biological properties they have been found to exhibit (Pereira *et al.*, 2015). The gradually expanding library of active compounds has lead to a growing interest into their solid- and solution-state characterization, including single-crystal X-ray diffraction. As part of our studies in this area, we now describe the synthesis and structure of the title compound, $C_{20}H_{16}C_{l2}N_4$.

The compound crystallizes in the monoclinic space group $P2_1/c$ with Z = 4. The asymmetric unit (Fig. 1) contains one molecule, featuring the 6,8-dichloroquinoxaline-based skeleton with two pyridyl-based substituents attached to positions 2 and 3 (atoms C1 and C2, respectively). The compound contains two chiral centres, namely atoms C3 and C14: in the arbitrarily chosen asymmetric unit, these both have an *R* configuration, but crystal symmetry generates a racemic mixture. The quinoxalinyl ring system and the 2-pyridyl groups are close to co-planar [N3—C9—C1—N1 = −179.61 (14), C8—N1—C1—C9 = 175.17 (13)°], with the third picolyl-containing substituent more notably rotated out of plane [C1—C2—C14—C16 = −166.73 (12)°] with respect to the quinoxalinyl group. In the quinoxaline moiety, partial saturation on C2 (position 3) occurs and C2 is sp^3-hybridized with bond angles of 113.58 (12)° (N2—C2—C14), 108.58 (12)° (N2—C2—C1) and 112.34 (12)° (C1—C2—C14). This leads C2 to be displaced by 0.383 (3) Å from the quinoxalinyl mean plane. Bonds lengths supporting the partially saturated

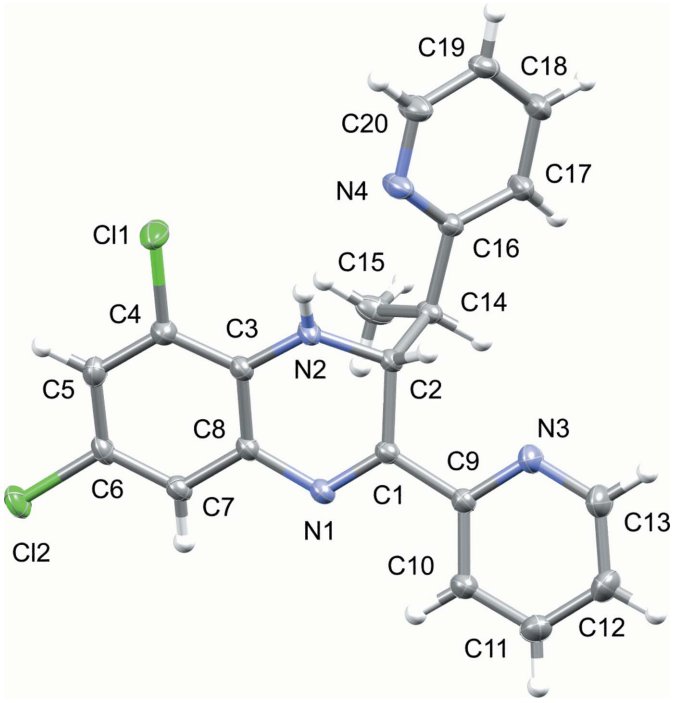


Figure 1
Perspective view of the molecular structure of the title compound showing displacement ellipsoids at the 50% probability level.

character include: 1.290 (2) Å (N1—C1), 1.522 (2) Å (C1—C2), 1.4586 (19) Å (C2—N2) and 1.550 (2) Å (C2—C14). The remaining C—C, C—Cl, and C—N bond lengths and angles agree well with similar pyridyl-containing quinoxaline systems (Wang *et al.*, 2015). A weak bifurcated intramolecular N—H···(N,Cl) hydrogen bond occurs (Table 1).

In the crystal, the compound packs as layers that extend down the *c*-axis interlinked by weak C—H···N hydrogen-bonding interactions (Fig. 2). No aromatic π–π stacking interactions were observed.

Synthesis and crystallization

Picolylamine (1 mmol), 2-methyl-2-(2-pyridyl)ethylamine (1 mmol) and 3,5-dichlorocyclohexan-1,2-dione (1 mmol) were added to a round-bottom flask with methanol (20 ml). The resulting solution was carefully heated to 50°C for approximately 2 h. The yellow solution was left to crystallize, after which yellow crystals of the title compound (which in this case represents the major product) were obtained.

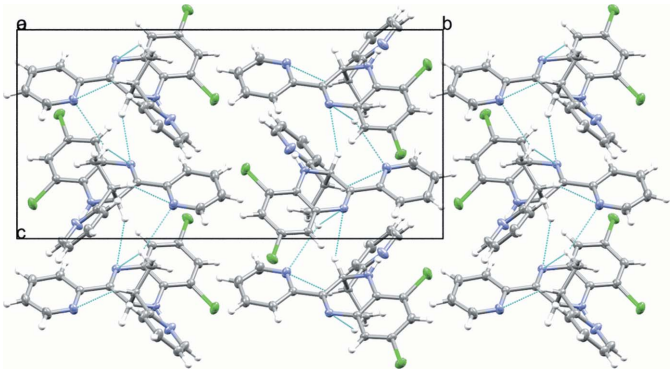


Figure 2
Packing viewed along the *a*-axis direction. Hydrogen-bonding interactions are indicated by means of cyan lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl1	0.88	2.64	2.9941 (13)	105
N2—H2···N4	0.88	2.50	2.815 (2)	102

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{16}Cl_2N_4$
M_r	383.27
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	8.4245 (3), 20.7040 (6), 10.2055 (3)
β (°)	96.448 (3)
V (Å^3)	1768.79 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.38
Crystal size (mm)	0.27 × 0.19 × 0.09
Data collection	
Diffractometer	XtaLAB Synergy R, DW system, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.576, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29036, 4742, 3981
R_{int}	0.112
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.719
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.137, 1.10
No. of reflections	4742
No. of parameters	236
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, −0.58

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The highest calculated residual electron density is 0.62 e Å^{-3} at 0.91 Å from N2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{20}H_{16}Cl_2N_4$
M_r = 383.27
Monoclinic, $P2_1/c$
a = 8.4245 (3) Å
b = 20.7040 (6) Å
c = 10.2055 (3) Å
β = 96.448 (3)°
V = 1768.79 (10) Å^3
Z = 4
$F(000)$ = 792
D_x = 1.439 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 18589 reflections
θ = 2.6–31.0°
μ = 0.38 mm^{-1}
T = 150 K
Blade, yellow
0.27 × 0.19 × 0.09 mm

Data collection

XtaLAB Synergy R, DW system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube, Rigaku (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2019)
T_{min} = 0.576, T_{max} = 1.000
29036 measured reflections
4742 independent reflections
3981 reflections with $I > 2\sigma(I)$
R_{int} = 0.112
θ_{max} = 30.8°, θ_{min} = 2.4°
h = −12→10
k = −28→26
l = −14→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.137
S = 1.10
4742 reflections
236 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.7299P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-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. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl2	1.12383 (5)	0.09926 (2)	0.40380 (4)	0.02882 (13)
Cl1	0.83348 (6)	0.03634 (2)	0.83287 (5)	0.03650 (15)
N1	0.81871 (15)	0.26674 (6)	0.64452 (13)	0.0189 (3)
N2	0.73638 (16)	0.17552 (6)	0.82624 (13)	0.0201 (3)
H2	0.7411	0.1527	0.8994	0.024*
N3	0.59274 (18)	0.36766 (7)	0.83720 (15)	0.0261 (3)
N4	0.45284 (17)	0.14108 (7)	0.93078 (16)	0.0279 (3)
C16	0.37494 (18)	0.18777 (7)	0.85957 (15)	0.0179 (3)
C8	0.85917 (17)	0.20116 (7)	0.63224 (15)	0.0181 (3)
C3	0.81853 (18)	0.15560 (7)	0.72517 (15)	0.0187 (3)
C9	0.69244 (18)	0.35242 (7)	0.74782 (15)	0.0189 (3)
C1	0.72267 (17)	0.28236 (7)	0.72928 (15)	0.0175 (3)
C2	0.64108 (17)	0.23446 (7)	0.81296 (14)	0.0169 (3)
H2A	0.6423	0.2536	0.9030	0.020*
C6	1.00485 (19)	0.12035 (8)	0.52627 (16)	0.0215 (3)
C14	0.46394 (18)	0.22276 (7)	0.75909 (15)	0.0190 (3)
H14	0.4123	0.2659	0.7422	0.023*
C7	0.95056 (18)	0.18329 (8)	0.53247 (15)	0.0205 (3)
H7	0.9755	0.2141	0.4690	0.025*
C10	0.76783 (19)	0.39916 (8)	0.67700 (17)	0.0224 (3)
H10	0.8372	0.3868	0.6142	0.027*
C5	0.96985 (19)	0.07447 (8)	0.61717 (16)	0.0236 (3)
H5	1.0082	0.0315	0.6126	0.028*
C4	0.8772 (2)	0.09267 (8)	0.71550 (17)	0.0230 (3)
C17	0.2167 (2)	0.20287 (8)	0.87252 (19)	0.0271 (4)
H17	0.1635	0.2360	0.8203	0.033*
C19	0.2179 (2)	0.12117 (8)	1.03820 (18)	0.0263 (3)
H19	0.1672	0.0977	1.1018	0.032*
C20	0.3742 (2)	0.10886 (9)	1.01806 (19)	0.0300 (4)
H20	0.4295	0.0757	1.0688	0.036*
C11	0.7391 (2)	0.46377 (8)	0.70050 (19)	0.0288 (4)
H11	0.7886	0.4965	0.6541	0.035*
C12	0.6367 (2)	0.47994 (9)	0.7931 (2)	0.0325 (4)
H12	0.6154	0.5238	0.8118	0.039*
C13	0.5664 (2)	0.43017 (9)	0.8576 (2)	0.0330 (4)
H13	0.4954	0.4414	0.9199	0.040*
C18	0.1374 (2)	0.16896 (9)	0.9625 (2)	0.0305 (4)
H18	0.0290	0.1784	0.9722	0.037*
C15	0.4450 (2)	0.18517 (10)	0.62926 (16)	0.0290 (4)
H15A	0.4889	0.1416	0.6441	0.044*
H15B	0.5026	0.2076	0.5644	0.044*
H15C	0.3315	0.1822	0.5961	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0285 (2)	0.0321 (2)	0.0284 (2)	0.00069 (15)	0.01460 (17)	−0.00866 (15)
Cl1	0.0531 (3)	0.0222 (2)	0.0386 (3)	0.00890 (18)	0.0247 (2)	0.00922 (17)
N1	0.0183 (6)	0.0205 (6)	0.0189 (6)	0.0000 (5)	0.0063 (5)	0.0003 (5)
N2	0.0214 (6)	0.0216 (6)	0.0188 (6)	0.0054 (5)	0.0087 (5)	0.0045 (5)
N3	0.0305 (7)	0.0215 (7)	0.0287 (7)	0.0010 (5)	0.0135 (6)	−0.0030 (5)
N4	0.0194 (7)	0.0333 (8)	0.0324 (8)	0.0030 (6)	0.0085 (6)	0.0137 (6)
C16	0.0175 (7)	0.0186 (7)	0.0182 (7)	−0.0023 (5)	0.0043 (5)	0.0000 (5)
C8	0.0163 (7)	0.0203 (7)	0.0184 (7)	0.0002 (5)	0.0054 (5)	−0.0002 (5)
C3	0.0170 (7)	0.0207 (7)	0.0192 (7)	0.0010 (5)	0.0054 (6)	0.0005 (5)
C9	0.0180 (7)	0.0188 (7)	0.0205 (7)	−0.0004 (5)	0.0044 (6)	−0.0006 (5)
C1	0.0159 (7)	0.0192 (7)	0.0179 (7)	−0.0007 (5)	0.0040 (5)	0.0012 (5)
C2	0.0168 (7)	0.0176 (7)	0.0172 (7)	0.0008 (5)	0.0056 (5)	0.0006 (5)
C6	0.0195 (7)	0.0256 (8)	0.0206 (7)	0.0008 (6)	0.0074 (6)	−0.0066 (6)
C14	0.0163 (7)	0.0217 (7)	0.0196 (7)	0.0002 (5)	0.0047 (5)	0.0053 (6)
C7	0.0209 (7)	0.0226 (8)	0.0190 (7)	−0.0017 (6)	0.0071 (6)	−0.0016 (6)
C10	0.0205 (7)	0.0220 (8)	0.0254 (8)	−0.0009 (6)	0.0062 (6)	0.0017 (6)
C5	0.0241 (8)	0.0208 (8)	0.0266 (8)	0.0031 (6)	0.0059 (6)	−0.0035 (6)
C4	0.0249 (8)	0.0204 (7)	0.0248 (8)	0.0014 (6)	0.0085 (6)	0.0018 (6)
C17	0.0213 (8)	0.0252 (8)	0.0368 (9)	0.0047 (6)	0.0116 (7)	0.0079 (7)
C19	0.0277 (8)	0.0256 (8)	0.0276 (8)	−0.0060 (6)	0.0120 (7)	0.0010 (6)
C20	0.0239 (8)	0.0332 (9)	0.0337 (9)	0.0010 (7)	0.0068 (7)	0.0146 (7)
C11	0.0287 (9)	0.0221 (8)	0.0361 (9)	−0.0044 (6)	0.0056 (7)	0.0010 (7)
C12	0.0383 (10)	0.0196 (8)	0.0407 (10)	0.0001 (7)	0.0093 (8)	−0.0041 (7)
C13	0.0409 (10)	0.0247 (9)	0.0363 (10)	0.0023 (7)	0.0177 (8)	−0.0053 (7)
C18	0.0231 (8)	0.0275 (9)	0.0442 (10)	0.0020 (6)	0.0176 (7)	0.0059 (7)
C15	0.0264 (8)	0.0428 (10)	0.0181 (7)	−0.0098 (7)	0.0033 (6)	−0.0003 (7)

Geometric parameters (Å, º)

Cl2—C6	1.7432 (16)	C9—C1	1.488 (2)
Cl1—C4	1.7406 (17)	C9—C10	1.402 (2)
N1—C8	1.409 (2)	C1—C2	1.522 (2)
N1—C1	1.290 (2)	C2—C14	1.550 (2)
N2—C3	1.3687 (19)	C6—C7	1.385 (2)
N2—C2	1.4586 (19)	C6—C5	1.382 (2)
N3—C9	1.345 (2)	C14—C15	1.529 (2)
N3—C13	1.333 (2)	C10—C11	1.385 (2)
N4—C16	1.336 (2)	C5—C4	1.391 (2)
N4—C20	1.346 (2)	C17—C18	1.385 (2)
C16—C14	1.520 (2)	C19—C20	1.379 (2)
C16—C17	1.390 (2)	C19—C18	1.385 (3)
C8—C3	1.407 (2)	C11—C12	1.390 (3)
C8—C7	1.394 (2)	C12—C13	1.391 (3)
C3—C4	1.401 (2)		

C1—N1—C8	118.51 (13)	C1—C2—C14	112.34 (12)
C3—N2—C2	120.11 (13)	C7—C6—Cl2	119.20 (13)
C13—N3—C9	117.45 (15)	C5—C6—Cl2	119.49 (12)
C16—N4—C20	118.06 (14)	C5—C6—C7	121.29 (14)
N4—C16—C14	117.53 (13)	C16—C14—C2	111.30 (12)
N4—C16—C17	121.91 (15)	C16—C14—C15	109.31 (13)
C17—C16—C14	120.53 (14)	C15—C14—C2	112.90 (13)
C3—C8—N1	120.43 (13)	C6—C7—C8	119.71 (15)
C7—C8—N1	118.68 (14)	C11—C10—C9	118.64 (16)
C7—C8—C3	120.70 (14)	C6—C5—C4	118.51 (15)
N2—C3—C8	119.20 (14)	C3—C4—Cl1	118.10 (12)
N2—C3—C4	123.06 (14)	C5—C4—Cl1	119.63 (12)
C4—C3—C8	117.49 (14)	C5—C4—C3	122.26 (15)
N3—C9—C1	116.33 (14)	C18—C17—C16	119.20 (15)
N3—C9—C10	122.77 (15)	C20—C19—C18	117.70 (16)
C10—C9—C1	120.88 (14)	N4—C20—C19	123.81 (16)
N1—C1—C9	117.29 (14)	C10—C11—C12	118.95 (17)
N1—C1—C2	124.72 (13)	C11—C12—C13	118.25 (17)
C9—C1—C2	117.98 (13)	N3—C13—C12	123.93 (17)
N2—C2—C1	108.58 (12)	C19—C18—C17	119.30 (16)
N2—C2—C14	113.58 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.88	2.64	2.9941 (13)	105
N2—H2···N4	0.88	2.50	2.815 (2)	102