

# N-[4-Chloro-2-methyl-6-(N-methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridyl)-3-trifluoromethyl-1H-pyrazole-5-carboxamide

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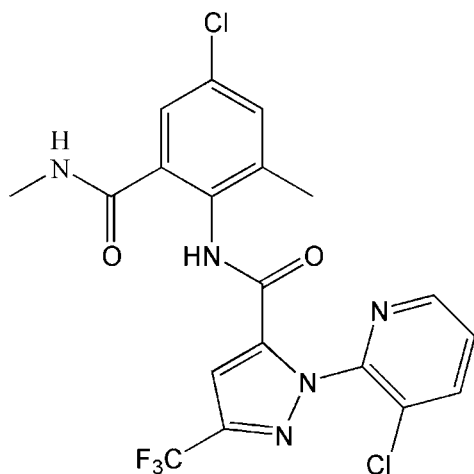
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; disorder in main residue;  $R$  factor = 0.034;  $wR$  factor = 0.082; data-to-parameter ratio = 11.5.

In the title compound,  $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{F}_3\text{N}_5\text{O}_2$ , which shows insecticidal activity, the dihedral angle between the pyrazole and pyridine rings is  $68.15(16)^\circ$ . In the crystal structure, the molecules are linked by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds and an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  interaction also occurs. The F atoms of the  $-\text{CF}_3$  group are disordered over two sets of sites in a 0.800 (8):0.200 (8) ratio.

## Related literature

For the synthesis and background to the insecticidal properties of the title compound, see: Lahm *et al.* (2003, 2005).



## Experimental

### Crystal data

$\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{F}_3\text{N}_5\text{O}_2$   
 $M_r = 472.25$   
 Orthorhombic,  $Fdd2$   
 $a = 26.4612(16)$  Å  
 $b = 32.8657(19)$  Å  
 $c = 9.4679(6)$  Å

$V = 8233.9(9)$  Å<sup>3</sup>  
 $Z = 16$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.37$  mm<sup>-1</sup>  
 $T = 296(2)$  K  
 $0.24 \times 0.20 \times 0.18$  mm

### Data collection

Bruker SMART CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{\min} = 0.917$ ,  $T_{\max} = 0.937$

10439 measured reflections  
 3565 independent reflections  
 3284 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.082$   
 $S = 1.04$   
 3565 reflections  
 310 parameters  
 49 restraints

H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1621 Friedel pairs  
 Flack parameter:  $-0.01(7)$

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N4}-\text{H4}\cdots\text{O2}$	0.86	2.37	2.673 (3)	101
$\text{N4}-\text{H4}\cdots\text{O2}^i$	0.86	2.25	3.107 (3)	176
$\text{N5}-\text{H5}\cdots\text{O1}^{ii}$	0.86	2.16	2.915 (3)	146
$\text{C8}-\text{H8}\cdots\text{O2}^i$	0.93	2.50	3.168 (4)	129

Symmetry codes: (i)  $-x + 1, -y + 2, z$ ; (ii)  $x + \frac{1}{4}, -y + \frac{7}{4}, z - \frac{1}{4}$

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2777).

## References

- Bruker (1999). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Lahm, G. P., Selby, T. P., Freudenberger, J. H., Stevenson, T. M., Myers, B. M., Seburyamo, G., Smith, B. K., Flexner, L., Clark, C. E. & Cordova, D. (2005). *Bioorg. Med. Chem. Lett.* **15**, 4898–4906.  
 Lahm, G. P., Selby, T. P. & Stevenson, T. M. (2003). International Patent Number WO 03/015 519.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

**supplementary materials**

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***N*-[4-Chloro-2-methyl-6-(*N*-methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridyl)-3-trifluoromethyl-1*H*-pyrazole-5-carboxamide**

**H. Yang, H. Yu and B. Li**

**Comment**

Anthranilamide compounds containing an *N*-pyridyl pyrazole grouping are a new class of insecticides showing potent activity against a broad spectrum of Lepidoptera and no-cross resistance to existing insecticides (Lahm *et al.*, 2003) and their mode of action has been established (Lahm *et al.*, 2005). Anthranilamides show little effect on mammalian ryanodine receptors and as a result they show excellent insect *versus* mammalian selectivity. As part of our studies in this area, we now report the crystal structures of the title compound, (I), (Fig. 1) which possesses high insecticidal activity.

The pyrazole ring and pyridine rings are not coplanar, the dihedral angle formed by the least-squares planes of the rings being equal to 68.15 (16)°. The dihedral angle between the mean plane of the pyrazole ring and the plane of the C10/O1/N4 group is 23.4 (2)° and the dihedral angle between the mean plane of the phenyl ring and the plane of the C10/O1/N4 group is 59.9 (2)°.

An intramolecular N—H···O hydrogen bond (Table 1) is observed, which helps to establish the molecular conformation. Intermolecular N—H···O and C—H···O bonds result in a three-dimensional network.

**Experimental**

The title compound was prepared by the literature method (Lahm *et al.*, 2003). The crude products were purified by silica-gel column chromatography and then grown from acetone to afford colourless blocks of (I).

Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 48.32; H, 2.99; N, 14.83. Found: C, 48.47; H, 3.04; N, 14.66. <sup>1</sup>H NMR(CDCl<sub>3</sub>): 2.19 (s, 3H, CH<sub>3</sub>), 2.70 (d, J=4.5 Hz, 3H, CH<sub>3</sub>), 7.30–7.31 (m, 2H, Ph), 7.57 (dd, 1H), 8.05 (d, J=8.1 Hz, 1H), 8.22 (br s, J=4.5 Hz, 1H, NH), 8.46 (d, J=4.8 Hz, 1H), 7.64 (s, 1H), 10.43 (s, 1H, NH).

**Refinement**

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions, with C—H distances in the range 0.93–0.96 Å and N—H distances of 0.86 Å, and included in the final refinement in the riding model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C, N})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . The F atoms of the -CF<sub>3</sub> are disordered over two sets of sites in a 0.800 (8):0.200 (8) ratio.

# supplementary materials

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## N-[4-Chloro-2-methyl-6-(N-methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridyl)-3-trifluoromethyl-1H-pyrazole-5-carboxamide

### Crystal data

$C_{19}H_{14}Cl_2F_3N_5O_2$

$M_r = 472.25$

Orthorhombic, *Fdd2*

$a = 26.4612(16) \text{ \AA}$

$b = 32.8657(19) \text{ \AA}$

$c = 9.4679(6) \text{ \AA}$

$V = 8233.9(9) \text{ \AA}^3$

$Z = 16$

$F(000) = 3840$

$D_x = 1.524 \text{ Mg m}^{-3}$

Melting point: 492(1) K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3952 reflections

$\theta = 2.4\text{--}23.9^\circ$

$\mu = 0.37 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colourless

$0.24 \times 0.20 \times 0.18 \text{ mm}$

### Data collection

Bruker SMART CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 1999)

$T_{\min} = 0.917$ ,  $T_{\max} = 0.937$

10439 measured reflections

3565 independent reflections

3284 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -31 \rightarrow 24$

$k = -34 \rightarrow 38$

$l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.082$

$S = 1.04$

3565 reflections

310 parameters

49 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 8.8659P]$

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

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

$\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Absolute structure: Flack (1983), 1621 Friedel pairs

Flack parameter:  $-0.01(7)$

### 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	0.28309 (3)	1.00598 (3)	0.40561 (10)	0.0647 (3)	
C12	0.46782 (4)	0.85540 (5)	-0.17854 (12)	0.1075 (5)	
F1	0.39895 (14)	1.06805 (12)	0.8595 (6)	0.1059 (17)	0.800 (8)
F2	0.4312 (2)	1.01859 (14)	0.9614 (4)	0.1148 (18)	0.800 (8)
F3	0.47071 (12)	1.04708 (16)	0.7981 (5)	0.0958 (15)	0.800 (8)
F1'	0.4028 (5)	1.0381 (5)	0.9535 (11)	0.074 (4)	0.200 (8)
F2'	0.4714 (4)	1.0263 (5)	0.8653 (18)	0.087 (5)	0.200 (8)
F3'	0.4283 (7)	1.0724 (3)	0.7878 (16)	0.106 (6)	0.200 (8)
O1	0.36097 (7)	0.91496 (6)	0.4022 (2)	0.0453 (5)	
O2	0.52136 (8)	0.96046 (6)	0.3535 (3)	0.0576 (6)	
N1	0.35642 (9)	0.99358 (8)	0.7518 (3)	0.0445 (6)	
N2	0.34753 (8)	0.97021 (6)	0.6376 (2)	0.0360 (5)	
N3	0.28654 (9)	0.92344 (8)	0.7109 (3)	0.0479 (6)	
N4	0.42127 (8)	0.95772 (6)	0.3170 (2)	0.0342 (5)	
H4	0.4359	0.9808	0.3291	0.041*	
N5	0.56488 (8)	0.90701 (7)	0.2779 (3)	0.0419 (6)	
H5	0.5672	0.8873	0.2186	0.050*	
C1	0.26575 (11)	0.96695 (9)	0.5174 (3)	0.0448 (7)	
C2	0.21856 (11)	0.94974 (11)	0.5056 (4)	0.0566 (9)	
H2	0.1958	0.9587	0.4375	0.068*	
C3	0.20605 (12)	0.91908 (11)	0.5966 (4)	0.0602 (10)	
H3	0.1747	0.9064	0.5899	0.072*	
C4	0.23980 (14)	0.90720 (10)	0.6975 (4)	0.0592 (9)	
H4A	0.2302	0.8869	0.7604	0.071*	
C5	0.29811 (10)	0.95245 (8)	0.6209 (3)	0.0379 (6)	
C6	0.40279 (10)	1.00776 (9)	0.7321 (3)	0.0434 (7)	
C7	0.42585 (12)	1.03518 (11)	0.8368 (4)	0.0596 (9)	
C8	0.42392 (10)	0.99401 (9)	0.6056 (3)	0.0429 (7)	
H8	0.4558	1.0000	0.5695	0.052*	
C9	0.38752 (10)	0.96987 (8)	0.5464 (3)	0.0346 (6)	
C10	0.38824 (9)	0.94496 (7)	0.4152 (3)	0.0329 (6)	
C11	0.43316 (10)	0.93476 (7)	0.1941 (3)	0.0323 (6)	
C12	0.48281 (9)	0.92011 (7)	0.1738 (3)	0.0319 (6)	
C13	0.49293 (10)	0.89622 (9)	0.0565 (3)	0.0415 (6)	
H13	0.5254	0.8864	0.0410	0.050*	
C14	0.45484 (12)	0.88718 (10)	-0.0367 (3)	0.0534 (8)	
C15	0.40693 (11)	0.90324 (10)	-0.0207 (3)	0.0507 (8)	
H15	0.3822	0.8976	-0.0875	0.061*	

## supplementary materials

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C16	0.39557 (10)	0.92751 (9)	0.0935 (3)	0.0401 (6)
C17	0.34412 (11)	0.94686 (11)	0.1030 (4)	0.0565 (8)
H17A	0.3290	0.9476	0.0108	0.085*
H17B	0.3474	0.9741	0.1385	0.085*
H17C	0.3232	0.9313	0.1656	0.085*
C18	0.52432 (10)	0.93058 (8)	0.2762 (3)	0.0334 (6)
C19	0.60538 (12)	0.91391 (11)	0.3778 (4)	0.0597 (9)
H19A	0.6216	0.9394	0.3571	0.090*
H19B	0.6296	0.8923	0.3708	0.090*
H19C	0.5918	0.9147	0.4718	0.090*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0572 (5)	0.0631 (5)	0.0737 (6)	0.0044 (4)	-0.0053 (4)	0.0203 (5)
C12	0.0781 (7)	0.1621 (12)	0.0821 (8)	0.0360 (7)	-0.0273 (6)	-0.0839 (8)
F1	0.090 (2)	0.090 (2)	0.137 (3)	0.0050 (19)	-0.020 (2)	-0.063 (2)
F2	0.168 (4)	0.117 (3)	0.059 (2)	-0.042 (3)	-0.040 (2)	-0.0052 (18)
F3	0.067 (2)	0.132 (3)	0.088 (3)	-0.0499 (19)	0.0139 (17)	-0.043 (2)
F1'	0.067 (6)	0.095 (6)	0.060 (6)	-0.014 (5)	0.009 (4)	-0.021 (5)
F2'	0.072 (6)	0.094 (6)	0.094 (7)	0.004 (5)	-0.017 (5)	-0.018 (5)
F3'	0.121 (8)	0.094 (7)	0.103 (7)	-0.008 (5)	-0.014 (5)	-0.004 (5)
O1	0.0485 (11)	0.0440 (11)	0.0433 (11)	-0.0146 (9)	0.0108 (10)	-0.0005 (9)
O2	0.0434 (12)	0.0537 (12)	0.0757 (17)	0.0105 (10)	-0.0185 (11)	-0.0324 (12)
N1	0.0407 (13)	0.0564 (15)	0.0365 (13)	-0.0054 (11)	0.0038 (10)	-0.0095 (11)
N2	0.0312 (11)	0.0441 (12)	0.0326 (12)	-0.0019 (9)	0.0043 (9)	-0.0051 (10)
N3	0.0511 (15)	0.0500 (14)	0.0426 (14)	-0.0052 (12)	0.0153 (11)	-0.0014 (12)
N4	0.0332 (11)	0.0331 (11)	0.0364 (13)	-0.0044 (9)	0.0052 (10)	-0.0030 (10)
N5	0.0347 (12)	0.0433 (13)	0.0478 (14)	0.0065 (10)	-0.0059 (10)	-0.0128 (11)
C1	0.0378 (16)	0.0472 (16)	0.0492 (18)	0.0027 (13)	0.0053 (13)	-0.0069 (14)
C2	0.0356 (17)	0.067 (2)	0.067 (2)	-0.0003 (15)	-0.0020 (16)	-0.0149 (18)
C3	0.0381 (17)	0.068 (2)	0.075 (2)	-0.0137 (16)	0.0124 (17)	-0.022 (2)
C4	0.065 (2)	0.0553 (19)	0.058 (2)	-0.0176 (17)	0.0271 (17)	-0.0078 (16)
C5	0.0335 (14)	0.0422 (15)	0.0380 (16)	-0.0023 (11)	0.0100 (12)	-0.0074 (12)
C6	0.0380 (16)	0.0545 (17)	0.0376 (16)	-0.0054 (13)	-0.0001 (12)	-0.0042 (13)
C7	0.0503 (19)	0.077 (2)	0.052 (2)	-0.0108 (18)	0.0062 (16)	-0.0155 (18)
C8	0.0326 (14)	0.0557 (17)	0.0405 (16)	-0.0058 (13)	0.0051 (12)	-0.0010 (13)
C9	0.0337 (14)	0.0392 (14)	0.0307 (13)	0.0022 (11)	0.0021 (11)	0.0020 (11)
C10	0.0288 (13)	0.0351 (13)	0.0347 (14)	0.0006 (11)	0.0028 (11)	0.0050 (11)
C11	0.0330 (13)	0.0329 (13)	0.0310 (14)	-0.0043 (11)	0.0016 (11)	0.0042 (10)
C12	0.0314 (13)	0.0310 (12)	0.0333 (14)	-0.0044 (10)	0.0008 (11)	0.0008 (11)
C13	0.0357 (14)	0.0499 (16)	0.0391 (15)	0.0027 (12)	0.0002 (12)	-0.0068 (13)
C14	0.0502 (18)	0.069 (2)	0.0405 (17)	0.0035 (16)	-0.0066 (13)	-0.0218 (16)
C15	0.0422 (17)	0.071 (2)	0.0392 (17)	-0.0054 (15)	-0.0108 (13)	-0.0092 (16)
C16	0.0319 (14)	0.0501 (16)	0.0383 (16)	-0.0040 (12)	0.0012 (11)	0.0034 (13)
C17	0.0365 (15)	0.085 (2)	0.0481 (19)	0.0068 (16)	-0.0051 (14)	0.0040 (16)
C18	0.0335 (14)	0.0308 (13)	0.0359 (15)	-0.0015 (11)	-0.0003 (11)	-0.0020 (11)
C19	0.0393 (17)	0.073 (2)	0.067 (2)	0.0107 (15)	-0.0141 (15)	-0.0186 (19)

*Geometric parameters (Å, °)*

C11—C1	1.725 (3)	C2—H2	0.9300
C12—C14	1.736 (3)	C3—C4	1.365 (5)
F1—C7	1.311 (4)	C3—H3	0.9300
F2—C7	1.307 (4)	C4—H4A	0.9300
F3—C7	1.303 (4)	C6—C8	1.397 (4)
F1'—C7	1.266 (8)	C6—C7	1.472 (4)
F2'—C7	1.269 (8)	C8—C9	1.368 (4)
F3'—C7	1.310 (8)	C8—H8	0.9300
O1—C10	1.228 (3)	C9—C10	1.488 (4)
O2—C18	1.227 (3)	C11—C16	1.397 (4)
N1—C6	1.326 (4)	C11—C12	1.412 (4)
N1—N2	1.347 (3)	C12—C13	1.387 (4)
N2—C9	1.366 (3)	C12—C18	1.505 (3)
N2—C5	1.441 (3)	C13—C14	1.372 (4)
N3—C5	1.315 (4)	C13—H13	0.9300
N3—C4	1.353 (4)	C14—C15	1.382 (4)
N4—C10	1.343 (3)	C15—C16	1.377 (4)
N4—C11	1.423 (3)	C15—H15	0.9300
N4—H4	0.8600	C16—C17	1.505 (4)
N5—C18	1.324 (3)	C17—H17A	0.9600
N5—C19	1.447 (4)	C17—H17B	0.9600
N5—H5	0.8600	C17—H17C	0.9600
C1—C2	1.375 (4)	C19—H19A	0.9600
C1—C5	1.386 (4)	C19—H19B	0.9600
C2—C3	1.367 (5)	C19—H19C	0.9600
C6—N1—N2	104.4 (2)	F3—C7—C6	111.8 (3)
N1—N2—C9	112.1 (2)	F2—C7—C6	113.4 (3)
N1—N2—C5	118.5 (2)	F3'—C7—C6	110.7 (7)
C9—N2—C5	129.1 (2)	F1—C7—C6	112.9 (3)
C5—N3—C4	116.0 (3)	C9—C8—C6	104.9 (2)
C10—N4—C11	123.0 (2)	C9—C8—H8	127.5
C10—N4—H4	118.5	C6—C8—H8	127.5
C11—N4—H4	118.5	N2—C9—C8	106.3 (2)
C18—N5—C19	121.1 (2)	N2—C9—C10	122.9 (2)
C18—N5—H5	119.5	C8—C9—C10	130.7 (2)
C19—N5—H5	119.5	O1—C10—N4	124.3 (2)
C2—C1—C5	118.5 (3)	O1—C10—C9	121.2 (2)
C2—C1—C11	119.8 (3)	N4—C10—C9	114.5 (2)
C5—C1—C11	121.7 (2)	C16—C11—C12	120.8 (2)
C3—C2—C1	118.1 (3)	C16—C11—N4	119.4 (2)
C3—C2—H2	120.9	C12—C11—N4	119.8 (2)
C1—C2—H2	120.9	C13—C12—C11	118.8 (2)
C4—C3—C2	119.6 (3)	C13—C12—C18	120.3 (2)
C4—C3—H3	120.2	C11—C12—C18	120.9 (2)
C2—C3—H3	120.2	C14—C13—C12	119.7 (3)
N3—C4—C3	123.4 (3)	C14—C13—H13	120.1

## supplementary materials

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N3—C4—H4A	118.3	C12—C13—H13	120.1
C3—C4—H4A	118.3	C13—C14—C15	121.4 (3)
N3—C5—C1	124.3 (3)	C13—C14—Cl2	118.8 (2)
N3—C5—N2	115.7 (3)	C15—C14—Cl2	119.8 (2)
C1—C5—N2	119.9 (2)	C16—C15—C14	120.5 (3)
N1—C6—C8	112.2 (3)	C16—C15—H15	119.7
N1—C6—C7	120.2 (3)	C14—C15—H15	119.7
C8—C6—C7	127.6 (3)	C15—C16—C11	118.6 (3)
F1'—C7—F2'	106.9 (8)	C15—C16—C17	119.3 (3)
F1'—C7—F3	131.5 (6)	C11—C16—C17	122.1 (3)
F2'—C7—F3	42.6 (7)	C16—C17—H17A	109.5
F1'—C7—F2	45.3 (7)	C16—C17—H17B	109.5
F2'—C7—F2	67.0 (8)	H17A—C17—H17B	109.5
F3—C7—F2	106.3 (4)	C16—C17—H17C	109.5
F1'—C7—F3'	105.2 (8)	H17A—C17—H17C	109.5
F2'—C7—F3'	104.1 (8)	H17B—C17—H17C	109.5
F3—C7—F3'	64.8 (8)	O2—C18—N5	120.9 (2)
F2—C7—F3'	134.7 (7)	O2—C18—C12	121.4 (2)
F1'—C7—F1	62.1 (7)	N5—C18—C12	117.7 (2)
F2'—C7—F1	132.1 (7)	N5—C19—H19A	109.5
F3—C7—F1	107.1 (4)	N5—C19—H19B	109.5
F2—C7—F1	104.8 (4)	H19A—C19—H19B	109.5
F3'—C7—F1	46.8 (8)	N5—C19—H19C	109.5
F1'—C7—C6	115.8 (6)	H19A—C19—H19C	109.5
F2'—C7—C6	113.3 (7)	H19B—C19—H19C	109.5
C6—N1—N2—C9	-0.5 (3)	N1—N2—C9—C10	177.2 (2)
C6—N1—N2—C5	-175.3 (2)	C5—N2—C9—C10	-8.7 (4)
C5—C1—C2—C3	-0.1 (4)	C6—C8—C9—N2	-0.2 (3)
Cl1—C1—C2—C3	-179.5 (3)	C6—C8—C9—C10	-176.6 (3)
C1—C2—C3—C4	1.5 (5)	C11—N4—C10—O1	-8.6 (4)
C5—N3—C4—C3	1.0 (4)	C11—N4—C10—C9	170.3 (2)
C2—C3—C4—N3	-2.0 (5)	N2—C9—C10—O1	-22.0 (4)
C4—N3—C5—C1	0.5 (4)	C8—C9—C10—O1	154.0 (3)
C4—N3—C5—N2	178.7 (2)	N2—C9—C10—N4	159.1 (2)
C2—C1—C5—N3	-1.0 (4)	C8—C9—C10—N4	-24.9 (4)
Cl1—C1—C5—N3	178.5 (2)	C10—N4—C11—C16	64.7 (3)
C2—C1—C5—N2	-179.1 (3)	C10—N4—C11—C12	-116.2 (3)
Cl1—C1—C5—N2	0.4 (4)	C16—C11—C12—C13	-3.9 (4)
N1—N2—C5—N3	-69.8 (3)	N4—C11—C12—C13	177.1 (2)
C9—N2—C5—N3	116.4 (3)	C16—C11—C12—C18	175.2 (2)
N1—N2—C5—C1	108.4 (3)	N4—C11—C12—C18	-3.8 (3)
C9—N2—C5—C1	-65.4 (4)	C11—C12—C13—C14	-0.3 (4)
N2—N1—C6—C8	0.4 (3)	C18—C12—C13—C14	-179.4 (3)
N2—N1—C6—C7	179.6 (3)	C12—C13—C14—C15	3.7 (5)
N1—C6—C7—F1'	11.8 (10)	C12—C13—C14—Cl2	-177.2 (2)
C8—C6—C7—F1'	-169.1 (10)	C13—C14—C15—C16	-2.8 (5)
N1—C6—C7—F2'	135.8 (10)	Cl2—C14—C15—C16	178.0 (3)
C8—C6—C7—F2'	-45.1 (11)	C14—C15—C16—C11	-1.4 (4)
N1—C6—C7—F3	-177.9 (4)	C14—C15—C16—C17	175.9 (3)



C8—C6—C7—F3	1.1 (6)	C12—C11—C16—C15	4.7 (4)
N1—C6—C7—F2	61.9 (5)	N4—C11—C16—C15	-176.2 (2)
C8—C6—C7—F2	-119.0 (5)	C12—C11—C16—C17	-172.5 (3)
N1—C6—C7—F3'	-107.7 (10)	N4—C11—C16—C17	6.6 (4)
C8—C6—C7—F3'	71.4 (11)	C19—N5—C18—O2	4.6 (4)
N1—C6—C7—F1	-57.1 (5)	C19—N5—C18—C12	-177.1 (3)
C8—C6—C7—F1	122.0 (4)	C13—C12—C18—O2	157.4 (3)
N1—C6—C8—C9	-0.2 (3)	C11—C12—C18—O2	-21.8 (4)
C7—C6—C8—C9	-179.3 (3)	C13—C12—C18—N5	-21.0 (4)
N1—N2—C9—C8	0.4 (3)	C11—C12—C18—N5	159.9 (2)
C5—N2—C9—C8	174.5 (3)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4...O2	0.86	2.37	2.673 (3)	101
N4—H4...O2 <sup>i</sup>	0.86	2.25	3.107 (3)	176
N5—H5...O1 <sup>ii</sup>	0.86	2.16	2.915 (3)	146
C8—H8...O2 <sup>i</sup>	0.93	2.50	3.168 (4)	129

Symmetry codes: (i)  $-x+1, -y+2, z$ ; (ii)  $x+1/4, -y+7/4, z-1/4$ .