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1-[[5-(4-Chlorophenyl)-1-(4-fluorophenyl)-1H-pyrazol-3-yl]carbonyl]piperidin-4-one

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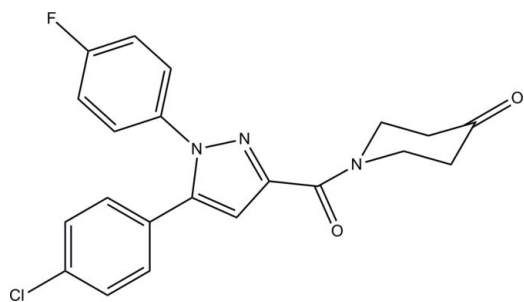
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.024; wR factor = 0.062; data-to-parameter ratio = 14.4.

In the title compound, $\text{C}_{21}\text{H}_{17}\text{ClFN}_3\text{O}_2$, the 1H-pyrazole ring makes dihedral angles of 36.73 (7), 18.73 (7) and 60.88 (8)°, respectively, with the mean planes of the chlorophenyl, 4-oxopiperidine and fluorophenyl rings. The molecular structure is stabilized by an intramolecular C—H···N hydrogen bond, which forms an $S(6)$ ring motif. In the crystal, intermolecular C—H···O hydrogen bonds link molecules into chains along [101]. In addition, intermolecular C—H···F hydrogen bonds with an $R_2^1(7)$ ring motif connect neighbouring chains into layers parallel to the ac plane.

Related literature

For pyrazole derivatives and their microbial activities, see: Ragavan *et al.* (2009, 2010). For a related structure, see: Shahani *et al.* (2010). For ring conformations, see: Cremer & Pople (1975). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



† Thomson Reuters ResearcherID: A-3561-2009.

Experimental

Crystal data

$\text{C}_{21}\text{H}_{17}\text{ClFN}_3\text{O}_2$
 $M_r = 397.83$
 Triclinic, $P1$
 $a = 6.0341$ (2) Å
 $b = 8.2500$ (3) Å
 $c = 10.2448$ (3) Å
 $\alpha = 108.837$ (1)°
 $\beta = 104.782$ (1)°
 $\gamma = 92.792$ (1)°
 $V = 461.90$ (3) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 100$ K
 $0.77 \times 0.21 \times 0.11$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.837$, $T_{\max} = 0.974$
 10178 measured reflections
 3646 independent reflections
 3596 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.062$
 $S = 1.05$
 3646 reflections
 253 parameters
 3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³
 Absolute structure: Flack (1983), 1556 Friedel pairs
 Flack parameter: 0.06 (3)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| C2—H2A···O1 ⁱ | 0.93 | 2.38 | 3.1196 (19) | 136 |
| C7—H7A···F1 ⁱⁱ | 0.93 | 2.50 | 3.2099 (15) | 133 |
| C14—H14A···F1 ⁱⁱ | 0.93 | 2.41 | 3.2614 (17) | 153 |
| C17—H17B···N2 | 0.97 | 2.16 | 2.9091 (18) | 133 |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2632).

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supplementary materials

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1-{{[5-(4-Chlorophenyl)-1-(4-fluorophenyl)-1*H*-pyrazol-3-yl]carbonyl}}piperidin-4-one

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Comment

Antibacterial and antifungal activities of the azoles are most widely studied and some of them are in clinical practice as anti-microbial agents. However, the azole-resistant strain had led to the development of new antimicrobial compounds. In particular, pyrazole derivatives are extensively studied and used as antimicrobial agents. Pyrazole is an important class of heterocyclic compounds and many pyrazole derivatives are reported to have the broad spectrum of biological properties such as anti-inflammatory, antifungal, herbicidal, anti-tumour, cytotoxic, molecular modelling and antiviral activities. Pyrazole derivatives also act as antiangiogenic agents, A3 adenosine receptor antagonists, neuropeptide YY5 receptor antagonists, kinase inhibitor for treatment of type 2 diabetes, hyperlipidemia, obesity and thrombopietinmimetics. Recently urea derivatives of pyrazoles have been reported as potent inhibitors of p38 kinase. Since the high electronegativity of halogens (particularly chlorine and fluorine) in the aromatic part of the drug molecules play an important role in enhancing their biological activity, we are interested to have 4-fluoro or 4-chloro substitution in the aryls of 1,5-diaryl pyrazoles. As part of our on-going research aiming the synthesis of new antimicrobial compounds, we have reported the synthesis of novel pyrazole derivatives and their microbial activities (Ragavan *et al.*, 2009; 2010). The structure of the title compound is presented here.

The asymmetric unit of the title compound (Fig. 1), consists of four rings, namely chlorophenyl (C7–C12/C11), 4-oxopiperidine-1-carbaldehyde (C16–C21/N3/O1/O2), fluorophenyl (C1–C6/F1) and 1*H*-pyrazole (N1/N2/C13–C15) rings. The 1*H*-pyrazole ring is essentially planar [maximum deviation of 0.002 (1) Å at atoms C13 and C15] and makes dihedral angles of 36.73 (7), 18.73 (7) and 60.88 (8)°, with the chlorophenyl [maximum deviation of 0.0077 (4) Å at atom C11], fluorophenyl [maximum deviation of 0.0084 (14) Å at atom C6] and 4-oxopiperidine-1-carbaldehyde [with the r.m.s. deviation of 0.3007 (15) Å] rings. Bond lengths (Allen *et al.*, 1987) and angles are normal and comparable to the related structure (Shahani *et al.*, 2010). The molecular structure is stabilized by an intramolecular C17—H17B···N2 hydrogen bond which forms an *S*(6) ring motif.

In the crystal packing (Fig. 2), intermolecular C14—H14A···F1ⁱⁱ and C7—H7A···F1ⁱⁱ hydrogen bonds (Table 1) connect the neighbouring molecules, generating an *R*₂¹(7) ring motif. Intermolecular C2—H2A···O1ⁱ hydrogen bonds (Table 1) further link the molecules into two-dimensional sheets parallel to the *ac* plane.

Experimental

The compound has been synthesized using the method available in the literature (Ragavan *et al.*, 2009) and recrystallized using the methanol-chloroform (1:1) mixture (yield 76%, m.p. 436.2–437.5 K).

Refinement

H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

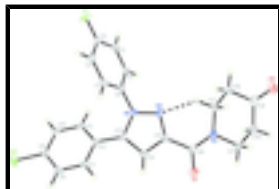


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids and the atom numbering scheme. Intermolecular hydrogen bonding (dashed lines) are omitted for clarity.

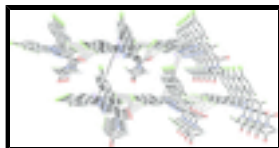


Fig. 2. The crystal packing of the title compound viewed along *a* axis. Intermolecular hydrogen bonds linked the molecules into two-dimensional sheets parallel to the *ac* plane.

1-[[5-(4-Chlorophenyl)-1-(4-fluorophenyl)-1*H*-pyrazol-3-yl]carbonyl]piperidin-4-one

Crystal data

| | |
|--------------------------------|---|
| $C_{21}H_{17}ClFN_3O_2$ | $Z = 1$ |
| $M_r = 397.83$ | $F(000) = 206$ |
| Triclinic, $P1$ | $D_x = 1.430 \text{ Mg m}^{-3}$ |
| Hall symbol: P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 6.0341 (2) \text{ \AA}$ | Cell parameters from 9510 reflections |
| $b = 8.2500 (3) \text{ \AA}$ | $\theta = 2.2\text{--}35.0^\circ$ |
| $c = 10.2448 (3) \text{ \AA}$ | $\mu = 0.24 \text{ mm}^{-1}$ |
| $\alpha = 108.837 (1)^\circ$ | $T = 100 \text{ K}$ |
| $\beta = 104.782 (1)^\circ$ | Needle, colourless |
| $\gamma = 92.792 (1)^\circ$ | $0.77 \times 0.21 \times 0.11 \text{ mm}$ |
| $V = 461.90 (3) \text{ \AA}^3$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEXII CCD area-detector diffractometer | 3646 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 3596 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.020$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2009) | $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.2^\circ$ |
| $T_{\text{min}} = 0.837$, $T_{\text{max}} = 0.974$ | $h = -7 \rightarrow 7$ |
| 10178 measured reflections | $k = -10 \rightarrow 10$ |
| | $l = -13 \rightarrow 13$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.024$ | H-atom parameters constrained |

| | |
|--|---|
| $wR(F^2) = 0.062$ | $w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.0616P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 3646 reflections | $(\Delta/\sigma)_{\max} = 0.001$ |
| 253 parameters | $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$ |
| 3 restraints | $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), 1556 Friedel pairs Flack parameter: 0.06 (3) |

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| C11 | -0.18751 (5) | -0.56629 (4) | -0.09987 (4) | 0.02699 (9) |
| F1 | 0.47475 (18) | -0.01865 (15) | -0.50052 (9) | 0.0397 (3) |
| O1 | 1.11635 (17) | 0.26727 (13) | 0.53957 (10) | 0.0225 (2) |
| O2 | 1.85032 (19) | 0.66828 (16) | 0.41014 (12) | 0.0326 (3) |
| N1 | 0.73866 (19) | 0.06297 (14) | 0.07455 (11) | 0.0160 (2) |
| N2 | 0.92725 (19) | 0.18040 (14) | 0.16028 (11) | 0.0171 (2) |
| N3 | 1.27132 (19) | 0.41856 (15) | 0.42751 (11) | 0.0197 (2) |
| C1 | 0.4556 (2) | 0.08181 (18) | -0.13442 (14) | 0.0192 (3) |
| H1A | 0.3585 | 0.1228 | -0.0774 | 0.023* |
| C2 | 0.3886 (3) | 0.06260 (19) | -0.27928 (14) | 0.0235 (3) |
| H2A | 0.2462 | 0.0894 | -0.3215 | 0.028* |
| C3 | 0.5399 (3) | 0.00258 (19) | -0.35841 (14) | 0.0254 (3) |
| C4 | 0.7542 (3) | -0.03780 (19) | -0.30190 (14) | 0.0243 (3) |
| H4A | 0.8525 | -0.0754 | -0.3587 | 0.029* |
| C5 | 0.8185 (2) | -0.02049 (18) | -0.15695 (14) | 0.0200 (3) |
| H5A | 0.9602 | -0.0487 | -0.1154 | 0.024* |
| C6 | 0.6687 (2) | 0.03934 (16) | -0.07542 (13) | 0.0161 (2) |
| C7 | 0.2588 (2) | -0.14175 (17) | 0.15655 (13) | 0.0173 (3) |
| H7A | 0.2749 | -0.0537 | 0.2437 | 0.021* |
| C8 | 0.0689 (2) | -0.27130 (18) | 0.10073 (14) | 0.0190 (3) |
| H8A | -0.0413 | -0.2705 | 0.1498 | 0.023* |
| C9 | 0.0469 (2) | -0.40181 (17) | -0.02954 (15) | 0.0192 (3) |

supplementary materials

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|------|------------|---------------|---------------|------------|
| C10 | 0.2091 (3) | -0.40594 (18) | -0.10451 (15) | 0.0199 (3) |
| H10A | 0.1914 | -0.4943 | -0.1918 | 0.024* |
| C11 | 0.3994 (2) | -0.27583 (17) | -0.04738 (14) | 0.0188 (3) |
| H11A | 0.5098 | -0.2778 | -0.0966 | 0.023* |
| C12 | 0.4254 (2) | -0.14175 (16) | 0.08395 (13) | 0.0160 (3) |
| C13 | 0.6292 (2) | -0.00678 (16) | 0.15007 (13) | 0.0151 (2) |
| C14 | 0.7564 (2) | 0.07058 (17) | 0.29276 (13) | 0.0172 (3) |
| H14A | 0.7284 | 0.0510 | 0.3719 | 0.021* |
| C15 | 0.9368 (2) | 0.18496 (17) | 0.29308 (13) | 0.0164 (3) |
| C16 | 1.1168 (2) | 0.29506 (17) | 0.42851 (13) | 0.0168 (3) |
| C17 | 1.2640 (2) | 0.49206 (18) | 0.31390 (14) | 0.0202 (3) |
| H17A | 1.2384 | 0.6119 | 0.3472 | 0.024* |
| H17B | 1.1365 | 0.4287 | 0.2296 | 0.024* |
| C18 | 1.4914 (3) | 0.48167 (19) | 0.27422 (15) | 0.0225 (3) |
| H18A | 1.5073 | 0.3614 | 0.2298 | 0.027* |
| H18B | 1.4901 | 0.5391 | 0.2051 | 0.027* |
| C19 | 1.6952 (3) | 0.56654 (19) | 0.40686 (15) | 0.0240 (3) |
| C20 | 1.6883 (2) | 0.5158 (2) | 0.53511 (15) | 0.0239 (3) |
| H20A | 1.8015 | 0.5955 | 0.6202 | 0.029* |
| H20B | 1.7320 | 0.4010 | 0.5200 | 0.029* |
| C21 | 1.4500 (2) | 0.51622 (19) | 0.56187 (14) | 0.0203 (3) |
| H21A | 1.4476 | 0.4642 | 0.6341 | 0.024* |
| H21B | 1.4190 | 0.6344 | 0.5975 | 0.024* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| C11 | 0.02313 (16) | 0.01987 (16) | 0.03408 (18) | -0.00462 (12) | 0.00415 (13) | 0.00849 (13) |
| F1 | 0.0393 (5) | 0.0625 (7) | 0.0143 (4) | -0.0089 (5) | 0.0024 (4) | 0.0159 (4) |
| O1 | 0.0247 (5) | 0.0267 (5) | 0.0153 (4) | 0.0003 (4) | 0.0023 (4) | 0.0092 (4) |
| O2 | 0.0231 (5) | 0.0389 (6) | 0.0328 (6) | -0.0016 (5) | 0.0122 (4) | 0.0060 (5) |
| N1 | 0.0171 (5) | 0.0171 (5) | 0.0133 (5) | -0.0006 (4) | 0.0035 (4) | 0.0058 (4) |
| N2 | 0.0162 (5) | 0.0173 (5) | 0.0150 (5) | -0.0008 (4) | 0.0013 (4) | 0.0048 (4) |
| N3 | 0.0203 (6) | 0.0210 (6) | 0.0139 (5) | -0.0026 (5) | -0.0014 (4) | 0.0065 (4) |
| C1 | 0.0194 (6) | 0.0214 (7) | 0.0187 (6) | -0.0005 (5) | 0.0056 (5) | 0.0097 (5) |
| C2 | 0.0222 (7) | 0.0291 (8) | 0.0196 (7) | -0.0038 (6) | 0.0001 (5) | 0.0145 (6) |
| C3 | 0.0308 (7) | 0.0295 (8) | 0.0129 (6) | -0.0090 (6) | 0.0024 (5) | 0.0085 (5) |
| C4 | 0.0281 (7) | 0.0243 (7) | 0.0183 (6) | -0.0055 (6) | 0.0098 (6) | 0.0033 (5) |
| C5 | 0.0199 (6) | 0.0182 (6) | 0.0196 (6) | -0.0016 (5) | 0.0057 (5) | 0.0041 (5) |
| C6 | 0.0197 (6) | 0.0160 (6) | 0.0127 (5) | -0.0023 (5) | 0.0040 (5) | 0.0062 (4) |
| C7 | 0.0203 (6) | 0.0173 (6) | 0.0151 (6) | 0.0034 (5) | 0.0039 (5) | 0.0075 (5) |
| C8 | 0.0187 (6) | 0.0213 (7) | 0.0206 (6) | 0.0038 (5) | 0.0061 (5) | 0.0114 (5) |
| C9 | 0.0175 (6) | 0.0159 (6) | 0.0244 (7) | -0.0009 (5) | 0.0019 (5) | 0.0109 (5) |
| C10 | 0.0240 (7) | 0.0165 (6) | 0.0182 (6) | 0.0011 (5) | 0.0051 (5) | 0.0055 (5) |
| C11 | 0.0211 (6) | 0.0174 (6) | 0.0184 (6) | 0.0012 (5) | 0.0062 (5) | 0.0068 (5) |
| C12 | 0.0179 (6) | 0.0149 (6) | 0.0155 (5) | 0.0021 (5) | 0.0017 (5) | 0.0081 (5) |
| C13 | 0.0174 (6) | 0.0142 (6) | 0.0154 (5) | 0.0035 (5) | 0.0055 (5) | 0.0065 (5) |
| C14 | 0.0206 (6) | 0.0178 (6) | 0.0138 (6) | 0.0028 (5) | 0.0045 (5) | 0.0065 (5) |

| | | | | | | |
|-----|------------|------------|------------|-------------|------------|------------|
| C15 | 0.0182 (6) | 0.0161 (6) | 0.0147 (6) | 0.0035 (5) | 0.0031 (5) | 0.0060 (5) |
| C16 | 0.0172 (6) | 0.0172 (6) | 0.0151 (6) | 0.0044 (5) | 0.0027 (5) | 0.0055 (5) |
| C17 | 0.0202 (6) | 0.0202 (6) | 0.0195 (6) | -0.0005 (5) | 0.0022 (5) | 0.0090 (5) |
| C18 | 0.0258 (7) | 0.0229 (7) | 0.0192 (6) | 0.0035 (6) | 0.0074 (5) | 0.0070 (5) |
| C19 | 0.0196 (7) | 0.0237 (7) | 0.0260 (7) | 0.0062 (6) | 0.0086 (5) | 0.0033 (6) |
| C20 | 0.0190 (7) | 0.0258 (7) | 0.0218 (7) | 0.0029 (6) | 0.0021 (5) | 0.0047 (5) |
| C21 | 0.0192 (6) | 0.0224 (7) | 0.0144 (6) | -0.0004 (5) | 0.0011 (5) | 0.0032 (5) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|--------------|-------------|
| C11—C9 | 1.7387 (14) | C8—C9 | 1.3877 (19) |
| F1—C3 | 1.3570 (14) | C8—H8A | 0.9300 |
| O1—C16 | 1.2317 (16) | C9—C10 | 1.385 (2) |
| O2—C19 | 1.2130 (19) | C10—C11 | 1.394 (2) |
| N1—N2 | 1.3558 (15) | C10—H10A | 0.9300 |
| N1—C13 | 1.3701 (17) | C11—C12 | 1.4045 (18) |
| N1—C6 | 1.4299 (15) | C11—H11A | 0.9300 |
| N2—C15 | 1.3352 (16) | C12—C13 | 1.4714 (18) |
| N3—C16 | 1.3515 (18) | C13—C14 | 1.3823 (17) |
| N3—C21 | 1.4657 (15) | C14—C15 | 1.4039 (19) |
| N3—C17 | 1.4684 (17) | C14—H14A | 0.9300 |
| C1—C6 | 1.3875 (19) | C15—C16 | 1.5004 (17) |
| C1—C2 | 1.3881 (18) | C17—C18 | 1.526 (2) |
| C1—H1A | 0.9300 | C17—H17A | 0.9700 |
| C2—C3 | 1.378 (2) | C17—H17B | 0.9700 |
| C2—H2A | 0.9300 | C18—C19 | 1.516 (2) |
| C3—C4 | 1.379 (2) | C18—H18A | 0.9700 |
| C4—C5 | 1.3927 (18) | C18—H18B | 0.9700 |
| C4—H4A | 0.9300 | C19—C20 | 1.511 (2) |
| C5—C6 | 1.3862 (18) | C20—C21 | 1.531 (2) |
| C5—H5A | 0.9300 | C20—H20A | 0.9700 |
| C7—C8 | 1.3903 (19) | C20—H20B | 0.9700 |
| C7—C12 | 1.3951 (19) | C21—H21A | 0.9700 |
| C7—H7A | 0.9300 | C21—H21B | 0.9700 |
| N2—N1—C13 | 112.88 (10) | C7—C12—C13 | 119.32 (11) |
| N2—N1—C6 | 118.05 (11) | C11—C12—C13 | 121.72 (12) |
| C13—N1—C6 | 128.81 (11) | N1—C13—C14 | 105.49 (12) |
| C15—N2—N1 | 104.32 (11) | N1—C13—C12 | 124.42 (11) |
| C16—N3—C21 | 118.56 (11) | C14—C13—C12 | 130.04 (12) |
| C16—N3—C17 | 128.10 (11) | C13—C14—C15 | 105.57 (12) |
| C21—N3—C17 | 112.47 (11) | C13—C14—H14A | 127.2 |
| C6—C1—C2 | 119.43 (13) | C15—C14—H14A | 127.2 |
| C6—C1—H1A | 120.3 | N2—C15—C14 | 111.75 (11) |
| C2—C1—H1A | 120.3 | N2—C15—C16 | 125.60 (12) |
| C3—C2—C1 | 117.83 (13) | C14—C15—C16 | 122.64 (11) |
| C3—C2—H2A | 121.1 | O1—C16—N3 | 122.03 (11) |
| C1—C2—H2A | 121.1 | O1—C16—C15 | 116.83 (12) |
| F1—C3—C2 | 118.27 (13) | N3—C16—C15 | 121.13 (11) |
| F1—C3—C4 | 117.82 (13) | N3—C17—C18 | 110.09 (11) |

supplementary materials

| | | | |
|----------------|--------------|-----------------|--------------|
| C2—C3—C4 | 123.90 (12) | N3—C17—H17A | 109.6 |
| C3—C4—C5 | 117.84 (13) | C18—C17—H17A | 109.6 |
| C3—C4—H4A | 121.1 | N3—C17—H17B | 109.6 |
| C5—C4—H4A | 121.1 | C18—C17—H17B | 109.6 |
| C6—C5—C4 | 119.19 (12) | H17A—C17—H17B | 108.2 |
| C6—C5—H5A | 120.4 | C19—C18—C17 | 110.61 (11) |
| C4—C5—H5A | 120.4 | C19—C18—H18A | 109.5 |
| C5—C6—C1 | 121.79 (12) | C17—C18—H18A | 109.5 |
| C5—C6—N1 | 119.07 (11) | C19—C18—H18B | 109.5 |
| C1—C6—N1 | 119.11 (12) | C17—C18—H18B | 109.5 |
| C8—C7—C12 | 121.09 (12) | H18A—C18—H18B | 108.1 |
| C8—C7—H7A | 119.5 | O2—C19—C20 | 122.68 (13) |
| C12—C7—H7A | 119.5 | O2—C19—C18 | 122.62 (14) |
| C9—C8—C7 | 118.83 (13) | C20—C19—C18 | 114.69 (13) |
| C9—C8—H8A | 120.6 | C19—C20—C21 | 113.13 (11) |
| C7—C8—H8A | 120.6 | C19—C20—H20A | 109.0 |
| C10—C9—C8 | 121.64 (13) | C21—C20—H20A | 109.0 |
| C10—C9—C11 | 118.91 (10) | C19—C20—H20B | 109.0 |
| C8—C9—C11 | 119.45 (11) | C21—C20—H20B | 109.0 |
| C9—C10—C11 | 119.11 (12) | H20A—C20—H20B | 107.8 |
| C9—C10—H10A | 120.4 | N3—C21—C20 | 109.72 (11) |
| C11—C10—H10A | 120.4 | N3—C21—H21A | 109.7 |
| C10—C11—C12 | 120.45 (13) | C20—C21—H21A | 109.7 |
| C10—C11—H11A | 119.8 | N3—C21—H21B | 109.7 |
| C12—C11—H11A | 119.8 | C20—C21—H21B | 109.7 |
| C7—C12—C11 | 118.89 (13) | H21A—C21—H21B | 108.2 |
| C13—N1—N2—C15 | -0.07 (13) | C6—N1—C13—C12 | 8.4 (2) |
| C6—N1—N2—C15 | 174.57 (11) | C7—C12—C13—N1 | -146.36 (12) |
| C6—C1—C2—C3 | -0.5 (2) | C11—C12—C13—N1 | 36.75 (19) |
| C1—C2—C3—F1 | 179.21 (13) | C7—C12—C13—C14 | 36.9 (2) |
| C1—C2—C3—C4 | -0.6 (2) | C11—C12—C13—C14 | -140.04 (14) |
| F1—C3—C4—C5 | -178.30 (12) | N1—C13—C14—C15 | 0.40 (14) |
| C2—C3—C4—C5 | 1.5 (2) | C12—C13—C14—C15 | 177.65 (12) |
| C3—C4—C5—C6 | -1.3 (2) | N1—N2—C15—C14 | 0.34 (14) |
| C4—C5—C6—C1 | 0.3 (2) | N1—N2—C15—C16 | 179.57 (11) |
| C4—C5—C6—N1 | -177.75 (12) | C13—C14—C15—N2 | -0.47 (15) |
| C2—C1—C6—C5 | 0.6 (2) | C13—C14—C15—C16 | -179.73 (11) |
| C2—C1—C6—N1 | 178.67 (12) | C21—N3—C16—O1 | 2.92 (18) |
| N2—N1—C6—C5 | 62.36 (15) | C17—N3—C16—O1 | -165.56 (13) |
| C13—N1—C6—C5 | -123.97 (15) | C21—N3—C16—C15 | -177.10 (11) |
| N2—N1—C6—C1 | -115.72 (14) | C17—N3—C16—C15 | 14.4 (2) |
| C13—N1—C6—C1 | 57.94 (19) | N2—C15—C16—O1 | -171.13 (13) |
| C12—C7—C8—C9 | -0.09 (18) | C14—C15—C16—O1 | 8.02 (18) |
| C7—C8—C9—C10 | 0.12 (19) | N2—C15—C16—N3 | 8.88 (19) |
| C7—C8—C9—C11 | 179.22 (10) | C14—C15—C16—N3 | -171.97 (12) |
| C8—C9—C10—C11 | 0.13 (19) | C16—N3—C17—C18 | -127.53 (14) |
| C11—C9—C10—C11 | -178.98 (10) | C21—N3—C17—C18 | 63.42 (14) |
| C9—C10—C11—C12 | -0.41 (19) | N3—C17—C18—C19 | -54.44 (15) |
| C8—C7—C12—C11 | -0.19 (18) | C17—C18—C19—O2 | -132.83 (14) |

| | | | |
|-----------------|--------------|-----------------|-------------|
| C8—C7—C12—C13 | -177.17 (11) | C17—C18—C19—C20 | 46.56 (16) |
| C10—C11—C12—C7 | 0.44 (19) | O2—C19—C20—C21 | 134.59 (15) |
| C10—C11—C12—C13 | 177.34 (12) | C18—C19—C20—C21 | -44.80 (16) |
| N2—N1—C13—C14 | -0.21 (14) | C16—N3—C21—C20 | 129.76 (13) |
| C6—N1—C13—C14 | -174.15 (12) | C17—N3—C21—C20 | -60.04 (15) |
| N2—N1—C13—C12 | -177.66 (11) | C19—C20—C21—N3 | 49.66 (16) |

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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| C2—H2A...O1 ⁱ | 0.93 | 2.38 | 3.1196 (19) | 136 |
| C7—H7A...F1 ⁱⁱ | 0.93 | 2.50 | 3.2099 (15) | 133 |
| C14—H14A...F1 ⁱⁱ | 0.93 | 2.41 | 3.2614 (17) | 153 |
| C17—H17B...N2 | 0.97 | 2.16 | 2.9091 (18) | 133 |

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

Fig. 1

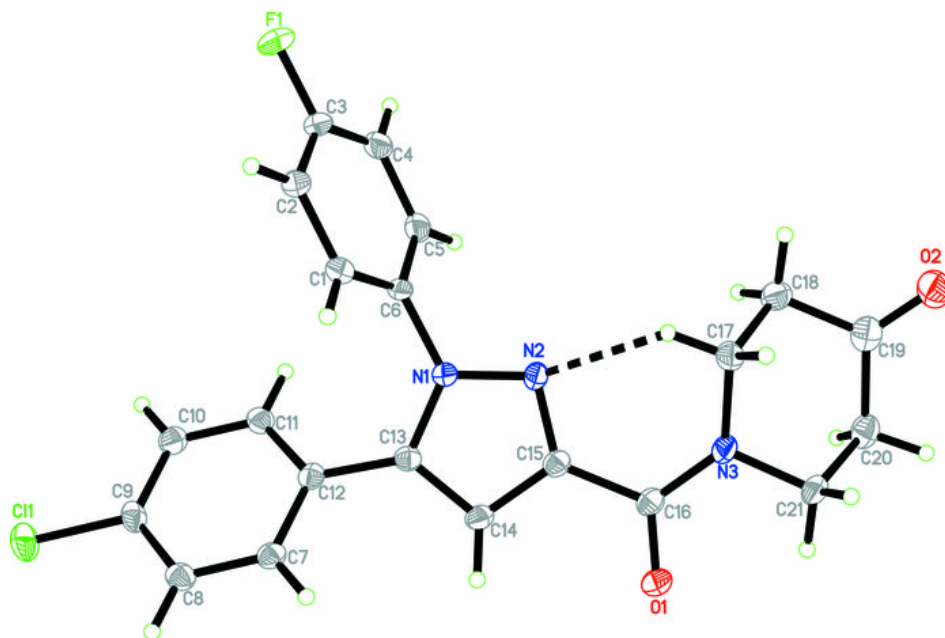
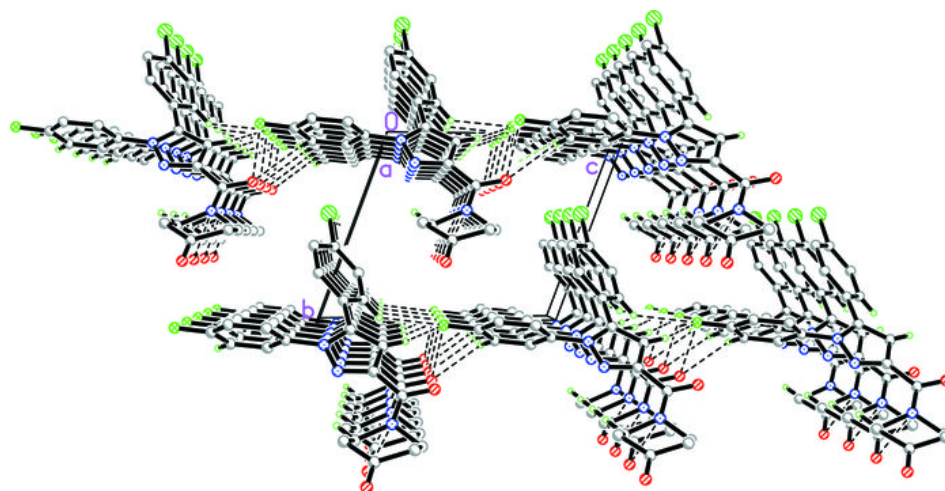


Fig. 2



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