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Ethyl 3-bromo-1-(3-chloropyridin-2-yl)-1H-pyrazole-5-carboxylate

Hai-Bing He, Shan Liu, Hai-Jun Tan, Ming Xia and Hong-Jun Zhu*

Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China
Correspondence e-mail: zhu hj@njut.edu.cn

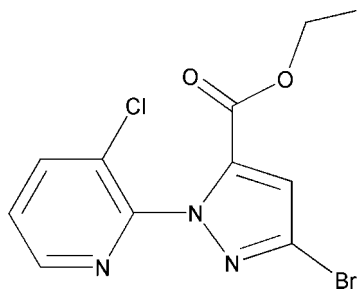
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.056; wR factor = 0.129; data-to-parameter ratio = 14.1.

The title compound, $\text{C}_{11}\text{H}_9\text{BrClN}_3\text{O}_2$, is an intermediate in the synthesis of Rynaxypyre, a new insecticidal anthranilic diamide used as a potent and selective ryanodine receptor activator. The dihedral angle between the aromatic ring planes is $78.7(2)^\circ$.

Related literature

For the synthetic procedure, see: Lahm *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{11}\text{H}_9\text{BrClN}_3\text{O}_2$
 $M_r = 330.57$
 Orthorhombic, $P2_12_12_1$
 $a = 7.404(2)$ Å
 $b = 10.024(2)$ Å
 $c = 17.072(3)$ Å

$V = 1267.0(4)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.45$ mm⁻¹
 $T = 298(2)$ K
 $0.40 \times 0.30 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.339$, $T_{\max} = 0.424$
 (expected range = 0.284–0.355)
 2295 measured reflections

1347 independent reflections
 959 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 3 standard reflections every 200 reflections
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.129$
 $S = 1.00$
 1347 reflections
 163 parameters
 H-atom parameters constrained

$\Delta\rho_{\max} = 0.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³
 Absolute structure: Flack (1983), 15 Friedel pairs
 Flack parameter: 0.37

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2086).

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supplementary materials

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Ethyl 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylate

H.-B. He, S. Liu, H.-J. Tan, M. Xia and H.-J. Zhu

Comment

Ethyl 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylate is one of the important intermediates in the synthesis of Rynaxypyre, a new insecticidal anthranilic diamide used as a potent and selective ryanodine receptor activator (Lahm *et al.*, 2007).

The molecular structure of (I) is shown in Fig. 1, a full list of geometric parameters is given in the supplementary material. The bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The dihedral angle of the rings A (C1—C5/N1) and B(C9—C11/N2/N3) is measured to 78.7 (2)°.

No obvious intra- or inter-molecular hydrogen bonds were observed in the crystal structure (Fig. 2).

Experimental

The title compound (I) was synthesized by a method reported in the literature (Lahm *et al.*, 2007). Crystals of the title compound were obtained by dissolving ethyl 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxylate (3.3 g, 10.0 mmol) in acetonitrile (60 ml) and evaporating the solvent slowly at room temperature for about 20 d.

Refinement

H atoms were positioned geometrically, with O—H = 0.82 Å and C—H = 0.93 Å for aromatic H, 0.97 Å for CH₂ and 0.96 Å for CH₃ groups. Hydrogen atoms were constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C/O})$, where $x = 1.2$ for aromatic H and $x = 1.5$ for other H.

Figures

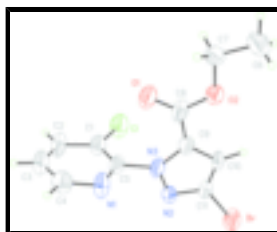


Fig. 1. A drawing of the title molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

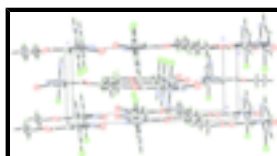


Fig. 2. A packing diagram for (I).

Ethyl 3-bromo-1-(3-chloropyridin-2-yl)-1H-pyrazole-5-carboxylate

Crystal data

$C_{11}H_9BrClN_3O_2$	$F_{000} = 656$
$M_r = 330.57$	$D_x = 1.733 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P 2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 7.404 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 10.024 (2) \text{ \AA}$	$\theta = 9\text{--}13^\circ$
$c = 17.072 (3) \text{ \AA}$	$\mu = 3.45 \text{ mm}^{-1}$
$V = 1267.0 (4) \text{ \AA}^3$	$T = 298 (2) \text{ K}$
$Z = 4$	Block, colourless
	$0.40 \times 0.30 \times 0.30 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.051$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.3^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.4^\circ$
$T = 293(2) \text{ K}$	$h = 0 \rightarrow 8$
$\omega/2\theta$ scans	$k = 0 \rightarrow 12$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$l = -20 \rightarrow 20$
$T_{\text{min}} = 0.339$, $T_{\text{max}} = 0.424$	3 standard reflections
2295 measured reflections	every 200 reflections
1347 independent reflections	intensity decay: 1%
959 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.5P]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1347 reflections	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
163 parameters	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 155 Friedel pairs
	Flack parameter: 0.37

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.03831 (14)	0.07498 (8)	0.79256 (5)	0.0580 (3)
Cl	0.2975 (3)	0.5607 (2)	0.90139 (15)	0.0661 (6)
O1	0.0029 (10)	0.4767 (5)	1.0803 (3)	0.0645 (19)
N1	-0.2392 (8)	0.5697 (7)	0.9219 (4)	0.0481 (16)
C1	0.0862 (11)	0.6189 (7)	0.9087 (5)	0.046 (2)
C2	0.0441 (15)	0.7564 (7)	0.9030 (4)	0.056 (2)
H2A	0.1355	0.8190	0.8964	0.067*
N2	-0.0180 (10)	0.3292 (5)	0.8505 (3)	0.0457 (17)
O2	0.0190 (8)	0.2604 (4)	1.1121 (3)	0.0483 (14)
N3	-0.0260 (10)	0.3932 (5)	0.9196 (3)	0.0442 (16)
C3	-0.1273 (14)	0.7949 (8)	0.9073 (6)	0.059 (2)
H3A	-0.1564	0.8848	0.9027	0.071*
C4	-0.2629 (11)	0.7014 (8)	0.9187 (5)	0.055 (2)
H4A	-0.3801	0.7333	0.9245	0.066*
C5	-0.0628 (13)	0.5354 (6)	0.9191 (4)	0.045 (2)
C6	0.0235 (18)	0.1666 (8)	1.2393 (5)	0.074 (3)
H6A	0.0324	0.1860	1.2943	0.111*
H6B	0.1218	0.1099	1.2241	0.111*
H6C	-0.0889	0.1224	1.2289	0.111*
C7	0.0317 (13)	0.2919 (7)	1.1945 (4)	0.0476 (19)
H7A	-0.0671	0.3499	1.2097	0.057*
H7B	0.1444	0.3377	1.2052	0.057*
C8	0.0085 (12)	0.3603 (7)	1.0617 (4)	0.046 (2)
C9	0.0042 (11)	0.3108 (6)	0.9816 (4)	0.041 (2)
C10	0.0303 (12)	0.1880 (6)	0.9503 (4)	0.0413 (17)
H10A	0.0526	0.1092	0.9773	0.050*
C11	0.0173 (11)	0.2032 (6)	0.8719 (4)	0.0383 (18)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0822 (6)	0.0377 (4)	0.0539 (4)	0.0033 (5)	0.0035 (5)	-0.0055 (4)

supplementary materials

Cl	0.0537 (13)	0.0473 (14)	0.0974 (17)	0.0016 (12)	0.0030 (12)	0.0009 (13)
O1	0.107 (6)	0.032 (3)	0.054 (3)	-0.003 (3)	-0.006 (4)	-0.004 (2)
N1	0.047 (4)	0.028 (4)	0.070 (4)	0.004 (4)	0.019 (3)	0.005 (4)
C1	0.045 (5)	0.034 (4)	0.058 (5)	0.004 (3)	0.002 (4)	0.000 (3)
C2	0.082 (7)	0.026 (4)	0.059 (5)	0.001 (5)	0.018 (6)	0.003 (3)
N2	0.067 (5)	0.028 (3)	0.042 (3)	0.003 (3)	-0.014 (4)	0.002 (2)
O2	0.070 (4)	0.035 (3)	0.040 (2)	0.000 (3)	-0.004 (3)	-0.001 (2)
N3	0.066 (4)	0.024 (3)	0.043 (3)	-0.003 (3)	-0.001 (3)	-0.001 (2)
C3	0.071 (7)	0.030 (5)	0.077 (6)	0.009 (5)	0.004 (6)	-0.003 (4)
C4	0.034 (5)	0.052 (5)	0.079 (6)	0.001 (4)	0.002 (5)	-0.001 (5)
C5	0.073 (6)	0.025 (4)	0.036 (4)	-0.010 (4)	-0.005 (4)	0.007 (3)
C6	0.113 (9)	0.058 (5)	0.050 (5)	0.006 (6)	-0.006 (6)	0.013 (4)
C7	0.059 (5)	0.043 (4)	0.041 (4)	0.010 (4)	-0.006 (4)	-0.005 (3)
C8	0.057 (7)	0.029 (4)	0.052 (4)	-0.008 (4)	0.009 (4)	0.001 (3)
C9	0.052 (6)	0.030 (4)	0.041 (4)	-0.001 (4)	0.000 (4)	0.001 (3)
C10	0.057 (5)	0.019 (3)	0.048 (4)	0.002 (4)	-0.003 (4)	0.003 (3)
C11	0.044 (5)	0.025 (3)	0.046 (4)	-0.004 (3)	0.003 (4)	0.001 (3)

Geometric parameters (\AA , $^\circ$)

Br—C11	1.874 (6)	N3—C5	1.452 (8)
Cl—C1	1.675 (8)	C3—C4	1.387 (12)
O1—C8	1.210 (7)	C3—H3A	0.9300
N1—C4	1.334 (9)	C4—H4A	0.9300
N1—C5	1.351 (11)	C6—C7	1.472 (9)
C1—C5	1.396 (11)	C6—H6A	0.9600
C1—C2	1.416 (10)	C6—H6B	0.9600
C2—C3	1.328 (12)	C6—H6C	0.9600
C2—H2A	0.9300	C7—H7A	0.9700
N2—C11	1.340 (8)	C7—H7B	0.9700
N2—N3	1.344 (7)	C8—C9	1.454 (10)
O2—C8	1.323 (8)	C9—C10	1.356 (9)
O2—C7	1.445 (7)	C10—C11	1.351 (9)
N3—C9	1.361 (8)	C10—H10A	0.9300
C4—N1—C5	112.2 (6)	H6A—C6—H6B	109.5
C5—C1—C2	114.7 (8)	C7—C6—H6C	109.5
C5—C1—Cl	122.6 (6)	H6A—C6—H6C	109.5
C2—C1—Cl	122.6 (7)	H6B—C6—H6C	109.5
C3—C2—C1	119.3 (9)	O2—C7—C6	108.5 (6)
C3—C2—H2A	120.4	O2—C7—H7A	110.0
C1—C2—H2A	120.4	C6—C7—H7A	110.0
C11—N2—N3	102.7 (5)	O2—C7—H7B	110.0
C8—O2—C7	118.2 (5)	C6—C7—H7B	110.0
N2—N3—C9	112.7 (5)	H7A—C7—H7B	108.4
N2—N3—C5	118.2 (5)	O1—C8—O2	124.1 (7)
C9—N3—C5	129.1 (5)	O1—C8—C9	125.1 (7)
C2—C3—C4	120.2 (8)	O2—C8—C9	110.8 (6)
C2—C3—H3A	119.9	C10—C9—N3	105.5 (6)
C4—C3—H3A	119.9	C10—C9—C8	132.6 (6)

N1—C4—C3	125.4 (8)	N3—C9—C8	121.9 (6)
N1—C4—H4A	117.3	C11—C10—C9	106.1 (6)
C3—C4—H4A	117.3	C11—C10—H10A	126.9
N1—C5—C1	128.0 (6)	C9—C10—H10A	126.9
N1—C5—N3	115.5 (7)	N2—C11—C10	113.0 (6)
C1—C5—N3	116.2 (8)	N2—C11—Br	117.8 (5)
C7—C6—H6A	109.5	C10—C11—Br	129.2 (5)
C7—C6—H6B	109.5		
C5—C1—C2—C3	-0.4 (12)	C8—O2—C7—C6	174.4 (8)
C1—C1—C2—C3	178.2 (8)	C7—O2—C8—O1	-2.5 (13)
C11—N2—N3—C9	0.4 (9)	C7—O2—C8—C9	177.6 (7)
C11—N2—N3—C5	180.0 (7)	N2—N3—C9—C10	-0.9 (10)
C1—C2—C3—C4	1.2 (15)	C5—N3—C9—C10	179.6 (8)
C5—N1—C4—C3	4.9 (12)	N2—N3—C9—C8	177.7 (7)
C2—C3—C4—N1	-3.8 (16)	C5—N3—C9—C8	-1.8 (14)
C4—N1—C5—C1	-4.2 (11)	O1—C8—C9—C10	171.0 (10)
C4—N1—C5—N3	-177.9 (6)	O2—C8—C9—C10	-9.1 (13)
C2—C1—C5—N1	2.1 (12)	O1—C8—C9—N3	-7.1 (14)
C1—C1—C5—N1	-176.5 (6)	O2—C8—C9—N3	172.8 (8)
C2—C1—C5—N3	175.8 (6)	N3—C9—C10—C11	0.9 (10)
C1—C1—C5—N3	-2.8 (10)	C8—C9—C10—C11	-177.4 (9)
N2—N3—C5—N1	89.5 (9)	N3—N2—C11—C10	0.2 (10)
C9—N3—C5—N1	-91.0 (10)	N3—N2—C11—Br	179.4 (6)
N2—N3—C5—C1	-85.1 (9)	C9—C10—C11—N2	-0.7 (10)
C9—N3—C5—C1	94.4 (10)	C9—C10—C11—Br	-179.8 (6)

Fig. 1

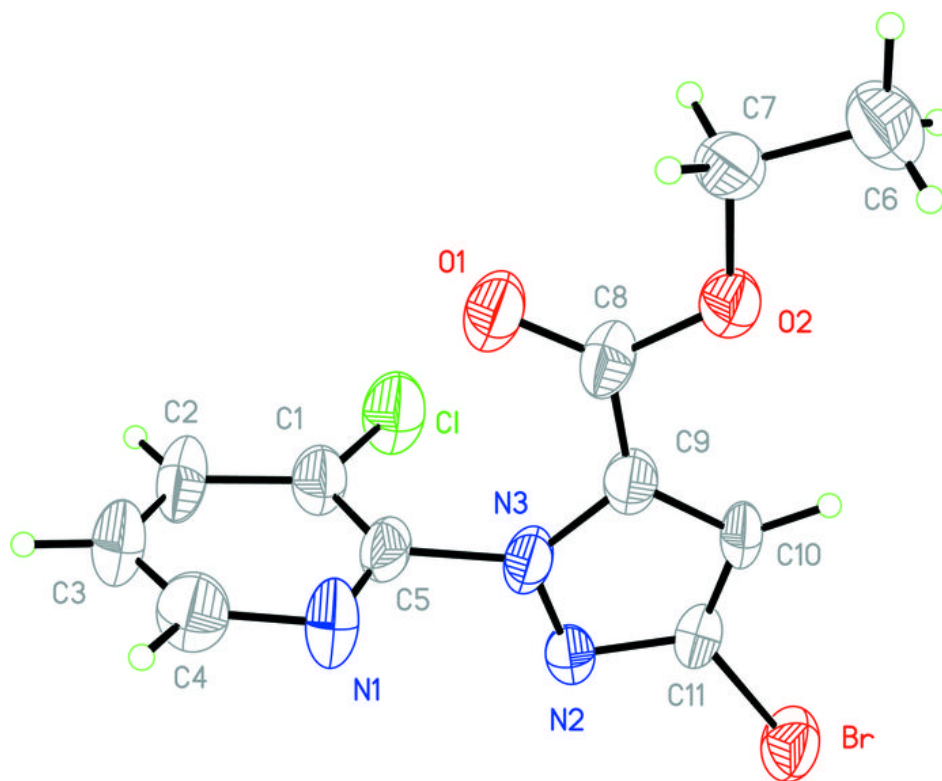


Fig. 2

