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# 4-[5-Amino-4-(4-fluorophenyl)-3-(pyridin-4-yl)-1*H*-pyrazol-1-yl]benzonitrile

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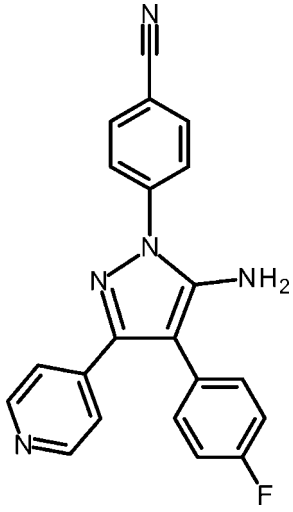
Key indicators: single-crystal X-ray study; $T$ = 193 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.038; $wR$ factor = 0.103; data-to-parameter ratio = 12.5.

In the crystal structure of the title compound, $C_{21}H_{14}FN_5$, the pyrazole ring forms dihedral angles of 38.0 (1), 40.0 (1) and 28.5 (1)° with the directly attached 4-fluorophenyl, pyridine and benzonitrile rings, respectively. The crystal packing is characterized by N—H···N hydrogen bonds, which result in a two-dimensional network parallel to the *ac*-plane.

## Related literature

For p38$\alpha$ MAP kinase inhibitors having a vicinal 4-fluorophenyl/pyridin-4-yl system connected to a five-membered heterocyclic core, see: Abu Thaher *et al.* (2009); Peifer *et al.* (2006). For the inhibitory activity and preparation of the title compound, see: Abu Thaher *et al.* (2012*a*). For related structures, see: Abu Thaher *et al.* (2012*b*,*c*).




## Experimental

### Crystal data

$C_{21}H_{14}FN_5$
$M_r$ = 355.37
Orthorhombic, $Pca2_1$
$a$ = 10.5189 (5) Å
$b$ = 8.1339 (3) Å
$c$ = 20.0009 (13) Å
$V$ = 1711.27 (15) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 0.76 mm$^{-1}$
$T$ = 193 K
0.50 × 0.30 × 0.30 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
3163 measured reflections
3059 independent reflections
3005 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
3 standard reflections every 60 min
intensity decay: 3%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
$S$ = 1.04
3059 reflections
244 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$
Absolute structure: Flack (1983), 1381 Friedel pairs
Flack parameter: −0.17 (18)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N6—H6$A$···N26$^{i}$ | 0.88 | 2.14 | 2.938 (2) | 150 |
| N6—H6$B$···N14$^{ii}$ | 0.86 | 2.58 | 3.292 (3) | 141 |

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+\frac{3}{2}, y, z-\frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2359).

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# supplementary materials

*Acta Cryst.* (2012). E**68**, o935 [doi:10.1107/S160053681200877X]

## 4-[5-Amino-4-(4-fluorophenyl)-3-(pyridin-4-yl)-1*H*-pyrazol-1-yl]benzonitrile

**Bassam Abu Thaher, Pierre Koch, Dieter Schollmeyer and Stefan Laufer**

### Comment

Compounds having a vicinal 4-fluorophenyl/pyridin-4-yl system connected to a five-membered heterocyclic core have been considered to be potential p38$\alpha$ MAP kinase inhibitors (Abu Thaher *et al.* 2009, Peifer *et al.* 2006). We showed that the regioisomeric switch from 3-(4-fluorophenyl)-4-(pyridin-4-yl)-1-(aryl)-1*H*-pyrazol-5-amine to 4-(4-fluorophenyl)-3-(pyridin-4-yl)-1-(aryl)-1*H*-pyrazol-5-amine completely changed the inhibitory profile from p38$\alpha$ MAP kinase to kinases relevant in cancer (Abu Thaher *et al.* 2012*a*). Recently, we reported similar crystal structures (Abu Thaher *et al.* 2012*b,c*).

In the crystal structure of the title compound (Fig. 1) the pyrazole ring forms dihedral angels of 38.0 (1)°, 40.0 (1)°, 28.5 (1)° with the directly attached 4-fluorophenyl, pyridine and benzonitrile rings, respectively. The 4-fluorophenyl ring encloses dihedral angels of 57.7 (1)° and 22.1 (9)° toward the pyridine and benzonitrile rings, respectively. The pyridine ring is oriented at a dihedral angle of 35.6 (1)° toward the benzonitrile ring.

The crystal packing (Fig. 2) shows that the amino function acts as a hydrogen bond donor of two intermolecular hydrogen bonds formed to two different molecules - one to the nitrogen atom (N26) of the pyridine ring and one to the nitrogen atom (N14) of the nitrile group. The length of the hydrogen bonds is 2.14Å and 2.58 Å, respectively (Table 1). The two hydrogen bonds result in a two dimensional network parallel to the *ac*-plane.

### Experimental

20 mmol of LDA were added to 30 ml of dry THF in a three neck flask and cooled to 194 K. 14 mmol of 4-fluorophenylacetonitril in 10 ml THF were added dropwise and the reaction mixture was stirred for 45 min. 5 mmol of *N*-(4-cyanophenyl)-4-pyridinecarbohydrazonoyl chloride were added slowly and stirring of the reaction mixture was continued for 1 h. After warming to 293 K, 50 ml of water were added to the reaction mixture which then was extracted with ethyl acetate (2x 50 mL). The combined organic layers were dried over $Na_2SO_4$. The organic solution was concentrated to about 5 ml and the product precipitated as pure pale brown crystalls which were washed with diethyl ether. Yield 62%.

### Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å ($sp^3$ C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the $U_{eq}$ of the parent atom).

### Computing details

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989); data reduction: CORINC (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

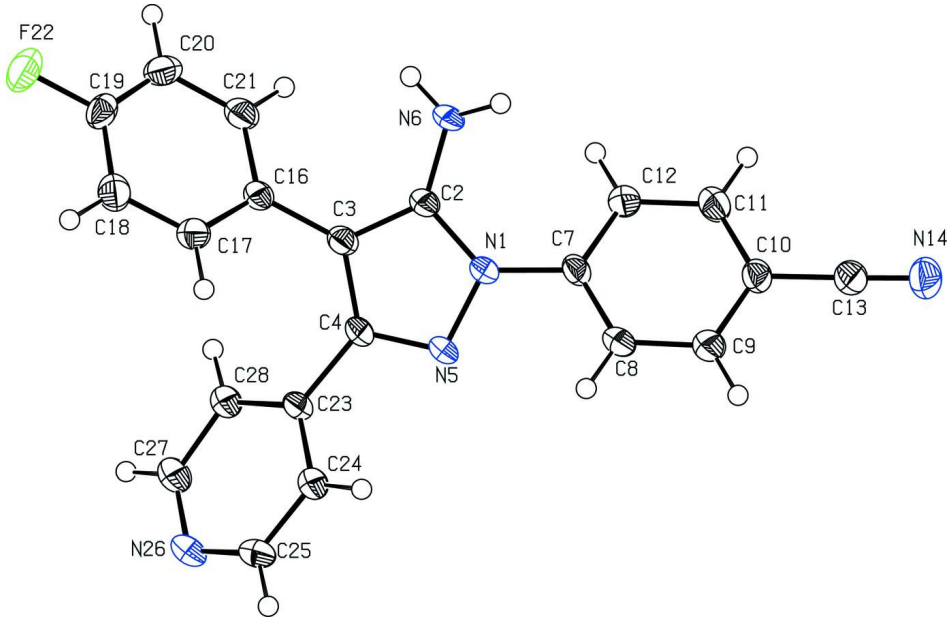


**Figure 1**

View of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are depicted as circles of arbitrary size.

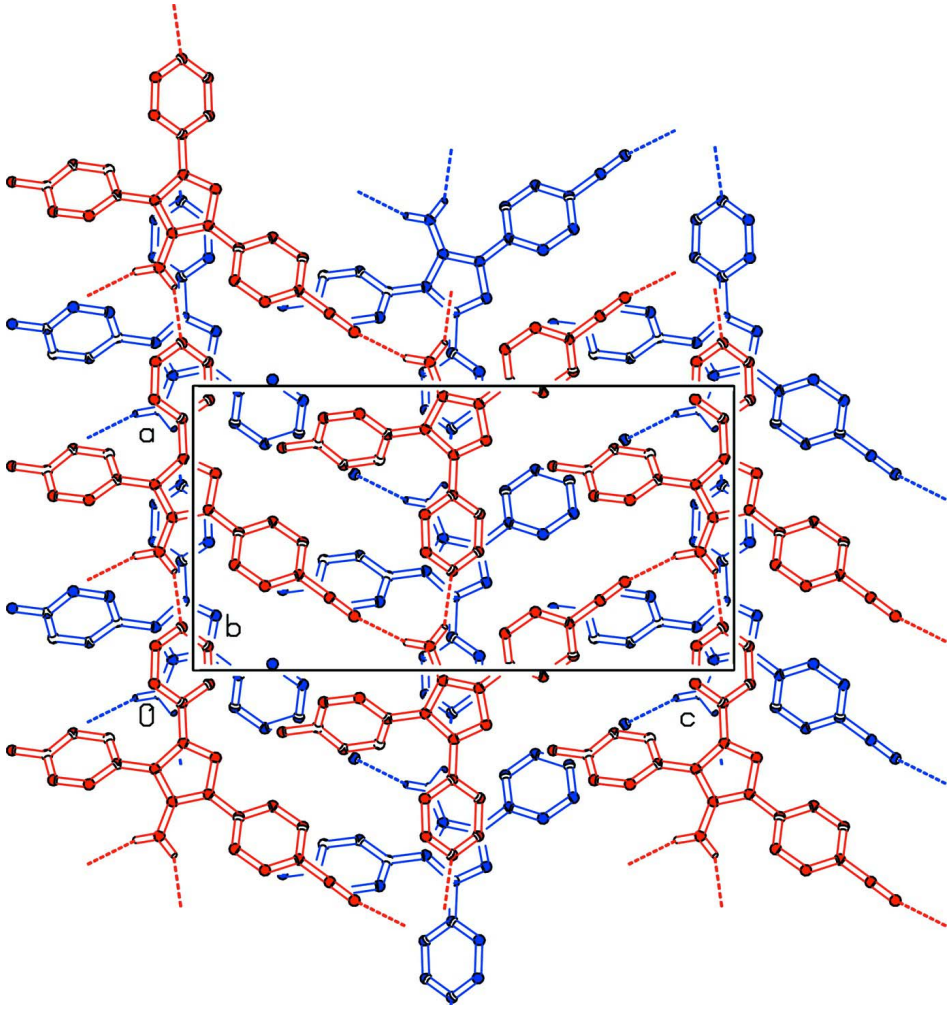


**Figure 2**

A packing section of the crystal viewed down the *b* axis. Hydrogen bonds are shown as dashed lines. Separated layers are indicated by different colours.

### 4-[5-Amino-4-(4-fluorophenyl)-3-(pyridin-4-yl)-1*H*- pyrazol-1-yl]benzonitrile

*Crystal data*

$C_{21}H_{14}FN_5$
$M_r = 355.37$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 10.5189$ (5) Å
$b = 8.1339$ (3) Å
$c = 20.0009$ (13) Å
$V = 1711.27$ (15) Å$^3$
$Z = 4$

$F(000) = 736$
$D_x = 1.379$ Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 65$–70°
$\mu = 0.76$ mm$^{-1}$
$T = 193$ K
Block, brown
0.50 × 0.30 × 0.30 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: rotating anode
Graphite monochromator
$\omega/2\theta$ scans
3163 measured reflections
3059 independent reflections
3005 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 69.9°$, $\theta_{min} = 4.4°$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 24$
3 standard reflections every 60 min
intensity decay: 3%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 1.04$
3059 reflections
244 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.2913P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{min} = -0.23$ e Å$^{-3}$
Absolute structure: Flack (1983), 1381 Friedel pairs
Flack parameter: −0.17 (18)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.43666 (14) | 0.21998 (19) | 0.52903 (8) | 0.0245 (3) |
| C2 | 0.46323 (15) | 0.2397 (2) | 0.46188 (10) | 0.0233 (4) |
| C3 | 0.34814 (17) | 0.2656 (2) | 0.43004 (10) | 0.0234 (4) |
| C4 | 0.25715 (16) | 0.2607 (2) | 0.48226 (9) | 0.0236 (4) |
| N5 | 0.30861 (14) | 0.23527 (19) | 0.54156 (8) | 0.0253 (3) |
| N6 | 0.58360 (15) | 0.2377 (2) | 0.43736 (9) | 0.0322 (4) |
| H6A | 0.6492 | 0.2547 | 0.4639 | 0.048* |
| H6B | 0.5975 | 0.2425 | 0.3949 | 0.048* |
| C7 | 0.51679 (16) | 0.1880 (2) | 0.58436 (10) | 0.0240 (4) |
| C8 | 0.47853 (17) | 0.2416 (3) | 0.64701 (11) | 0.0307 (4) |
| H8 | 0.4014 | 0.3013 | 0.6516 | 0.037* |
| C9 | 0.55154 (18) | 0.2090 (3) | 0.70281 (10) | 0.0319 (4) |
| H9 | 0.5245 | 0.2446 | 0.7457 | 0.038* |
| C10 | 0.66595 (17) | 0.1229 (2) | 0.69545 (9) | 0.0269 (4) |
| C11 | 0.70398 (19) | 0.0686 (2) | 0.63280 (10) | 0.0309 (4) |

| | | | | |
|---|---|---|---|---|
| H11 | 0.7816 | 0.0102 | 0.6281 | 0.037* |
| C12 | 0.62949 (18) | 0.0992 (2) | 0.57720 (10) | 0.0287 (4) |
| H12 | 0.6548 | 0.0600 | 0.5345 | 0.034* |
| C13 | 0.74546 (19) | 0.0933 (2) | 0.75280 (11) | 0.0306 (4) |
| N14 | 0.81025 (18) | 0.0714 (3) | 0.79805 (10) | 0.0402 (4) |
| C16 | 0.33007 (16) | 0.3156 (2) | 0.35985 (9) | 0.0235 (4) |
| C17 | 0.24094 (18) | 0.4368 (2) | 0.34404 (10) | 0.0279 (4) |
| H17 | 0.1915 | 0.4843 | 0.3788 | 0.033* |
| C18 | 0.22306 (19) | 0.4892 (2) | 0.27863 (11) | 0.0315 (4) |
| H18 | 0.1605 | 0.5693 | 0.2681 | 0.038* |
| C19 | 0.29837 (19) | 0.4220 (3) | 0.22958 (9) | 0.0303 (4) |
| C20 | 0.38681 (19) | 0.3029 (3) | 0.24196 (10) | 0.0329 (4) |
| H20 | 0.4369 | 0.2585 | 0.2068 | 0.039* |
| C21 | 0.40156 (19) | 0.2480 (3) | 0.30763 (10) | 0.0294 (4) |
| H21 | 0.4611 | 0.1634 | 0.3170 | 0.035* |
| F22 | 0.28240 (13) | 0.47710 (18) | 0.16555 (6) | 0.0439 (3) |
| C23 | 0.11619 (16) | 0.2723 (2) | 0.47901 (10) | 0.0247 (4) |
| C24 | 0.04902 (17) | 0.3515 (3) | 0.52898 (10) | 0.0301 (4) |
| H24 | 0.0927 | 0.4043 | 0.5646 | 0.036* |
| C25 | −0.08274 (18) | 0.3532 (3) | 0.52667 (11) | 0.0357 (5) |
| H25 | −0.1273 | 0.4093 | 0.5611 | 0.043* |
| N26 | −0.15029 (15) | 0.2799 (2) | 0.47859 (10) | 0.0370 (4) |
| C27 | −0.08439 (19) | 0.2038 (3) | 0.43060 (12) | 0.0362 (5) |
| H27 | −0.1306 | 0.1511 | 0.3959 | 0.043* |
| C28 | 0.04695 (18) | 0.1972 (3) | 0.42836 (11) | 0.0301 (4) |
| H28 | 0.0891 | 0.1422 | 0.3928 | 0.036* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0145 (6) | 0.0350 (8) | 0.0241 (8) | −0.0011 (6) | 0.0004 (6) | 0.0023 (7) |
| C2 | 0.0160 (8) | 0.0292 (9) | 0.0246 (10) | −0.0018 (6) | 0.0001 (7) | −0.0011 (7) |
| C3 | 0.0177 (8) | 0.0267 (8) | 0.0259 (9) | −0.0007 (6) | 0.0000 (7) | −0.0014 (8) |
| C4 | 0.0149 (8) | 0.0299 (8) | 0.0259 (9) | −0.0019 (6) | −0.0023 (7) | 0.0007 (7) |
| N5 | 0.0128 (7) | 0.0366 (8) | 0.0265 (9) | 0.0008 (5) | −0.0004 (6) | 0.0013 (7) |
| N6 | 0.0119 (7) | 0.0586 (11) | 0.0260 (8) | −0.0022 (7) | 0.0012 (6) | −0.0019 (8) |
| C7 | 0.0164 (8) | 0.0288 (9) | 0.0268 (9) | −0.0026 (7) | −0.0035 (7) | 0.0019 (8) |
| C8 | 0.0175 (8) | 0.0447 (11) | 0.0298 (10) | 0.0032 (7) | 0.0008 (8) | −0.0026 (9) |
| C9 | 0.0228 (9) | 0.0469 (11) | 0.0261 (10) | −0.0006 (8) | −0.0003 (7) | −0.0042 (9) |
| C10 | 0.0224 (8) | 0.0318 (9) | 0.0265 (10) | −0.0038 (7) | −0.0041 (7) | 0.0022 (8) |
| C11 | 0.0252 (9) | 0.0357 (10) | 0.0320 (10) | 0.0068 (8) | −0.0031 (8) | −0.0003 (9) |
| C12 | 0.0254 (9) | 0.0363 (9) | 0.0244 (9) | 0.0042 (8) | 0.0003 (7) | −0.0028 (8) |
| C13 | 0.0260 (8) | 0.0365 (10) | 0.0291 (9) | −0.0040 (8) | −0.0014 (8) | 0.0014 (8) |
| N14 | 0.0332 (9) | 0.0541 (11) | 0.0333 (9) | −0.0074 (8) | −0.0090 (8) | 0.0054 (9) |
| C16 | 0.0172 (7) | 0.0292 (9) | 0.0241 (9) | −0.0039 (7) | −0.0008 (6) | −0.0019 (7) |
| C17 | 0.0248 (9) | 0.0328 (9) | 0.0261 (10) | −0.0002 (7) | 0.0017 (7) | −0.0024 (8) |
| C18 | 0.0297 (10) | 0.0336 (10) | 0.0314 (10) | −0.0008 (8) | −0.0043 (8) | 0.0041 (8) |
| C19 | 0.0300 (9) | 0.0406 (10) | 0.0202 (9) | −0.0136 (8) | −0.0034 (7) | 0.0013 (8) |
| C20 | 0.0277 (9) | 0.0456 (11) | 0.0254 (10) | −0.0079 (8) | 0.0058 (8) | −0.0078 (9) |
| C21 | 0.0202 (9) | 0.0367 (10) | 0.0313 (10) | −0.0014 (7) | 0.0004 (8) | −0.0033 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| F22 | 0.0503 (8) | 0.0578 (8) | 0.0236 (6) | −0.0142 (6) | −0.0051 (5) | 0.0065 (6) |
| C23 | 0.0156 (8) | 0.0316 (9) | 0.0268 (9) | 0.0008 (6) | 0.0006 (7) | 0.0040 (7) |
| C24 | 0.0205 (8) | 0.0449 (11) | 0.0250 (9) | 0.0002 (7) | −0.0024 (7) | −0.0022 (9) |
| C25 | 0.0213 (9) | 0.0538 (12) | 0.0318 (10) | 0.0055 (8) | 0.0055 (8) | −0.0036 (9) |
| N26 | 0.0160 (7) | 0.0569 (11) | 0.0382 (10) | −0.0002 (7) | 0.0001 (7) | 0.0016 (9) |
| C27 | 0.0206 (9) | 0.0542 (12) | 0.0337 (11) | −0.0049 (8) | −0.0040 (8) | −0.0026 (10) |
| C28 | 0.0210 (8) | 0.0428 (11) | 0.0265 (9) | −0.0017 (7) | −0.0020 (8) | −0.0022 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—N5 | 1.376 (2) | C13—N14 | 1.147 (3) |
| N1—C2 | 1.381 (3) | C16—C17 | 1.397 (3) |
| N1—C7 | 1.415 (2) | C16—C21 | 1.399 (3) |
| C2—N6 | 1.358 (2) | C17—C18 | 1.389 (3) |
| C2—C3 | 1.384 (2) | C17—H17 | 0.9500 |
| C3—C4 | 1.417 (3) | C18—C19 | 1.374 (3) |
| C3—C16 | 1.474 (3) | C18—H18 | 0.9500 |
| C4—N5 | 1.320 (2) | C19—C20 | 1.366 (3) |
| C4—C23 | 1.487 (2) | C19—F22 | 1.367 (2) |
| N6—H6A | 0.8816 | C20—C21 | 1.396 (3) |
| N6—H6B | 0.8621 | C20—H20 | 0.9500 |
| C7—C8 | 1.386 (3) | C21—H21 | 0.9500 |
| C7—C12 | 1.395 (3) | C23—C24 | 1.383 (3) |
| C8—C9 | 1.380 (3) | C23—C28 | 1.389 (3) |
| C8—H8 | 0.9500 | C24—C25 | 1.387 (3) |
| C9—C10 | 1.400 (3) | C24—H24 | 0.9500 |
| C9—H9 | 0.9500 | C25—N26 | 1.336 (3) |
| C10—C11 | 1.388 (3) | C25—H25 | 0.9500 |
| C10—C13 | 1.440 (3) | N26—C27 | 1.336 (3) |
| C11—C12 | 1.383 (3) | C27—C28 | 1.383 (3) |
| C11—H11 | 0.9500 | C27—H27 | 0.9500 |
| C12—H12 | 0.9500 | C28—H28 | 0.9500 |
| | | | |
| N5—N1—C2 | 111.40 (14) | C17—C16—C21 | 117.97 (18) |
| N5—N1—C7 | 117.21 (15) | C17—C16—C3 | 119.80 (17) |
| C2—N1—C7 | 131.39 (15) | C21—C16—C3 | 122.22 (17) |
| N6—C2—N1 | 122.58 (16) | C18—C17—C16 | 121.39 (18) |
| N6—C2—C3 | 130.64 (18) | C18—C17—H17 | 119.3 |
| N1—C2—C3 | 106.74 (15) | C16—C17—H17 | 119.3 |
| C2—C3—C4 | 104.33 (17) | C19—C18—C17 | 118.20 (18) |
| C2—C3—C16 | 126.37 (16) | C19—C18—H18 | 120.9 |
| C4—C3—C16 | 128.50 (17) | C17—C18—H18 | 120.9 |
| N5—C4—C3 | 112.93 (16) | C20—C19—F22 | 119.08 (19) |
| N5—C4—C23 | 117.26 (16) | C20—C19—C18 | 123.03 (18) |
| C3—C4—C23 | 129.75 (18) | F22—C19—C18 | 117.90 (18) |
| C4—N5—N1 | 104.59 (15) | C19—C20—C21 | 118.24 (19) |
| C2—N6—H6A | 120.7 | C19—C20—H20 | 120.9 |
| C2—N6—H6B | 120.9 | C21—C20—H20 | 120.9 |
| H6A—N6—H6B | 117.0 | C20—C21—C16 | 121.13 (19) |
| C8—C7—C12 | 120.14 (18) | C20—C21—H21 | 119.4 |

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| C8—C7—N1 | 118.43 (16) | C16—C21—H21 | 119.4 |
| C12—C7—N1 | 121.39 (18) | C24—C23—C28 | 117.64 (16) |
| C9—C8—C7 | 120.58 (17) | C24—C23—C4 | 120.48 (17) |
| C9—C8—H8 | 119.7 | C28—C23—C4 | 121.79 (17) |
| C7—C8—H8 | 119.7 | C23—C24—C25 | 119.40 (18) |
| C8—C9—C10 | 119.30 (19) | C23—C24—H24 | 120.3 |
| C8—C9—H9 | 120.4 | C25—C24—H24 | 120.3 |
| C10—C9—H9 | 120.4 | N26—C25—C24 | 123.45 (19) |
| C11—C10—C9 | 120.12 (18) | N26—C25—H25 | 118.3 |
| C11—C10—C13 | 119.92 (17) | C24—C25—H25 | 118.3 |
| C9—C10—C13 | 119.95 (18) | C27—N26—C25 | 116.60 (16) |
| C12—C11—C10 | 120.38 (18) | N26—C27—C28 | 124.0 (2) |
| C12—C11—H11 | 119.8 | N26—C27—H27 | 118.0 |
| C10—C11—H11 | 119.8 | C28—C27—H27 | 118.0 |
| C11—C12—C7 | 119.46 (19) | C27—C28—C23 | 118.87 (19) |
| C11—C12—H12 | 120.3 | C27—C28—H28 | 120.6 |
| C7—C12—H12 | 120.3 | C23—C28—H28 | 120.6 |
| N14—C13—C10 | 178.9 (2) | | |

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| N5—N1—C2—N6 | 176.84 (17) | C8—C7—C12—C11 | −1.5 (3) |
| C7—N1—C2—N6 | −3.2 (3) | N1—C7—C12—C11 | −179.04 (17) |
| N5—N1—C2—C3 | −1.1 (2) | C2—C3—C16—C17 | −136.16 (19) |
| C7—N1—C2—C3 | 178.89 (17) | C4—C3—C16—C17 | 32.0 (3) |
| N6—C2—C3—C4 | −177.24 (19) | C2—C3—C16—C21 | 42.5 (3) |
| N1—C2—C3—C4 | 0.45 (19) | C4—C3—C16—C21 | −149.42 (18) |
| N6—C2—C3—C16 | −6.8 (3) | C21—C16—C17—C18 | 0.1 (3) |
| N1—C2—C3—C16 | 170.87 (17) | C3—C16—C17—C18 | 178.76 (17) |
| C2—C3—C4—N5 | 0.3 (2) | C16—C17—C18—C19 | −1.9 (3) |
| C16—C3—C4—N5 | −169.81 (17) | C17—C18—C19—C20 | 2.1 (3) |
| C2—C3—C4—C23 | −176.61 (17) | C17—C18—C19—F22 | −178.44 (16) |
| C16—C3—C4—C23 | 13.2 (3) | F22—C19—C20—C21 | −179.87 (17) |
| C3—C4—N5—N1 | −0.97 (19) | C18—C19—C20—C21 | −0.4 (3) |
| C23—C4—N5—N1 | 176.39 (15) | C19—C20—C21—C16 | −1.5 (3) |
| C2—N1—N5—C4 | 1.26 (19) | C17—C16—C21—C20 | 1.7 (3) |
| C7—N1—N5—C4 | −178.71 (15) | C3—C16—C21—C20 | −176.99 (18) |
| N5—N1—C7—C8 | −27.3 (2) | N5—C4—C23—C24 | 38.6 (3) |
| C2—N1—C7—C8 | 152.71 (19) | C3—C4—C23—C24 | −144.6 (2) |
| N5—N1—C7—C12 | 150.24 (17) | N5—C4—C23—C28 | −137.84 (19) |
| C2—N1—C7—C12 | −29.7 (3) | C3—C4—C23—C28 | 39.0 (3) |
| C12—C7—C8—C9 | 0.5 (3) | C28—C23—C24—C25 | 0.0 (3) |
| N1—C7—C8—C9 | 178.05 (18) | C4—C23—C24—C25 | −176.60 (18) |
| C7—C8—C9—C10 | 0.9 (3) | C23—C24—C25—N26 | 0.8 (3) |
| C8—C9—C10—C11 | −1.1 (3) | C24—C25—N26—C27 | −0.8 (3) |
| C8—C9—C10—C13 | 177.70 (19) | C25—N26—C27—C28 | 0.1 (3) |
| C9—C10—C11—C12 | 0.1 (3) | N26—C27—C28—C23 | 0.6 (4) |
| C13—C10—C11—C12 | −178.77 (19) | C24—C23—C28—C27 | −0.6 (3) |
| C10—C11—C12—C7 | 1.3 (3) | C4—C23—C28—C27 | 175.92 (19) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N6—H6*A*···N26$^{i}$ | 0.88 | 2.14 | 2.938 (2) | 150 |
| N6—H6*B*···N14$^{ii}$ | 0.86 | 2.58 | 3.292 (3) | 141 |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+3/2, *y*, *z*−1/2.