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## 2-[4-(2-Chlorobenzyl)-3-methyl-6-oxo-1,6-dihydropyridazin-1-yl]-N-(4-fluorophenyl)-acetamide

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**Keywords:** crystal structure; pyridazine; hydrogen bond;  $\pi$ -stacking; arylacetamide; crystal structure.

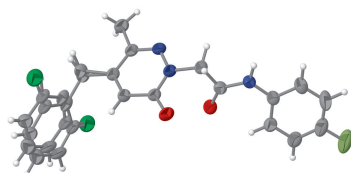
**CCDC reference:** 2301289

**Structural data:** full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

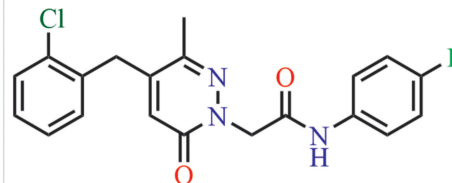
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The conformation of the title molecule, C<sub>20</sub>H<sub>17</sub>ClFN<sub>3</sub>O<sub>2</sub>, is partly determined by an intramolecular C—H...O hydrogen bond, which leads to a dihedral angle of 14.7(4)° between the fluorobenzene ring and the acetamide group. The 2-chlorobenzyl group is rotationally disordered over two orientations in a 0.656(2):0.344(2) ratio. In the crystal, a layered structure is formed by N—H...O, C—H...O and C—H...F hydrogen bonds plus slipped  $\pi$ - $\pi$  stacking interactions.

3D view



Chemical scheme



### Structure description

Pyridazinone derivatives possess a number of biological activities including anti-oxidant (Khokra *et al.*, 2016), anti-bacterial and antifungal (Abiha *et al.* 2018), anti-cancer (Kamble *et al.* 2017), analgesic and anti-inflammatory (Ibrahim *et al.* 2017), anti-depressant (Boukharsa *et al.* 2016) and anti-ulcer properties (Yamada *et al.*, 1981). In addition, *N*-arylacetamide derivatives with their wide spectrum of activities (*e.g.*, Missioui *et al.*, 2022) have significant importance as intermediates in organic chemistry. As a continuation of our work in synthesizing new *N*-arylacetamide derivatives (*e.g.*, Mortada *et al.*, 2023), and developing new pyridazine-3(2*H*)-one compounds (*e.g.*, Zaoui *et al.*, 2022), the title compound C<sub>20</sub>H<sub>17</sub>ClFN<sub>3</sub>O<sub>2</sub> was synthesized and its crystal structure is reported here.

The title molecule adopts an 'extended' conformation with a dihedral angle between the mean plane of the C15–C20 fluorobenzene ring and that defined by N2, C14, C13 and

**Table 1**

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>
N3—H3···O1 <sup>i</sup>	0.88	1.95	2.815 (5)	168
C7—H7A···O2 <sup>ii</sup>	0.99	2.32	3.282 (15)	164
C16—H16···O2	0.95	2.29	2.900 (6)	121
C19—H19···F1 <sup>iii</sup>	0.95	2.42	3.336 (7)	162

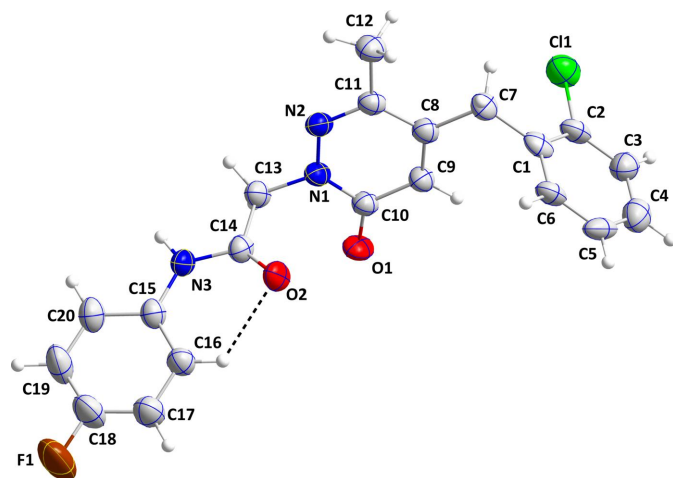
Symmetry codes: (i)  $-x + 2, y + \frac{1}{2}, -z + 1$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + 1$ ; (iii)  $-x + 2, y + \frac{1}{2}, -z$ .

O2 of 14.7 (4)°. This is likely due in part to the intramolecular C16—H16···O2 hydrogen bond (Table 1 and Fig. 1). The dihedral angle between this latter plane and the mean plane of the C8—C11/N1/N2 ring is 72.07 (16)° while that between the mean planes of the C8—C11/N1/N2 and the C1—C6 rings is 80.38 (16)°. The disorder in this part of the molecule features a 177.2 (5)° rotation of the 2-chlorophenyl between the two components of the disorder in a 0.656 (2): 0.344 (2) ratio.

In the crystal, N3—H3···O1 hydrogen bonds form chains of molecules extending along the *b*-axis direction. These are reinforced by slipped  $\pi$ -stacking interactions between a pyridazine and a 4-fluorophenyl ring at  $-x + 2, y + \frac{1}{2}, -z + 1$  [centroid-centroid separation = 3.706 (3) Å, dihedral angle = 8.7 (2)°, slippage = 1.18 Å] (Fig. 2). These chains are connected into layers by C19—H19···F1 hydrogen bonds with the layers further connected by C7—H7A···O2 hydrogen bonds (Fig. 3).

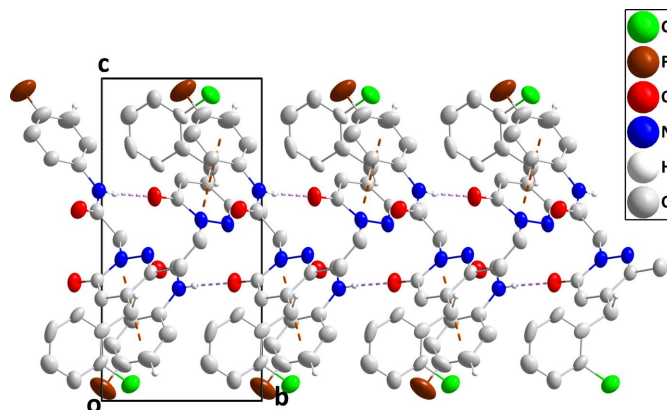
### Synthesis and crystallization

A mixture of 3-benzylidene-4-oxopentanoic acid derivative (0.010 mol) and hydrazine hydrate (0.020 mol) in ethanol was refluxed to obtain the 5-(2-chlorobenzyl)-6-methylpyridazin-3(2*H*)-one precursor. To this pyridazine-3(2*H*)-one (0.010 mol) was added 0.010 mol of 2-chloro-*N*-(4-fluorophenyl)acetamide, followed by 0.020 mol of potassium bicarbonate and a spatula tip of BTBA (benzyltributylammonium bromide). The mixture was kept stirring at room temperature



**Figure 1**

The title molecule with labeling scheme and 50% probability ellipsoids. The intramolecular C—H···O hydrogen bond is depicted by a dashed line and only the major component of the disorder is shown.

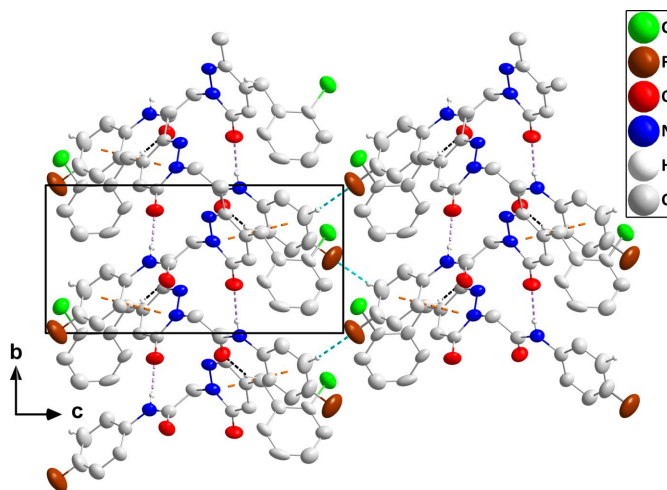


**Figure 2**

A portion of one chain of molecules viewed along the *a*-axis direction with N—H···O hydrogen bonds and slipped,  $\pi$ -stacking interactions depicted, respectively, by violet and orange dashed lines. Non-interacting hydrogen atoms are omitted for clarity.

for 24 h and the progress of the reaction was monitored by TLC. Then, 200 ml of distilled water were added to the reaction mixture, the precipitated product was filtered off, dried and recrystallized from acetone solution to yield colorless crystals of the title compound.

Yield 82%; m.p: 477–479 K. <sup>1</sup>H NMR [300 MHz DMSO-*d*<sub>6</sub>,  $\delta$ (p.p.m.)]: 2.25 (*s*, 3H, CH<sub>3</sub>); 3.96 (*s*, 2H, phenyl-CH<sub>2</sub>-pyridazinone); 4.78 (*s*, 2H, N—CH<sub>2</sub>—CO); 6.06 (*s*, 1H, pyridazinone); 7.07–7.58 (*m*, 8H, two phenyl); 10.32 (*s*, 1H, NH). <sup>13</sup>C NMR [126 MHz DMSO-*d*<sub>6</sub>,  $\delta$ (p.p.m.)]: 19.06 (CH<sub>3</sub>); 35.32 (phenyle-CH<sub>2</sub>-pyridazinone); 54.61 (pyridazinone-CH<sub>2</sub>—CO); 115.84 (*d*, *J* = 22.5 Hz) (C aromatic acetamide); 121.32 (*d*, *J* = 7.7 Hz) (C aromatic acetamide); 126.55 (CH pyridazinone); 128.32 (C aromatic); 129.73 (C aromatic); 130.17 (C aromatic); 132.08 (C aromatic); 134.02 (C aromatic); 134.87 (C aromatic-CH<sub>2</sub>); 135.67 (*d*, *J* = 2,5 Hz) (C aromatic-NH); 144.88



**Figure 3**

Packing viewed along the *a*-axis direction with N—H···O, C—H···O and C—H···F hydrogen bonds depicted, respectively, by violet, black and light blue dashed lines. Slipped  $\pi$ -stacking interactions are depicted by orange dashed lines and non-interacting hydrogen atoms are omitted for clarity.

(CH<sub>2</sub>–C pyridazinone); 145.96 (C pyridazinone–CH<sub>3</sub>); 157.63 (*d*, *J* = 293,9 Hz) (C aromatic-F); 159.83 (C pyridazinone=O); 165.68 (NH–C=O). MS (ESI+): *m/z* = 386.10.

## Refinement

Crystal data, data collection and refinement details are presented in Table 2. The *o*-chlorobenzyl group is rotationally disordered over two orientations in a 0.656 (2): 0.344 (2) ratio with the components refined with restraints to make their geometries comparable. One reflection affected by the beamstop was omitted from the final refinement.

## Acknowledgements

Author contributions are as follows. Conceptualization, MA and IAE; methodology, YR; investigation, HA and AEAA; writing (original draft), JMT and YR; writing (review and editing of the manuscript), YR; formal analysis, AS and YR; supervision, MA and YR; crystal structure determination and validation, JTM.

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## References

- Abiha, G. B., Bahar, L. & Utku, S. (2018). *Rev. Rom. Med. Lab.* **26**, 231–241.
- Boukharsa, Y., Meddah, B., Tiendrebeogo, R. Y., Ibrahim, A., Taoufik, J., Cherrah, Y., Benomar, A., Faouzi, M. E. A. & Ansar, M. (2016). *Med. Chem. Res.* **25**, 494–500.
- Brandenburg, K. & Putz, H. (2012). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.
- Bruker (2021). *APEX4 and SAINT*. Bruker AXS LLC, Madison, Wisconsin, USA.
- Ibrahim, T. H., Loksha, Y. M., Elshihawy, H. A., Khodeer, D. M. & Said, M. M. (2017). *Arch. Pharm. Chem. Life Sci.* **350**, e1700093.
- Kamble, V. T., Sawant, A.-S., Sawant, S. S., Pisal, P. M., Gacche, R. N., Kamble, S. S., Shegokar, H. D. & Kamble, V. A. (2017). *J. Basic Appl. Res. Int.* **21**, 10–39.
- Khokra, S. L., Khan, S. A., Thakur, P., Chowdhary, D., Ahmad, A. & Husain, A. (2016). *J. Chin. Chem. Soc.* **63**, 739–750.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Missioui, M., Said, M. A., Demirtaş, G., Mague, J. T. & Ramli, Y. (2022). *J. Mol. Struct.* **1247**, 131420.

**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>20</sub> H <sub>17</sub> ClFN <sub>3</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	385.82
Crystal system, space group	Monoclinic, <i>P2</i> <sub>1</sub>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.0602 (13), 6.7704 (9), 14.524 (2)
$\beta$ (°)	110.168 (2)
<i>V</i> (Å <sup>3</sup> )	928.6 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.24
Crystal size (mm)	0.19 × 0.14 × 0.08
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 3 diffractometer
Absorption correction	Numerical ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.80, 0.98
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	6266, 2856, 2376
<i>R</i> <sub>int</sub>	0.039
$\theta$ <sub>max</sub> (°)	23.9
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.570
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.048, 0.131, 1.03
No. of reflections	2856
No. of parameters	240
No. of restraints	17
H-atom treatment	H-atom parameters constrained
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	0.27, -0.28
Absolute structure	Flack <i>x</i> determined using 904 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.01 (7)

Computer programs: *APEX4* and *SAINTE* (Bruker, 2021), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/1* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

- Mortada, S., Guerrab, W., Missioui, M., Salhi, N., Naceiri Mrabti, H., Rouass, L., Benkirane, S., Hassane, M., Masrar, A., Mezzour, H., Faouzi, M. E. A. & Ramli, Y. (2023). *J. Biomol. Struct. Dyn.* pp. 1–15.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015*a*). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.
- Yamada, T., Nobuhara, Y., Shimamura, H., Yoshihara, K., Yamaguchi, A. & Ohki, M. (1981). *Chem. Pharm. Bull.* **29**, 3433–3439.
- Zaoui, Y., Assila, H., Mague, J. T., Alsubari, A., Taoufik, J., Ramli, Y. & Ansar, M. (2022). *IUCrData*, **7**, x220582.

## full crystallographic data

*IUCrData* (2023). **8**, x230901 [https://doi.org/10.1107/S241431462300901X]

## 2-[4-(2-Chlorobenzyl)-3-methyl-6-oxo-1,6-dihydropyridazin-1-yl]-N-(4-fluorophenyl)acetamide

Hamza Assila, Issam Ameziane El Hassani, Abderrazzak El Moutaouakil Ala Allah, Abdulsalam Alsubari, Joel T Mague, Youssef Ramli and MHammed Ansar

### 2-[4-(2-Chlorobenzyl)-3-methyl-6-oxo-1,6-dihydropyridazin-1-yl]-N-(4-fluorophenyl)acetamide

#### Crystal data

C<sub>20</sub>H<sub>17</sub>ClFN<sub>3</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 385.82  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 10.0602 (13) Å  
*b* = 6.7704 (9) Å  
*c* = 14.524 (2) Å  
 $\beta$  = 110.168 (2)°  
*V* = 928.6 (2) Å<sup>3</sup>  
*Z* = 2

*F*(000) = 400  
*D<sub>x</sub>* = 1.380 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 3275 reflections  
 $\theta$  = 3.0–23.6°  
 $\mu$  = 0.24 mm<sup>-1</sup>  
*T* = 150 K  
 Plate, colourless  
 0.19 × 0.14 × 0.08 mm

#### Data collection

Bruker D8 QUEST PHOTON 3  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution: 7.3910 pixels mm<sup>-1</sup>  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: numerical  
 (*SADABS*; Krause *et al.*, 2015)  
*T<sub>min</sub>* = 0.80, *T<sub>max</sub>* = 0.98

6266 measured reflections  
 2856 independent reflections  
 2376 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.039  
 $\theta_{\max}$  = 23.9°,  $\theta_{\min}$  = 3.0°  
*h* = -11→11  
*k* = -7→7  
*l* = -16→16

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR* (*F*<sup>2</sup>) = 0.131  
*S* = 1.03  
 2856 reflections  
 240 parameters  
 17 restraints  
 Primary atom site location: dual  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.1965P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack *x* determined using  
 904 quotients [(*I*<sup>+</sup>)-(*I*)]/[(*I*<sup>+</sup>)+(*I*)] (Parsons *et al.*, 2013)  
 Absolute structure parameter: -0.01 (7)

*Special details*

**Experimental.** The diffraction data were collected in three sets of 363 frames ( $0.5^\circ$  width in  $\omega$ ) at  $\varphi = 0, 120$  and  $240^\circ$ . A scan time of 40 sec/frame was used.

**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.** 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  $F^2 > 2\sigma(F^2)$  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. H-atoms attached to carbon were placed in calculated positions ( $C-H = 0.95 - 0.99 \text{ \AA}$ ) and were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. That attached to nitrogen was located in a difference map and refined with a DFIX 0.91 0.01 instruction. The *o*-chlorobenzyl group is rotationally disordered over two sites  $177.2 (5)^\circ$  apart in a  $0.656 (2)/0.344 (2)$  ratio. The two components were refined as rigid hexagons with additional restraints to make their geometries comparable. One reflection affected by the beam stop was omitted from the final refinement.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$	Occ. (<1)
Cl1	0.7132 (2)	0.6802 (4)	0.94862 (15)	0.0618 (6)	0.656 (2)
Cl1A	0.3896 (4)	0.3635 (7)	0.6576 (3)	0.0618 (6)	0.344 (2)
F1	0.9061 (5)	0.0075 (7)	0.0379 (3)	0.1107 (17)	
O1	0.9168 (3)	0.3291 (5)	0.6332 (3)	0.0492 (9)	
O2	0.7561 (3)	0.3559 (5)	0.4072 (2)	0.0485 (9)	
N1	0.8281 (4)	0.6205 (5)	0.5611 (3)	0.0390 (9)	
N2	0.7474 (4)	0.7866 (6)	0.5485 (3)	0.0400 (9)	
N3	0.9225 (4)	0.4816 (6)	0.3484 (3)	0.0391 (9)	
H3	0.983416	0.579248	0.357540	0.047*	
C7	0.5560 (15)	0.6816 (12)	0.7246 (10)	0.046 (3)	0.656 (2)
H7A	0.463053	0.714697	0.674956	0.055*	0.656 (2)
H7B	0.585469	0.795035	0.770111	0.055*	0.656 (2)
C1	0.5373 (5)	0.5015 (6)	0.7825 (3)	0.041 (2)	0.656 (2)
C2	0.6067 (5)	0.4920 (7)	0.8834 (3)	0.0432 (13)	0.656 (2)
C3	0.5904 (6)	0.3270 (8)	0.9354 (3)	0.052 (2)	0.656 (2)
H3A	0.637871	0.320515	1.004371	0.063*	0.656 (2)
C4	0.5046 (6)	0.1717 (7)	0.8867 (4)	0.059 (2)	0.656 (2)
H4	0.493389	0.058937	0.922286	0.071*	0.656 (2)
C5	0.4351 (5)	0.1812 (7)	0.7858 (4)	0.056 (2)	0.656 (2)
H5	0.376434	0.075013	0.752518	0.067*	0.656 (2)
C6	0.4514 (5)	0.3461 (8)	0.7338 (3)	0.0432 (13)	0.656 (2)
H6	0.403960	0.352669	0.664833	0.052*	0.656 (2)
C7A	0.583 (4)	0.712 (2)	0.741 (2)	0.046 (3)	0.344 (2)
H7C	0.484915	0.750414	0.700522	0.055*	0.344 (2)
H7D	0.628844	0.828556	0.780181	0.055*	0.344 (2)
C1A	0.5776 (10)	0.5441 (14)	0.8094 (7)	0.041 (2)	0.344 (2)
C2A	0.6600 (10)	0.5581 (14)	0.9082 (7)	0.0432 (13)	0.344 (2)
H2A	0.718157	0.670747	0.931670	0.052*	0.344 (2)

C3A	0.6572 (11)	0.4075 (16)	0.9725 (6)	0.052 (2)	0.344 (2)
H3B	0.713505	0.417063	1.039937	0.063*	0.344 (2)
C4A	0.5721 (13)	0.2427 (14)	0.9381 (8)	0.059 (2)	0.344 (2)
H4A	0.570209	0.139715	0.982019	0.071*	0.344 (2)
C5A	0.4897 (12)	0.2286 (14)	0.8393 (9)	0.056 (2)	0.344 (2)
H5A	0.431564	0.116050	0.815834	0.067*	0.344 (2)
C6A	0.4925 (10)	0.3793 (18)	0.7750 (6)	0.0432 (13)	0.344 (2)
C8	0.6632 (4)	0.6569 (7)	0.6726 (3)	0.0385 (11)	
C9	0.7456 (5)	0.4970 (7)	0.6832 (4)	0.0393 (10)	
H9	0.743747	0.398076	0.729138	0.047*	
C10	0.8370 (4)	0.4717 (7)	0.6265 (3)	0.0374 (10)	
C11	0.6674 (4)	0.8051 (7)	0.6030 (3)	0.0381 (11)	
C12	0.5826 (5)	0.9905 (8)	0.5867 (4)	0.0513 (13)	
H12A	0.606286	1.063382	0.648541	0.077*	
H12B	0.481472	0.957689	0.562809	0.077*	
H12C	0.604076	1.072240	0.537915	0.077*	
C13	0.9116 (5)	0.6132 (7)	0.4974 (4)	0.0429 (12)	
H13A	1.009880	0.574945	0.536509	0.052*	
H13B	0.914605	0.746647	0.470293	0.052*	
C14	0.8535 (5)	0.4690 (7)	0.4135 (3)	0.0393 (11)	
C15	0.9084 (4)	0.3573 (7)	0.2676 (3)	0.0410 (11)	
C16	0.8316 (5)	0.1846 (8)	0.2489 (3)	0.0450 (11)	
H16	0.778599	0.147835	0.289062	0.054*	
C17	0.8311 (6)	0.0641 (9)	0.1718 (4)	0.0572 (14)	
H17	0.779684	-0.056479	0.159180	0.069*	
C18	0.9065 (6)	0.1228 (10)	0.1143 (4)	0.0662 (17)	
C19	0.9804 (7)	0.2951 (11)	0.1287 (4)	0.0687 (17)	
H19	1.029488	0.333303	0.086165	0.082*	
C20	0.9824 (5)	0.4130 (9)	0.2065 (4)	0.0526 (14)	
H20	1.034536	0.532974	0.218520	0.063*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0550 (10)	0.0672 (12)	0.0641 (11)	-0.0116 (9)	0.0217 (8)	-0.0154 (10)
Cl1A	0.0550 (10)	0.0672 (12)	0.0641 (11)	-0.0116 (9)	0.0217 (8)	-0.0154 (10)
F1	0.134 (4)	0.130 (4)	0.094 (3)	-0.030 (3)	0.072 (3)	-0.054 (3)
O1	0.0436 (18)	0.038 (2)	0.074 (2)	0.0100 (16)	0.0311 (17)	-0.0024 (17)
O2	0.0387 (17)	0.052 (2)	0.063 (2)	-0.0123 (17)	0.0283 (16)	-0.0098 (18)
N1	0.035 (2)	0.034 (2)	0.054 (2)	0.0004 (17)	0.0227 (18)	-0.0041 (18)
N2	0.037 (2)	0.032 (2)	0.054 (2)	-0.0014 (17)	0.0195 (19)	-0.0036 (18)
N3	0.034 (2)	0.039 (2)	0.050 (2)	-0.0057 (18)	0.0216 (17)	-0.0019 (19)
C7	0.043 (6)	0.044 (4)	0.060 (5)	0.008 (5)	0.029 (6)	0.002 (5)
C1	0.026 (4)	0.049 (5)	0.050 (4)	0.007 (4)	0.017 (3)	-0.012 (4)
C2	0.037 (3)	0.043 (3)	0.051 (4)	-0.005 (2)	0.017 (3)	-0.021 (3)
C3	0.054 (5)	0.043 (5)	0.067 (6)	0.001 (4)	0.030 (5)	0.001 (4)
C4	0.055 (5)	0.060 (5)	0.074 (5)	0.007 (4)	0.036 (4)	0.009 (4)
C5	0.048 (5)	0.033 (4)	0.100 (8)	-0.008 (4)	0.041 (5)	-0.021 (5)

C6	0.037 (3)	0.043 (3)	0.051 (4)	-0.005 (2)	0.017 (3)	-0.021 (3)
C7A	0.043 (6)	0.044 (4)	0.060 (5)	0.008 (5)	0.029 (6)	0.002 (5)
C1A	0.026 (4)	0.049 (5)	0.050 (4)	0.007 (4)	0.017 (3)	-0.012 (4)
C2A	0.037 (3)	0.043 (3)	0.051 (4)	-0.005 (2)	0.017 (3)	-0.021 (3)
C3A	0.054 (5)	0.043 (5)	0.067 (6)	0.001 (4)	0.030 (5)	0.001 (4)
C4A	0.055 (5)	0.060 (5)	0.074 (5)	0.007 (4)	0.036 (4)	0.009 (4)
C5A	0.048 (5)	0.033 (4)	0.100 (8)	-0.008 (4)	0.041 (5)	-0.021 (5)
C6A	0.037 (3)	0.043 (3)	0.051 (4)	-0.005 (2)	0.017 (3)	-0.021 (3)
C8	0.035 (2)	0.037 (3)	0.045 (3)	0.001 (2)	0.016 (2)	-0.003 (2)
C9	0.036 (2)	0.037 (3)	0.051 (3)	0.003 (2)	0.022 (2)	-0.001 (2)
C10	0.035 (2)	0.033 (2)	0.046 (3)	0.002 (2)	0.017 (2)	-0.002 (2)
C11	0.033 (2)	0.035 (3)	0.048 (3)	0.000 (2)	0.015 (2)	-0.006 (2)
C12	0.050 (3)	0.043 (3)	0.067 (3)	0.006 (2)	0.028 (3)	-0.002 (3)
C13	0.037 (2)	0.041 (3)	0.059 (3)	-0.007 (2)	0.028 (2)	-0.009 (2)
C14	0.031 (2)	0.040 (3)	0.052 (3)	0.000 (2)	0.020 (2)	0.001 (2)
C15	0.033 (2)	0.048 (3)	0.045 (3)	0.000 (2)	0.017 (2)	0.001 (2)
C16	0.043 (3)	0.047 (3)	0.047 (3)	-0.003 (2)	0.018 (2)	-0.006 (3)
C17	0.058 (3)	0.058 (3)	0.059 (3)	-0.007 (3)	0.025 (3)	-0.013 (3)
C18	0.070 (4)	0.079 (4)	0.057 (3)	-0.007 (3)	0.031 (3)	-0.024 (3)
C19	0.068 (4)	0.096 (5)	0.057 (3)	-0.012 (4)	0.041 (3)	-0.010 (3)
C20	0.044 (3)	0.065 (4)	0.055 (3)	-0.003 (3)	0.026 (3)	0.003 (3)

*Geometric parameters (Å, °)*

C11—C2	1.723 (4)	C1A—C6A	1.3900
C11A—C6A	1.666 (9)	C2A—C3A	1.3900
F1—C18	1.355 (7)	C2A—H2A	0.9500
O1—C10	1.237 (5)	C3A—C4A	1.3900
O2—C14	1.222 (5)	C3A—H3B	0.9500
N1—N2	1.362 (5)	C4A—C5A	1.3900
N1—C10	1.366 (6)	C4A—H4A	0.9500
N1—C13	1.450 (6)	C5A—C6A	1.3900
N2—C11	1.314 (6)	C5A—H5A	0.9500
N3—C14	1.356 (5)	C8—C9	1.340 (6)
N3—C15	1.410 (6)	C8—C11	1.435 (7)
N3—H3	0.8800	C9—C10	1.441 (6)
C7—C8	1.525 (6)	C9—H9	0.9500
C7—C1	1.529 (6)	C11—C12	1.490 (6)
C7—H7A	0.9900	C12—H12A	0.9800
C7—H7B	0.9900	C12—H12B	0.9800
C1—C2	1.3900	C12—H12C	0.9800
C1—C6	1.3900	C13—C14	1.512 (7)
C2—C3	1.3900	C13—H13A	0.9900
C3—C4	1.3900	C13—H13B	0.9900
C3—H3A	0.9500	C15—C16	1.376 (7)
C4—C5	1.3900	C15—C20	1.393 (6)
C4—H4	0.9500	C16—C17	1.384 (7)
C5—C6	1.3900	C16—H16	0.9500

C5—H5	0.9500	C17—C18	1.367 (8)
C6—H6	0.9500	C17—H17	0.9500
C7A—C8	1.524 (7)	C18—C19	1.360 (9)
C7A—C1A	1.529 (6)	C19—C20	1.378 (8)
C7A—H7C	0.9900	C19—H19	0.9500
C7A—H7D	0.9900	C20—H20	0.9500
C1A—C2A	1.3900		
N2—N1—C10	126.5 (4)	C6A—C5A—H5A	120.0
N2—N1—C13	113.1 (4)	C5A—C6A—C1A	120.0
C10—N1—C13	120.3 (4)	C5A—C6A—C11A	119.4 (7)
C11—N2—N1	117.3 (4)	C1A—C6A—C11A	120.5 (8)
C14—N3—C15	127.9 (4)	C9—C8—C11	118.6 (4)
C14—N3—H3	116.0	C9—C8—C7A	124.8 (6)
C15—N3—H3	116.0	C11—C8—C7A	115.8 (5)
C8—C7—C1	115.3 (4)	C9—C8—C7	123.1 (5)
C8—C7—H7A	108.4	C11—C8—C7	118.0 (4)
C1—C7—H7A	108.4	C8—C9—C10	121.4 (4)
C8—C7—H7B	108.4	C8—C9—H9	119.3
C1—C7—H7B	108.4	C10—C9—H9	119.3
H7A—C7—H7B	107.5	O1—C10—N1	121.0 (4)
C2—C1—C6	120.0	O1—C10—C9	124.9 (4)
C2—C1—C7	120.3 (7)	N1—C10—C9	114.1 (4)
C6—C1—C7	119.7 (7)	N2—C11—C8	122.0 (4)
C1—C2—C3	120.0	N2—C11—C12	114.9 (4)
C1—C2—C11	122.4 (3)	C8—C11—C12	123.1 (4)
C3—C2—C11	117.6 (3)	C11—C12—H12A	109.5
C4—C3—C2	120.0	C11—C12—H12B	109.5
C4—C3—H3A	120.0	H12A—C12—H12B	109.5
C2—C3—H3A	120.0	C11—C12—H12C	109.5
C3—C4—C5	120.0	H12A—C12—H12C	109.5
C3—C4—H4	120.0	H12B—C12—H12C	109.5
C5—C4—H4	120.0	N1—C13—C14	112.8 (4)
C6—C5—C4	120.0	N1—C13—H13A	109.0
C6—C5—H5	120.0	C14—C13—H13A	109.0
C4—C5—H5	120.0	N1—C13—H13B	109.0
C5—C6—C1	120.0	C14—C13—H13B	109.0
C5—C6—H6	120.0	H13A—C13—H13B	107.8
C1—C6—H6	120.0	O2—C14—N3	125.2 (4)
C8—C7A—C1A	112.7 (6)	O2—C14—C13	122.9 (4)
C8—C7A—H7C	109.1	N3—C14—C13	111.9 (4)
C1A—C7A—H7C	109.1	C16—C15—C20	119.4 (4)
C8—C7A—H7D	109.1	C16—C15—N3	124.1 (4)
C1A—C7A—H7D	109.1	C20—C15—N3	116.5 (4)
H7C—C7A—H7D	107.8	C15—C16—C17	120.4 (5)
C2A—C1A—C6A	120.0	C15—C16—H16	119.8
C2A—C1A—C7A	118.8 (17)	C17—C16—H16	119.8
C6A—C1A—C7A	121.2 (17)	C18—C17—C16	118.4 (5)



C1A—C2A—C3A	120.0	C18—C17—H17	120.8
C1A—C2A—H2A	120.0	C16—C17—H17	120.8
C3A—C2A—H2A	120.0	F1—C18—C19	117.9 (5)
C4A—C3A—C2A	120.0	F1—C18—C17	119.1 (5)
C4A—C3A—H3B	120.0	C19—C18—C17	123.0 (5)
C2A—C3A—H3B	120.0	C18—C19—C20	118.4 (5)
C5A—C4A—C3A	120.0	C18—C19—H19	120.8
C5A—C4A—H4A	120.0	C20—C19—H19	120.8
C3A—C4A—H4A	120.0	C19—C20—C15	120.4 (5)
C4A—C5A—C6A	120.0	C19—C20—H20	119.8
C4A—C5A—H5A	120.0	C15—C20—H20	119.8
C10—N1—N2—C11	-1.5 (6)	C7—C8—C9—C10	174.7 (9)
C13—N1—N2—C11	179.6 (4)	N2—N1—C10—O1	-178.3 (4)
C8—C7—C1—C2	98.6 (11)	C13—N1—C10—O1	0.6 (6)
C8—C7—C1—C6	-80.7 (11)	N2—N1—C10—C9	2.5 (6)
C6—C1—C2—C3	0.0	C13—N1—C10—C9	-178.7 (4)
C7—C1—C2—C3	-179.3 (3)	C8—C9—C10—O1	179.2 (5)
C6—C1—C2—C11	-179.3 (4)	C8—C9—C10—N1	-1.6 (6)
C7—C1—C2—C11	1.4 (4)	N1—N2—C11—C8	-0.5 (6)
C1—C2—C3—C4	0.0	N1—N2—C11—C12	179.5 (4)
C11—C2—C3—C4	179.3 (4)	C9—C8—C11—N2	1.2 (7)
C2—C3—C4—C5	0.0	C7A—C8—C11—N2	171.4 (18)
C3—C4—C5—C6	0.0	C7—C8—C11—N2	-173.8 (8)
C4—C5—C6—C1	0.0	C9—C8—C11—C12	-178.7 (4)
C2—C1—C6—C5	0.0	C7A—C8—C11—C12	-8.6 (18)
C7—C1—C6—C5	179.3 (3)	C7—C8—C11—C12	6.2 (10)
C8—C7A—C1A—C2A	107 (2)	N2—N1—C13—C14	-105.4 (4)
C8—C7A—C1A—C6A	-73 (2)	C10—N1—C13—C14	75.6 (5)
C6A—C1A—C2A—C3A	0.0	C15—N3—C14—O2	-7.4 (7)
C7A—C1A—C2A—C3A	179.9 (4)	C15—N3—C14—C13	172.5 (4)
C1A—C2A—C3A—C4A	0.0	N1—C13—C14—O2	-7.6 (7)
C2A—C3A—C4A—C5A	0.0	N1—C13—C14—N3	172.5 (4)
C3A—C4A—C5A—C6A	0.0	C14—N3—C15—C16	-8.1 (7)
C4A—C5A—C6A—C1A	0.0	C14—N3—C15—C20	174.3 (4)
C4A—C5A—C6A—C11A	-178.2 (7)	C20—C15—C16—C17	1.9 (7)
C2A—C1A—C6A—C5A	0.0	N3—C15—C16—C17	-175.5 (5)
C7A—C1A—C6A—C5A	-179.9 (4)	C15—C16—C17—C18	-1.1 (8)
C2A—C1A—C6A—C11A	178.2 (7)	C16—C17—C18—F1	-179.4 (5)
C7A—C1A—C6A—C11A	-1.8 (8)	C16—C17—C18—C19	-0.8 (9)
C1A—C7A—C8—C9	-13 (3)	F1—C18—C19—C20	-179.6 (6)
C1A—C7A—C8—C11	177.5 (16)	C17—C18—C19—C20	1.8 (10)
C1—C7—C8—C9	-5.9 (15)	C18—C19—C20—C15	-1.0 (9)
C1—C7—C8—C11	168.9 (8)	C16—C15—C20—C19	-0.9 (8)
C11—C8—C9—C10	-0.1 (7)	N3—C15—C20—C19	176.8 (5)
C7A—C8—C9—C10	-169.2 (19)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N3—H3 $\cdots$ O1 <sup>i</sup>	0.88	1.95	2.815 (5)	168
C7—H7A $\cdots$ O2 <sup>ii</sup>	0.99	2.32	3.282 (15)	164
C16—H16 $\cdots$ O2	0.95	2.29	2.900 (6)	121
C19—H19 $\cdots$ F1 <sup>iii</sup>	0.95	2.42	3.336 (7)	162

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