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N-(2-Bromo-4-methylphenyl)-2-(5-methyl-2-phenylpyrazolo[1,5-a]pyrimidin-7-yl)acetamide

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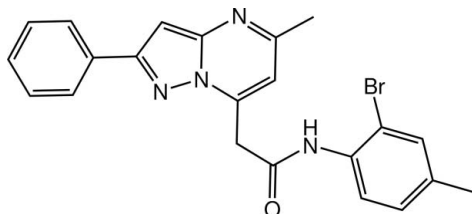
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.041; wR factor = 0.107; data-to-parameter ratio = 25.2.

The fused pyrazole and pyrimidine rings in the title compound, $\text{C}_{22}\text{H}_{19}\text{BrN}_4\text{O}$, are almost coplanar, their planes being inclined to one another by $2.08(13)^\circ$. The dihedral angles formed by the mean plane of the fused ring system and the phenyl and benzene rings are $16.21(4)$ and $82.84(4)^\circ$, respectively. An intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond is observed. In the crystal, molecules form inversion dimers *via* pairs of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. $\pi-\pi$ interactions, with centroid-centroid distances of $3.4916(9)$ Å, connect the dimers into a three-dimensional network.

Related literature

For pharmacological and biochemical properties of pyrazolo[1,5-*a*]pyrimidine derivatives, see: Selleri *et al.* (2005); Almansa *et al.* (2001); Suzuki *et al.* (2001); Chen *et al.* (2004). For related structures, see: Bassoude *et al.* (2013*a,b*).



Experimental

Crystal data

 $\text{C}_{22}\text{H}_{19}\text{BrN}_4\text{O}$
 $M_r = 435.32$

Monoclinic, $P2_1/c$
 $a = 9.8102(6)$ Å
 $b = 7.2915(4)$ Å
 $c = 27.0162(14)$ Å
 $\beta = 92.942(3)^\circ$
 $V = 1929.95(19)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.15$ mm⁻¹
 $T = 296$ K
 $0.42 \times 0.33 \times 0.25$ mm

Data collection

Bruker X8 APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.739$, $T_{\max} = 0.867$

29996 measured reflections
 6371 independent reflections
 3830 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.107$
 $S = 1.02$
 6371 reflections

253 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N4}-\text{H4A}\cdots\text{N2}$ | 0.86 | 2.17 | 2.927 (2) | 147 |
| $\text{C14}-\text{H14}\cdots\text{O1}^i$ | 0.93 | 2.43 | 3.189 (2) | 139 |

 Symmetry code: (i) $-x + 2, -y + 1, -z$.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2009) and publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5060).

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supporting information

Acta Cryst. (2013). E69, o829 [doi:10.1107/S1600536813011811]

***N*-(2-Bromo-4-methylphenyl)-2-(5-methyl-2-phenylpyrazolo[1,5-*a*]pyrimidin-7-yl)acetamide**

Ibtissam Bassoude, Sabine Berteina-Raboin, El Mokhtar Essassi, Gérald Guillaumet and Lahcen El Ammari

S1. Comment

Pyrazolo[1,5-*a*]pyrimidines have attracted considerable interest because of their biological activity. For instance, they are known for their potent utility as selective peripheral benzodiazepine receptor ligands (Selleri *et al.*, 2005), COX-2 selective inhibitors (Almansa *et al.*, 2001), HMG-CoA reductase inhibitors (Suzuki *et al.*, 2001) and CRF1 antagonists (Chen *et al.*, 2004). Our research group targeted at the development of heterocycles with a bridgehead nitrogen atom such the title compound and related compounds recently published (Bassoude *et al.* 2013*a*, 2013*b*).

The crystal structure of the title compound is built up from two fused five (N2/N3/C3–C5) and six-membered (N1/N3/C1–C3/C6) rings linked to one phenyl ring (C17–C22) and to a 2-bromo-4-methylphenyl ring (Br1/C9–C14) through an acetamide group as shown in Fig. 1. The pyrazole and pyrimidine rings are essentially planar with the maximum deviation of 0.0039 (15) and 0.0076 (15) Å for atom C3. The plane through the fused ring system makes a dihedral angles of 16.21 (4)° and 82.84 (4)° with the phenyl ring and with the 2-bromo-4-methylphenyl ring, respectively.

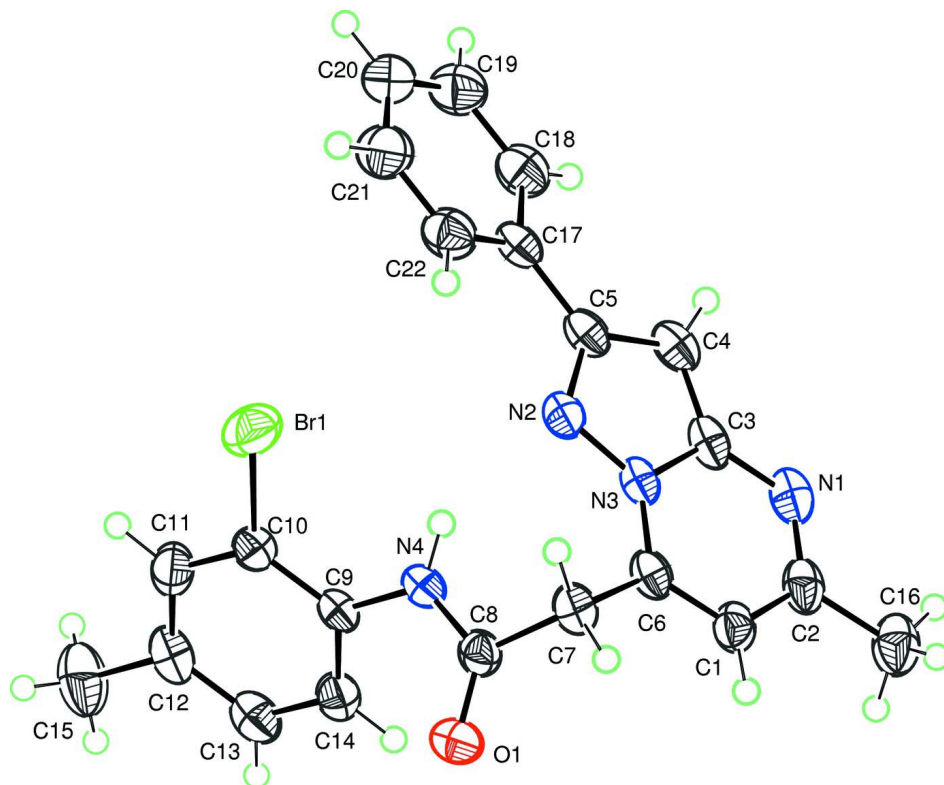
In the crystal (Fig. 2) molecules form inversion dimers *via* pairs of C14—H14···O1 hydrogen bonds. In addition, π – π interactions connect the dimers into a three-dimensional network, with centroid–centroid distances of 3.4916 (9) Å. An intramolecular N4—H4A···N2 hydrogen bond my help to define the conformation of the molecule.

S2. Experimental

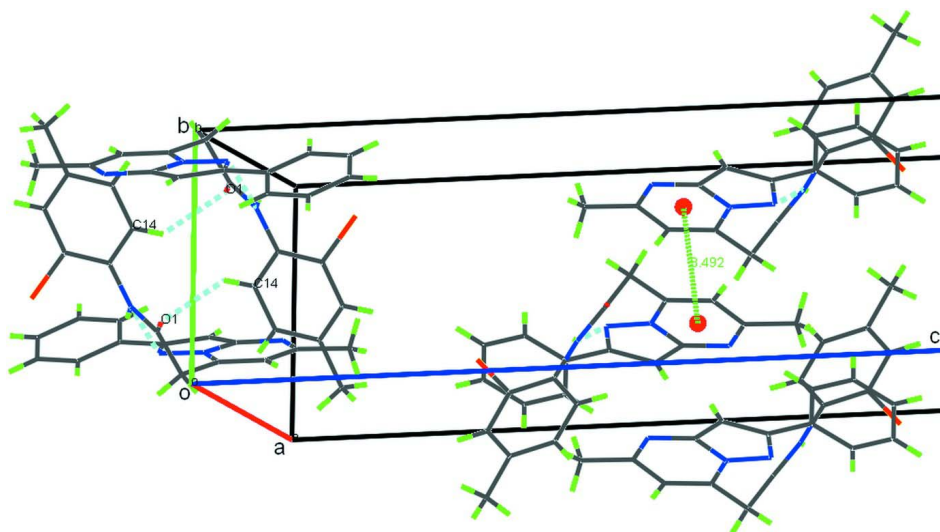
To a solution of 2-bromo-4-methylaniline (0.1 ml, 0.78 mmol) in 4 ml dichloromethane, under argon and at 273 K, were added 0.8 ml of trimethylaluminium in toluene (2M, 1.6 mmol), then the mixture was stirred for 15 min followed by addition of 0.2 g (0.68 mmol) of 7-ethoxycarbonyl-methyl-5-methylpyrazolo[1,5-*a*]pyrimidine. The reaction mixture was stirred to room temperature for 30 min then heated to reflux for 5 h. After evaporation of solvent under reduced pressure, the residue was extracted with CH₂Cl₂ and washed with a saturated NaCl solution. The combined organic layers were dried with MgSO₄ and concentrated under vacuum. The residue was purified on silica gel by column chromatography using mixture of petroleum ether and ethyl acetate (9:1 *v/v*) as eluent. The compound was recrystallized from a mixture of cyclohexane/ diethyl ether (1:1 *v/v*) to give colourless crystals.

S3. Refinement

All H atoms could be located in a difference Fourier map and were treated as riding, with C—H = 0.93–0.97 Å, N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms. Two outliers (1 0 0; 0 0 2) were omitted from the last refinement cycles

**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small circles of arbitrary radii.

**Figure 2**

Partial crystal packing of the title compound showing C14-H14A...O1 and N4-H4...N2 hydrogen bonds as blue dashed lines and a π ... π contact as green line. The red spheres represent the centroids of the pyrimidine rings.

N*-(2-Bromo-4-methylphenyl)-2-(5-methyl-2-phenylpyrazolo[1,5-*a*]pyrimidin-7-yl)acetamideCrystal data*C₂₂H₁₉BrN₄O $M_r = 435.32$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 9.8102$ (6) Å $b = 7.2915$ (4) Å $c = 27.0162$ (14) Å $\beta = 92.942$ (3)° $V = 1929.95$ (19) Å³ $Z = 4$ $F(000) = 888$ $D_x = 1.498$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6371 reflections

 $\theta = 2.5$ – 31.4 ° $\mu = 2.15$ mm⁻¹ $T = 296$ K

Block, colourless

 $0.42 \times 0.33 \times 0.25$ mm*Data collection*

Bruker X8 APEXII area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.739$, $T_{\max} = 0.867$

29996 measured reflections

6371 independent reflections

3830 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.044$ $\theta_{\max} = 31.4$ °, $\theta_{\min} = 2.5$ ° $h = -14 \rightarrow 14$ $k = -10 \rightarrow 10$ $l = -39 \rightarrow 39$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.041$ $wR(F^2) = 0.107$ $S = 1.02$

6371 reflections

253 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.2795P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.41$ e Å⁻³ $\Delta\rho_{\min} = -0.62$ e Å⁻³*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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|------------|--------------|----------------------------------|
| C1 | 0.6173 (2) | 0.8274 (2) | -0.03898 (7) | 0.0377 (4) |
| H1 | 0.6836 | 0.8688 | -0.0597 | 0.045* |
| C2 | 0.4907 (2) | 0.7594 (2) | -0.05997 (7) | 0.0389 (4) |
| C3 | 0.41574 (19) | 0.7044 (2) | 0.01713 (7) | 0.0363 (4) |

| | | | | |
|------|--------------|--------------|--------------|--------------|
| C4 | 0.3365 (2) | 0.6608 (2) | 0.05592 (7) | 0.0389 (4) |
| H4 | 0.2478 | 0.6155 | 0.0539 | 0.047* |
| C5 | 0.41646 (19) | 0.6987 (2) | 0.09908 (7) | 0.0345 (4) |
| C6 | 0.64217 (19) | 0.8324 (2) | 0.01096 (7) | 0.0329 (4) |
| C7 | 0.76984 (19) | 0.9055 (2) | 0.03730 (7) | 0.0366 (4) |
| H7A | 0.7446 | 0.9745 | 0.0661 | 0.044* |
| H7B | 0.8141 | 0.9894 | 0.0154 | 0.044* |
| C8 | 0.87117 (19) | 0.7571 (2) | 0.05392 (7) | 0.0330 (4) |
| C9 | 0.89437 (18) | 0.4831 (2) | 0.10641 (7) | 0.0332 (4) |
| C10 | 0.89659 (19) | 0.4341 (2) | 0.15591 (7) | 0.0361 (4) |
| C11 | 0.9568 (2) | 0.2718 (3) | 0.17291 (8) | 0.0422 (5) |
| H11 | 0.9557 | 0.2416 | 0.2063 | 0.051* |
| C12 | 1.0184 (2) | 0.1551 (3) | 0.14043 (8) | 0.0436 (5) |
| C13 | 1.0160 (2) | 0.2037 (3) | 0.09087 (8) | 0.0432 (5) |
| H13 | 1.0567 | 0.1265 | 0.0685 | 0.052* |
| C14 | 0.9547 (2) | 0.3641 (3) | 0.07366 (8) | 0.0397 (4) |
| H14 | 0.9538 | 0.3925 | 0.0401 | 0.048* |
| C15 | 1.0869 (3) | -0.0203 (3) | 0.15829 (10) | 0.0691 (7) |
| H15A | 1.1706 | 0.0085 | 0.1766 | 0.104* |
| H15B | 1.1060 | -0.0955 | 0.1303 | 0.104* |
| H15C | 1.0274 | -0.0854 | 0.1793 | 0.104* |
| C16 | 0.4645 (2) | 0.7598 (3) | -0.11515 (8) | 0.0512 (5) |
| H16C | 0.4995 | 0.8709 | -0.1287 | 0.077* |
| H16A | 0.3680 | 0.7523 | -0.1229 | 0.077* |
| H16B | 0.5091 | 0.6563 | -0.1292 | 0.077* |
| C17 | 0.38277 (19) | 0.6745 (2) | 0.15115 (7) | 0.0361 (4) |
| C18 | 0.2742 (2) | 0.5647 (3) | 0.16391 (9) | 0.0470 (5) |
| H18 | 0.2209 | 0.5064 | 0.1392 | 0.056* |
| C19 | 0.2447 (2) | 0.5415 (3) | 0.21290 (9) | 0.0541 (6) |
| H19 | 0.1721 | 0.4670 | 0.2209 | 0.065* |
| C20 | 0.3217 (2) | 0.6275 (3) | 0.25011 (9) | 0.0533 (6) |
| H20 | 0.3013 | 0.6116 | 0.2831 | 0.064* |
| C21 | 0.4294 (2) | 0.7376 (3) | 0.23797 (9) | 0.0518 (5) |
| H21 | 0.4818 | 0.7966 | 0.2628 | 0.062* |
| C22 | 0.4595 (2) | 0.7604 (3) | 0.18897 (8) | 0.0452 (5) |
| H22 | 0.5326 | 0.8345 | 0.1812 | 0.054* |
| N1 | 0.39309 (17) | 0.6994 (2) | -0.03282 (6) | 0.0405 (4) |
| N2 | 0.54163 (15) | 0.7640 (2) | 0.08894 (6) | 0.0338 (3) |
| N3 | 0.53930 (15) | 0.76798 (18) | 0.03862 (6) | 0.0317 (3) |
| N4 | 0.82608 (16) | 0.6428 (2) | 0.08896 (6) | 0.0370 (4) |
| H4A | 0.7499 | 0.6695 | 0.1016 | 0.044* |
| O1 | 0.98349 (14) | 0.74725 (19) | 0.03713 (5) | 0.0453 (3) |
| Br1 | 0.81300 (3) | 0.58958 (3) | 0.201758 (8) | 0.05961 (10) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|------------|-------------|------------|-------------|------------|
| C1 | 0.0391 (11) | 0.0356 (9) | 0.0378 (10) | 0.0071 (8) | -0.0030 (9) | 0.0039 (8) |

| | | | | | | |
|-----|-------------|--------------|--------------|--------------|--------------|--------------|
| C2 | 0.0459 (12) | 0.0288 (8) | 0.0409 (11) | 0.0120 (8) | -0.0089 (9) | -0.0027 (7) |
| C3 | 0.0315 (10) | 0.0304 (8) | 0.0458 (12) | 0.0060 (7) | -0.0103 (9) | -0.0036 (7) |
| C4 | 0.0268 (10) | 0.0370 (9) | 0.0523 (12) | 0.0007 (8) | -0.0044 (9) | -0.0031 (8) |
| C5 | 0.0282 (10) | 0.0278 (8) | 0.0473 (11) | 0.0048 (7) | -0.0008 (8) | -0.0028 (7) |
| C6 | 0.0303 (10) | 0.0275 (8) | 0.0405 (10) | 0.0056 (7) | -0.0035 (8) | 0.0011 (7) |
| C7 | 0.0330 (10) | 0.0341 (9) | 0.0420 (11) | 0.0014 (8) | -0.0036 (8) | 0.0021 (7) |
| C8 | 0.0294 (10) | 0.0381 (9) | 0.0309 (9) | 0.0008 (7) | -0.0032 (8) | -0.0041 (7) |
| C9 | 0.0223 (9) | 0.0400 (9) | 0.0371 (10) | 0.0042 (7) | -0.0009 (8) | 0.0022 (7) |
| C10 | 0.0291 (10) | 0.0442 (10) | 0.0350 (10) | 0.0004 (8) | 0.0005 (8) | 0.0002 (8) |
| C11 | 0.0409 (12) | 0.0462 (10) | 0.0387 (11) | -0.0011 (9) | -0.0055 (9) | 0.0086 (8) |
| C12 | 0.0366 (11) | 0.0381 (9) | 0.0549 (13) | 0.0032 (8) | -0.0102 (10) | 0.0024 (9) |
| C13 | 0.0359 (11) | 0.0409 (10) | 0.0522 (13) | 0.0050 (8) | -0.0026 (9) | -0.0077 (9) |
| C14 | 0.0345 (11) | 0.0466 (10) | 0.0377 (11) | 0.0048 (8) | -0.0027 (9) | -0.0010 (8) |
| C15 | 0.0758 (19) | 0.0495 (12) | 0.0796 (18) | 0.0205 (13) | -0.0183 (15) | 0.0084 (12) |
| C16 | 0.0619 (15) | 0.0482 (11) | 0.0422 (12) | 0.0110 (10) | -0.0118 (11) | -0.0065 (9) |
| C17 | 0.0277 (10) | 0.0335 (9) | 0.0470 (12) | 0.0077 (7) | 0.0010 (8) | -0.0020 (8) |
| C18 | 0.0373 (12) | 0.0483 (11) | 0.0551 (13) | -0.0024 (9) | 0.0001 (10) | -0.0032 (9) |
| C19 | 0.0418 (13) | 0.0624 (13) | 0.0588 (15) | -0.0058 (11) | 0.0085 (11) | 0.0066 (11) |
| C20 | 0.0467 (14) | 0.0681 (14) | 0.0455 (13) | 0.0084 (11) | 0.0074 (11) | 0.0030 (10) |
| C21 | 0.0453 (13) | 0.0632 (13) | 0.0466 (13) | -0.0024 (11) | 0.0013 (10) | -0.0085 (10) |
| C22 | 0.0366 (11) | 0.0490 (11) | 0.0501 (13) | -0.0034 (9) | 0.0015 (10) | -0.0048 (9) |
| N1 | 0.0393 (10) | 0.0358 (8) | 0.0451 (10) | 0.0055 (7) | -0.0107 (8) | -0.0041 (7) |
| N2 | 0.0292 (8) | 0.0355 (7) | 0.0362 (9) | 0.0033 (6) | -0.0027 (7) | -0.0015 (6) |
| N3 | 0.0276 (8) | 0.0296 (7) | 0.0371 (9) | 0.0048 (6) | -0.0056 (7) | -0.0012 (6) |
| N4 | 0.0279 (9) | 0.0454 (8) | 0.0379 (9) | 0.0098 (7) | 0.0046 (7) | 0.0059 (7) |
| O1 | 0.0352 (8) | 0.0541 (8) | 0.0474 (8) | 0.0065 (6) | 0.0094 (7) | 0.0049 (6) |
| Br1 | 0.0728 (2) | 0.06541 (16) | 0.04192 (14) | 0.01753 (12) | 0.01561 (12) | 0.00091 (10) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|----------|-----------|
| C1—C6 | 1.359 (3) | C11—H11 | 0.9300 |
| C1—C2 | 1.428 (3) | C12—C13 | 1.384 (3) |
| C1—H1 | 0.9300 | C12—C15 | 1.512 (3) |
| C2—N1 | 1.311 (3) | C13—C14 | 1.385 (3) |
| C2—C16 | 1.500 (3) | C13—H13 | 0.9300 |
| C3—N1 | 1.357 (2) | C14—H14 | 0.9300 |
| C3—C4 | 1.374 (3) | C15—H15A | 0.9600 |
| C3—N3 | 1.396 (2) | C15—H15B | 0.9600 |
| C4—C5 | 1.399 (3) | C15—H15C | 0.9600 |
| C4—H4 | 0.9300 | C16—H16C | 0.9600 |
| C5—N2 | 1.358 (2) | C16—H16A | 0.9600 |
| C5—C17 | 1.472 (3) | C16—H16B | 0.9600 |
| C6—N3 | 1.369 (2) | C17—C22 | 1.387 (3) |
| C6—C7 | 1.506 (3) | C17—C18 | 1.390 (3) |
| C7—C8 | 1.521 (2) | C18—C19 | 1.380 (3) |
| C7—H7A | 0.9700 | C18—H18 | 0.9300 |
| C7—H7B | 0.9700 | C19—C20 | 1.377 (3) |
| C8—O1 | 1.215 (2) | C19—H19 | 0.9300 |

| | | | |
|-------------|-------------|---------------|-------------|
| C8—N4 | 1.353 (2) | C20—C21 | 1.380 (3) |
| C9—C10 | 1.383 (3) | C20—H20 | 0.9300 |
| C9—C14 | 1.393 (3) | C21—C22 | 1.381 (3) |
| C9—N4 | 1.412 (2) | C21—H21 | 0.9300 |
| C10—C11 | 1.390 (3) | C22—H22 | 0.9300 |
| C10—Br1 | 1.8962 (19) | N2—N3 | 1.359 (2) |
| C11—C12 | 1.384 (3) | N4—H4A | 0.8600 |
| C6—C1—C2 | 120.76 (19) | C13—C14—C9 | 120.30 (19) |
| C6—C1—H1 | 119.6 | C13—C14—H14 | 119.8 |
| C2—C1—H1 | 119.6 | C9—C14—H14 | 119.8 |
| N1—C2—C1 | 122.65 (18) | C12—C15—H15A | 109.5 |
| N1—C2—C16 | 117.63 (19) | C12—C15—H15B | 109.5 |
| C1—C2—C16 | 119.7 (2) | H15A—C15—H15B | 109.5 |
| N1—C3—C4 | 133.01 (18) | C12—C15—H15C | 109.5 |
| N1—C3—N3 | 121.12 (18) | H15A—C15—H15C | 109.5 |
| C4—C3—N3 | 105.85 (16) | H15B—C15—H15C | 109.5 |
| C3—C4—C5 | 105.95 (17) | C2—C16—H16C | 109.5 |
| C3—C4—H4 | 127.0 | C2—C16—H16A | 109.5 |
| C5—C4—H4 | 127.0 | H16C—C16—H16A | 109.5 |
| N2—C5—C4 | 112.04 (17) | C2—C16—H16B | 109.5 |
| N2—C5—C17 | 118.99 (17) | H16C—C16—H16B | 109.5 |
| C4—C5—C17 | 128.97 (18) | H16A—C16—H16B | 109.5 |
| C1—C6—N3 | 115.66 (17) | C22—C17—C18 | 118.12 (19) |
| C1—C6—C7 | 125.52 (18) | C22—C17—C5 | 120.65 (18) |
| N3—C6—C7 | 118.81 (16) | C18—C17—C5 | 121.24 (18) |
| C6—C7—C8 | 113.78 (14) | C19—C18—C17 | 120.7 (2) |
| C6—C7—H7A | 108.8 | C19—C18—H18 | 119.7 |
| C8—C7—H7A | 108.8 | C17—C18—H18 | 119.7 |
| C6—C7—H7B | 108.8 | C20—C19—C18 | 120.7 (2) |
| C8—C7—H7B | 108.8 | C20—C19—H19 | 119.7 |
| H7A—C7—H7B | 107.7 | C18—C19—H19 | 119.7 |
| O1—C8—N4 | 124.06 (17) | C19—C20—C21 | 119.3 (2) |
| O1—C8—C7 | 121.57 (17) | C19—C20—H20 | 120.4 |
| N4—C8—C7 | 114.36 (16) | C21—C20—H20 | 120.4 |
| C10—C9—C14 | 117.85 (17) | C20—C21—C22 | 120.1 (2) |
| C10—C9—N4 | 121.28 (16) | C20—C21—H21 | 119.9 |
| C14—C9—N4 | 120.76 (17) | C22—C21—H21 | 119.9 |
| C9—C10—C11 | 121.64 (18) | C21—C22—C17 | 121.1 (2) |
| C9—C10—Br1 | 119.42 (14) | C21—C22—H22 | 119.4 |
| C11—C10—Br1 | 118.93 (15) | C17—C22—H22 | 119.4 |
| C12—C11—C10 | 120.42 (19) | C2—N1—C3 | 117.42 (17) |
| C12—C11—H11 | 119.8 | C5—N2—N3 | 103.92 (14) |
| C10—C11—H11 | 119.8 | N2—N3—C6 | 125.34 (15) |
| C11—C12—C13 | 118.01 (18) | N2—N3—C3 | 112.24 (15) |
| C11—C12—C15 | 121.3 (2) | C6—N3—C3 | 122.38 (16) |
| C13—C12—C15 | 120.7 (2) | C8—N4—C9 | 125.11 (15) |
| C12—C13—C14 | 121.77 (19) | C8—N4—H4A | 117.4 |

| | | | |
|-------------|-------|-----------|-------|
| C12—C13—H13 | 119.1 | C9—N4—H4A | 117.4 |
| C14—C13—H13 | 119.1 | | |

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> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N4—H4A \cdots N2 | 0.86 | 2.17 | 2.927 (2) | 147 |
| C14—H14 \cdots O1 ⁱ | 0.93 | 2.43 | 3.189 (2) | 139 |

Symmetry code: (i) $-x+2, -y+1, -z$.