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6-(1*H*-Indol-3-yl)-4-phenyl-2,2'-bi-pyridine-5-carbonitrileWeijun Zhu,^{a*} Yan Xiang^b and Songlei Zhu^c

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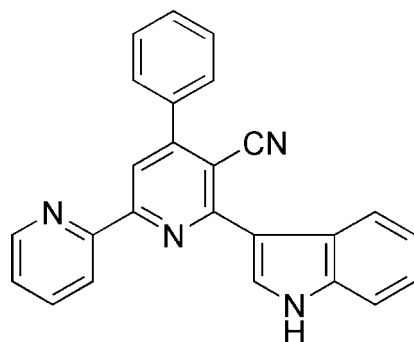
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.054; wR factor = 0.126; data-to-parameter ratio = 12.7.

In the molecule of the title compound, $\text{C}_{25}\text{H}_{16}\text{N}_4$, the pyridine rings are oriented at a dihedral angle of 0.92 (3)°, while the dihedral angle between the benzene ring and the adjacent pyridine ring is 56.51 (3)°. In the crystal structure, intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into centrosymmetric dimers, forming $R_2^2(16)$ ring motifs. $\pi-\pi$ contacts between the pyridine ring and the indole ring system and between the pyridine rings [centroid-centroid distances = 3.923 (2) and 3.724 (2) Å] may further stabilize the structure. Two weak $\text{C}-\text{H}\cdots\pi$ interactions are also present.

Related literature

For general background, see: da Silva *et al.* (2001); Joshi & Chand (1982); Namba *et al.* (2005). For a related structure, see: Zhu *et al.*, (2008). For bond-length data, see: Allen *et al.* (1987). For ring-motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{25}\text{H}_{16}\text{N}_4$
 $M_r = 372.42$
Triclinic, $P1$

$a = 9.7744$ (16) Å
 $b = 9.7927$ (11) Å
 $c = 11.233$ (2) Å

$\alpha = 73.121$ (13)°
 $\beta = 86.008$ (16)°
 $\gamma = 63.853$ (10)°
 $V = 921.5$ (3) Å³
 $Z = 2$

Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 291$ K
 $0.55 \times 0.35 \times 0.30$ mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: multi-scan
(*ABSCOR*; Jacobson, 1998)
 $T_{\min} = 0.966$, $T_{\max} = 0.976$

8987 measured reflections
3349 independent reflections
2614 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.126$
 $S = 1.12$
3349 reflections

263 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.16$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N4}-\text{H4}\cdots\text{N3}^{\text{i}}$ | 0.86 | 2.23 | 3.066 (2) | 164 |
| $\text{C12}-\text{H12}\cdots\text{Cg5}^{\text{ii}}$ | 0.93 | 2.84 | 3.649 (3) | 146 |
| $\text{C23}-\text{H23}\cdots\text{Cg4}^{\text{iii}}$ | 0.93 | 2.91 | 3.711 (3) | 145 |

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y + 2, -z + 1$; (iii) $x, y, z - 1$. Cg4 and Cg5 are the centroids of the $\text{C11}-\text{C16}$ and $\text{C20}-\text{C25}$ rings, respectively.

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2679).

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Zhu, S. L., Ji, S. J., Zhao, K. & Liu, Y. (2008). *Tetrahedron Lett.* **49**, 2578–2582.

supplementary materials

Acta Cryst. (2009). E65, o1187 [doi:10.1107/S1600536809016195]

6-(1*H*-Indol-3-yl)-4-phenyl-2,2'-bipyridine-5-carbonitrile

W. Zhu, Y. Xiang and S. Zhu

Comment

Indole nucleus is a well known heterocycle (da Silva *et al.*, 2001). Compounds carrying the indole moiety exhibit antibacterial and fungicidal activities (Joshi & Chand, 1982). Moreover, the bipyridines and the related complexes have also found numerous applications in asymmetric catalysis, photoinduced electron transfer, and polymer and dendrimer science (Namba *et al.*, 2005). As a part of our programme devoted to the preparation of functionalized indole derivatives, we synthesized a series of indole substituted heterocycles (Zhu *et al.*, 2008). We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The indole ring system A (N4/C18-C25) is planar with a maximum deviation of -0.021 (3) Å for atom C25. Rings B (N1/C1-C5), C (N2/C6-C10) and D (C11-C16) are, of course, planar, and they are oriented at dihedral angles of A/B = 23.01 (3), A/C = 23.61 (3), A/D = 74.90 (3), B/C = 0.92 (3), B/D = 56.51 (3) and C/D = 56.51 (3) °. So, rings B and C are nearly coplanar.

In the crystal structure, intermolecular N-H...N hydrogen bonds (Table 1) link the molecules into centrosymmetric dimers forming R₂²(16) ring motifs (Fig. 2) (Bernstein *et al.*, 1995), in which they may be effective in the stabilization of the structure. The π-π contacts between the pyridine ring and the indole ring system and the pyridine rings, Cg1—Cg2ⁱ and Cg2—Cg3ⁱⁱ [symmetry codes: (i) -x, 2 - y, 1 - z, (ii) -x, 1 - y, 1 - z, where Cg1, Cg2 and Cg3 are centroids of the rings (N4/C18-C20/C25), B (N1/C1-C5) and C (N2/C6-C10), respectively] may further stabilize the structure, with centroid-centroid distances of 3.923 (2) and 3.724 (2) Å. There also exist two weak C—H...π interactions (Table 1).

Experimental

The title compound was prepared by one-pot reaction of 3-cyanoacetyl indole (2 mmol), benzaldehyde (2 mmol) and 2-acetyl pyridine (2 mmol) in present of ammonium acetate in ethanol. After refluxing for 5 h, the reaction mixture was cooled and washed with small amount of cool ethanol. The crude product was filtered and single crystals of the title compound were obtained from ethanol solution by slow evaporation at room temperature (yield; 80%, m.p. 567-568 K). Spectroscopic analysis: IR (KBr, n, cm⁻¹): 3337, 3050, 2218, 1573, 1535, 1438, 1214, 1145, 850, 745, 703. ¹H NMR (400 MHz, DMSO-d₆): 11.89 (br s, 1H, NH), 8.78 (d, J = 4.4 Hz, 1H, ArH), 8.58 (d, J = 8.0 Hz, 1H, ArH), 8.41 (d, J = 5.2 Hz, 2H, ArH), 8.31 (s, 1H, ArH), 8.11 (m, 1H, ArH), 7.79-7.81 (m, 2H, ArH), 7.56-7.66 (m, 5H, ArH), 7.24-7.29 (m, 2H, ArH)

Refinement

H atoms were positioned geometrically, with N-H = 0.86 Å (for NH) and C-H = 0.93 Å for aromatic H and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C,N).

Figures

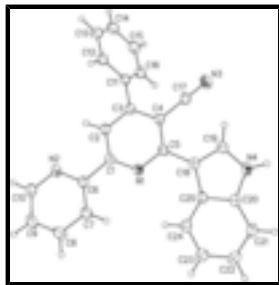


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

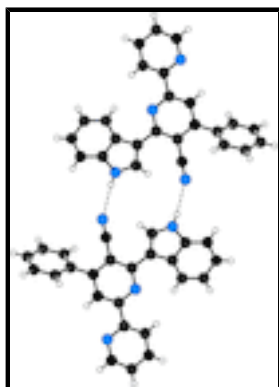


Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

6-(1H-Indol-3-yl)-4-phenyl-2,2'-bipyridine-5-carbonitrile

Crystal data

$C_{25}H_{16}N_4$

$M_r = 372.42$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 9.7744$ (16) Å

$b = 9.7927$ (11) Å

$c = 11.233$ (2) Å

$\alpha = 73.121$ (13)°

$\beta = 86.008$ (16)°

$\gamma = 63.853$ (10)°

$V = 921.5$ (3) Å³

$Z = 2$

$F_{000} = 388$

$D_x = 1.342$ Mg m⁻³

Melting point = 567–568 K

Mo $K\alpha$ radiation

$\lambda = 0.71070$ Å

Cell parameters from 3008 reflections

$\theta = 3.1$ – 25.3 °

$\mu = 0.08$ mm⁻¹

$T = 291$ K

Block, yellow

$0.55 \times 0.35 \times 0.30$ mm

Data collection

Rigaku Mercury
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 7.31 pixels mm⁻¹

$T = 291$ K

3349 independent reflections

2614 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$

$\theta_{max} = 25.3$ °

$\theta_{min} = 3.1$ °

ω scans $h = -11 \rightarrow 11$
 Absorption correction: multi-scan $k = -10 \rightarrow 11$
 (ABSCOR; Jacobson, 1998)
 $T_{\min} = 0.966$, $T_{\max} = 0.976$ $l = -13 \rightarrow 13$
 8987 measured reflections

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.054$ H-atom parameters constrained
 $wR(F^2) = 0.126$ $w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.1499P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.12$ $(\Delta/\sigma)_{\max} < 0.001$
 3349 reflections $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 263 parameters $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|---------------|--------------|----------------------------------|
| N1 | 0.94201 (16) | 0.20772 (17) | 0.54741 (13) | 0.0355 (4) |
| N2 | 1.20413 (18) | 0.3774 (2) | 0.44026 (14) | 0.0455 (4) |
| N3 | 0.5855 (2) | 0.1895 (2) | 0.28547 (16) | 0.0606 (5) |
| N4 | 0.64100 (17) | -0.04598 (18) | 0.69177 (14) | 0.0422 (4) |
| H4 | 0.5936 | -0.1043 | 0.7025 | 0.051* |
| C1 | 1.01436 (19) | 0.2799 (2) | 0.46717 (16) | 0.0347 (4) |
| C2 | 0.98275 (19) | 0.3310 (2) | 0.33960 (16) | 0.0371 (4) |
| H2 | 1.0382 | 0.3776 | 0.2873 | 0.045* |
| C3 | 0.86846 (19) | 0.3126 (2) | 0.28960 (16) | 0.0353 (4) |
| C4 | 0.79281 (19) | 0.2362 (2) | 0.37308 (16) | 0.0348 (4) |
| C5 | 0.83308 (19) | 0.1829 (2) | 0.50305 (16) | 0.0334 (4) |
| C6 | 1.13427 (19) | 0.3032 (2) | 0.52184 (16) | 0.0354 (4) |
| C7 | 1.1727 (2) | 0.2494 (2) | 0.64913 (18) | 0.0449 (5) |

supplementary materials

| | | | | |
|-----|------------|-------------|---------------|------------|
| H7 | 1.1226 | 0.1981 | 0.7039 | 0.054* |
| C8 | 1.2862 (2) | 0.2731 (3) | 0.6929 (2) | 0.0519 (5) |
| H8 | 1.3135 | 0.2383 | 0.7779 | 0.062* |
| C9 | 1.3586 (2) | 0.3482 (2) | 0.6104 (2) | 0.0494 (5) |
| H9 | 1.4361 | 0.3648 | 0.6378 | 0.059* |
| C10 | 1.3136 (2) | 0.3981 (3) | 0.4861 (2) | 0.0521 (5) |
| H10 | 1.3625 | 0.4497 | 0.4302 | 0.063* |
| C11 | 0.8284 (2) | 0.3777 (2) | 0.15322 (16) | 0.0379 (4) |
| C12 | 0.9407 (2) | 0.3356 (2) | 0.07066 (17) | 0.0445 (5) |
| H12 | 1.0400 | 0.2617 | 0.1010 | 0.053* |
| C13 | 0.9065 (3) | 0.4026 (3) | -0.05660 (18) | 0.0529 (6) |
| H13 | 0.9823 | 0.3725 | -0.1114 | 0.063* |
| C14 | 0.7602 (3) | 0.5140 (3) | -0.10229 (19) | 0.0555 (6) |
| H14 | 0.7376 | 0.5599 | -0.1878 | 0.067* |
| C15 | 0.6484 (3) | 0.5570 (3) | -0.02151 (19) | 0.0532 (6) |
| H15 | 0.5498 | 0.6323 | -0.0525 | 0.064* |
| C16 | 0.6809 (2) | 0.4891 (2) | 0.10587 (18) | 0.0460 (5) |
| H16 | 0.6039 | 0.5181 | 0.1600 | 0.055* |
| C17 | 0.6772 (2) | 0.2108 (2) | 0.32443 (17) | 0.0423 (5) |
| C18 | 0.7603 (2) | 0.1025 (2) | 0.59690 (16) | 0.0352 (4) |
| C19 | 0.6856 (2) | 0.0176 (2) | 0.58127 (17) | 0.0385 (4) |
| H19 | 0.6682 | 0.0056 | 0.5054 | 0.046* |
| C20 | 0.6833 (2) | -0.0028 (2) | 0.78422 (17) | 0.0380 (4) |
| C21 | 0.6582 (2) | -0.0376 (2) | 0.90989 (18) | 0.0476 (5) |
| H21 | 0.6081 | -0.1001 | 0.9444 | 0.057* |
| C22 | 0.7105 (3) | 0.0240 (3) | 0.98141 (19) | 0.0568 (6) |
| H22 | 0.6957 | 0.0029 | 1.0663 | 0.068* |
| C23 | 0.7851 (3) | 0.1175 (3) | 0.92946 (19) | 0.0601 (6) |
| H23 | 0.8188 | 0.1581 | 0.9803 | 0.072* |
| C24 | 0.8104 (2) | 0.1515 (3) | 0.80452 (18) | 0.0507 (5) |
| H24 | 0.8605 | 0.2143 | 0.7711 | 0.061* |
| C25 | 0.7595 (2) | 0.0901 (2) | 0.72879 (16) | 0.0366 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0353 (8) | 0.0367 (9) | 0.0374 (8) | -0.0191 (7) | 0.0027 (7) | -0.0097 (7) |
| N2 | 0.0430 (9) | 0.0583 (11) | 0.0475 (9) | -0.0321 (8) | 0.0058 (8) | -0.0173 (8) |
| N3 | 0.0675 (12) | 0.0748 (13) | 0.0507 (10) | -0.0502 (11) | -0.0130 (9) | 0.0006 (9) |
| N4 | 0.0439 (9) | 0.0449 (9) | 0.0476 (9) | -0.0298 (8) | 0.0052 (7) | -0.0109 (7) |
| C1 | 0.0320 (9) | 0.0349 (10) | 0.0378 (10) | -0.0153 (8) | 0.0024 (8) | -0.0102 (8) |
| C2 | 0.0336 (9) | 0.0415 (11) | 0.0369 (10) | -0.0206 (8) | 0.0024 (8) | -0.0058 (8) |
| C3 | 0.0354 (10) | 0.0346 (10) | 0.0355 (10) | -0.0159 (8) | 0.0005 (8) | -0.0081 (8) |
| C4 | 0.0346 (9) | 0.0346 (10) | 0.0362 (10) | -0.0172 (8) | 0.0001 (8) | -0.0082 (8) |
| C5 | 0.0329 (9) | 0.0314 (9) | 0.0385 (10) | -0.0157 (8) | 0.0034 (8) | -0.0114 (8) |
| C6 | 0.0319 (9) | 0.0355 (10) | 0.0407 (10) | -0.0152 (8) | 0.0036 (8) | -0.0134 (8) |
| C7 | 0.0452 (11) | 0.0490 (12) | 0.0415 (11) | -0.0237 (10) | -0.0025 (9) | -0.0083 (9) |
| C8 | 0.0514 (12) | 0.0575 (13) | 0.0492 (12) | -0.0256 (11) | -0.0101 (10) | -0.0131 (10) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C9 | 0.0334 (10) | 0.0567 (13) | 0.0663 (14) | -0.0199 (10) | -0.0016 (10) | -0.0281 (11) |
| C10 | 0.0458 (12) | 0.0661 (14) | 0.0611 (13) | -0.0364 (11) | 0.0121 (10) | -0.0249 (11) |
| C11 | 0.0418 (10) | 0.0419 (11) | 0.0360 (10) | -0.0255 (9) | 0.0003 (8) | -0.0080 (8) |
| C12 | 0.0459 (11) | 0.0509 (12) | 0.0399 (11) | -0.0266 (10) | 0.0016 (9) | -0.0089 (9) |
| C13 | 0.0668 (14) | 0.0664 (15) | 0.0398 (11) | -0.0420 (13) | 0.0114 (10) | -0.0171 (10) |
| C14 | 0.0770 (16) | 0.0650 (15) | 0.0357 (11) | -0.0472 (13) | -0.0048 (11) | -0.0026 (10) |
| C15 | 0.0566 (13) | 0.0545 (13) | 0.0463 (12) | -0.0306 (11) | -0.0118 (11) | 0.0018 (10) |
| C16 | 0.0448 (11) | 0.0539 (12) | 0.0410 (10) | -0.0260 (10) | -0.0005 (9) | -0.0085 (9) |
| C17 | 0.0457 (11) | 0.0469 (12) | 0.0382 (10) | -0.0283 (10) | 0.0001 (9) | -0.0042 (9) |
| C18 | 0.0334 (9) | 0.0345 (10) | 0.0388 (10) | -0.0164 (8) | 0.0030 (8) | -0.0098 (8) |
| C19 | 0.0408 (10) | 0.0398 (11) | 0.0387 (10) | -0.0215 (9) | 0.0030 (8) | -0.0109 (8) |
| C20 | 0.0339 (10) | 0.0373 (10) | 0.0436 (11) | -0.0174 (8) | 0.0041 (8) | -0.0105 (8) |
| C21 | 0.0476 (12) | 0.0545 (13) | 0.0449 (11) | -0.0305 (10) | 0.0111 (9) | -0.0091 (10) |
| C22 | 0.0709 (15) | 0.0729 (15) | 0.0377 (11) | -0.0436 (13) | 0.0129 (10) | -0.0146 (11) |
| C23 | 0.0815 (16) | 0.0805 (16) | 0.0432 (12) | -0.0570 (14) | 0.0122 (11) | -0.0205 (11) |
| C24 | 0.0656 (14) | 0.0626 (13) | 0.0424 (11) | -0.0457 (12) | 0.0096 (10) | -0.0145 (10) |
| C25 | 0.0356 (10) | 0.0374 (10) | 0.0394 (10) | -0.0199 (8) | 0.0033 (8) | -0.0091 (8) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-------------|-----------|
| N1—C1 | 1.339 (2) | C11—C12 | 1.385 (3) |
| N1—C5 | 1.347 (2) | C11—C16 | 1.391 (3) |
| N2—C10 | 1.334 (2) | C12—C13 | 1.384 (3) |
| N2—C6 | 1.341 (2) | C12—H12 | 0.9300 |
| N3—C17 | 1.144 (2) | C13—C14 | 1.378 (3) |
| N4—C19 | 1.354 (2) | C13—H13 | 0.9300 |
| N4—C20 | 1.377 (2) | C14—C15 | 1.369 (3) |
| N4—H4 | 0.8600 | C14—H14 | 0.9300 |
| C1—C2 | 1.381 (2) | C15—C16 | 1.384 (3) |
| C1—C6 | 1.490 (2) | C15—H15 | 0.9300 |
| C2—C3 | 1.385 (2) | C16—H16 | 0.9300 |
| C2—H2 | 0.9300 | C18—C19 | 1.375 (2) |
| C3—C4 | 1.404 (2) | C18—C25 | 1.451 (2) |
| C3—C11 | 1.484 (2) | C19—H19 | 0.9300 |
| C4—C5 | 1.420 (2) | C20—C21 | 1.384 (3) |
| C4—C17 | 1.432 (2) | C20—C25 | 1.405 (2) |
| C5—C18 | 1.465 (2) | C21—C22 | 1.372 (3) |
| C6—C7 | 1.388 (2) | C21—H21 | 0.9300 |
| C7—C8 | 1.377 (3) | C22—C23 | 1.389 (3) |
| C7—H7 | 0.9300 | C22—H22 | 0.9300 |
| C8—C9 | 1.368 (3) | C23—C24 | 1.376 (3) |
| C8—H8 | 0.9300 | C23—H23 | 0.9300 |
| C9—C10 | 1.371 (3) | C24—C25 | 1.398 (3) |
| C9—H9 | 0.9300 | C24—H24 | 0.9300 |
| C10—H10 | 0.9300 | | |
| C1—N1—C5 | 119.18 (15) | C13—C12—H12 | 119.7 |
| C10—N2—C6 | 117.30 (17) | C11—C12—H12 | 119.7 |
| C19—N4—C20 | 109.41 (15) | C14—C13—C12 | 120.1 (2) |
| C19—N4—H4 | 125.3 | C14—C13—H13 | 119.9 |

supplementary materials

| | | | |
|---------------|--------------|-----------------|--------------|
| C20—N4—H4 | 125.3 | C12—C13—H13 | 119.9 |
| N1—C1—C2 | 123.09 (15) | C15—C14—C13 | 119.85 (19) |
| N1—C1—C6 | 116.67 (15) | C15—C14—H14 | 120.1 |
| C2—C1—C6 | 120.24 (16) | C13—C14—H14 | 120.1 |
| C1—C2—C3 | 119.94 (16) | C14—C15—C16 | 120.5 (2) |
| C1—C2—H2 | 120.0 | C14—C15—H15 | 119.8 |
| C3—C2—H2 | 120.0 | C16—C15—H15 | 119.8 |
| C2—C3—C4 | 117.25 (16) | C15—C16—C11 | 120.2 (2) |
| C2—C3—C11 | 119.47 (16) | C15—C16—H16 | 119.9 |
| C4—C3—C11 | 123.25 (15) | C11—C16—H16 | 119.9 |
| C3—C4—C5 | 120.12 (15) | N3—C17—C4 | 179.5 (2) |
| C3—C4—C17 | 118.82 (15) | C19—C18—C25 | 105.64 (15) |
| C5—C4—C17 | 121.05 (16) | C19—C18—C5 | 128.12 (16) |
| N1—C5—C4 | 120.37 (15) | C25—C18—C5 | 126.18 (15) |
| N1—C5—C18 | 115.71 (15) | N4—C19—C18 | 110.50 (16) |
| C4—C5—C18 | 123.91 (15) | N4—C19—H19 | 124.7 |
| N2—C6—C7 | 122.15 (16) | C18—C19—H19 | 124.7 |
| N2—C6—C1 | 115.83 (15) | N4—C20—C21 | 129.29 (17) |
| C7—C6—C1 | 122.01 (16) | N4—C20—C25 | 107.56 (15) |
| C8—C7—C6 | 118.82 (18) | C21—C20—C25 | 123.15 (17) |
| C8—C7—H7 | 120.6 | C22—C21—C20 | 117.15 (18) |
| C6—C7—H7 | 120.6 | C22—C21—H21 | 121.4 |
| C9—C8—C7 | 119.50 (19) | C20—C21—H21 | 121.4 |
| C9—C8—H8 | 120.2 | C21—C22—C23 | 121.23 (19) |
| C7—C8—H8 | 120.2 | C21—C22—H22 | 119.4 |
| C8—C9—C10 | 118.03 (18) | C23—C22—H22 | 119.4 |
| C8—C9—H9 | 121.0 | C24—C23—C22 | 121.5 (2) |
| C10—C9—H9 | 121.0 | C24—C23—H23 | 119.2 |
| N2—C10—C9 | 124.20 (19) | C22—C23—H23 | 119.2 |
| N2—C10—H10 | 117.9 | C23—C24—C25 | 118.88 (18) |
| C9—C10—H10 | 117.9 | C23—C24—H24 | 120.6 |
| C12—C11—C16 | 118.78 (17) | C25—C24—H24 | 120.6 |
| C12—C11—C3 | 119.99 (16) | C24—C25—C20 | 118.06 (17) |
| C16—C11—C3 | 121.11 (17) | C24—C25—C18 | 135.01 (17) |
| C13—C12—C11 | 120.51 (19) | C20—C25—C18 | 106.88 (15) |
| C5—N1—C1—C2 | 0.0 (3) | C16—C11—C12—C13 | -0.3 (3) |
| C5—N1—C1—C6 | -179.68 (15) | C3—C11—C12—C13 | -176.21 (17) |
| N1—C1—C2—C3 | 2.0 (3) | C11—C12—C13—C14 | 1.0 (3) |
| C6—C1—C2—C3 | -178.34 (16) | C12—C13—C14—C15 | -0.7 (3) |
| C1—C2—C3—C4 | -2.2 (3) | C13—C14—C15—C16 | -0.1 (3) |
| C1—C2—C3—C11 | 175.87 (17) | C14—C15—C16—C11 | 0.8 (3) |
| C2—C3—C4—C5 | 0.7 (3) | C12—C11—C16—C15 | -0.5 (3) |
| C11—C3—C4—C5 | -177.30 (16) | C3—C11—C16—C15 | 175.28 (17) |
| C2—C3—C4—C17 | -178.14 (16) | N1—C5—C18—C19 | -157.15 (17) |
| C11—C3—C4—C17 | 3.8 (3) | C4—C5—C18—C19 | 24.1 (3) |
| C1—N1—C5—C4 | -1.6 (2) | N1—C5—C18—C25 | 19.5 (3) |
| C1—N1—C5—C18 | 179.67 (15) | C4—C5—C18—C25 | -159.21 (17) |
| C3—C4—C5—N1 | 1.2 (3) | C20—N4—C19—C18 | 0.8 (2) |
| C17—C4—C5—N1 | -179.95 (17) | C25—C18—C19—N4 | -0.5 (2) |

| | | | |
|---------------|--------------|-----------------|--------------|
| C3—C4—C5—C18 | 179.84 (16) | C5—C18—C19—N4 | 176.68 (17) |
| C17—C4—C5—C18 | -1.3 (3) | C19—N4—C20—C21 | 178.41 (19) |
| C10—N2—C6—C7 | 0.0 (3) | C19—N4—C20—C25 | -0.8 (2) |
| C10—N2—C6—C1 | -179.08 (16) | N4—C20—C21—C22 | -178.64 (19) |
| N1—C1—C6—N2 | -179.21 (15) | C25—C20—C21—C22 | 0.5 (3) |
| C2—C1—C6—N2 | 1.1 (3) | C20—C21—C22—C23 | 0.1 (3) |
| N1—C1—C6—C7 | 1.7 (3) | C21—C22—C23—C24 | -0.3 (4) |
| C2—C1—C6—C7 | -178.01 (17) | C22—C23—C24—C25 | 0.0 (4) |
| N2—C6—C7—C8 | 0.0 (3) | C23—C24—C25—C20 | 0.6 (3) |
| C1—C6—C7—C8 | 179.07 (17) | C23—C24—C25—C18 | 177.8 (2) |
| C6—C7—C8—C9 | -0.3 (3) | N4—C20—C25—C24 | 178.46 (16) |
| C7—C8—C9—C10 | 0.4 (3) | C21—C20—C25—C24 | -0.8 (3) |
| C6—N2—C10—C9 | 0.2 (3) | N4—C20—C25—C18 | 0.5 (2) |
| C8—C9—C10—N2 | -0.4 (3) | C21—C20—C25—C18 | -178.79 (17) |
| C2—C3—C11—C12 | 54.4 (2) | C19—C18—C25—C24 | -177.5 (2) |
| C4—C3—C11—C12 | -127.63 (19) | C5—C18—C25—C24 | 5.3 (3) |
| C2—C3—C11—C16 | -121.39 (19) | C19—C18—C25—C20 | 0.0 (2) |
| C4—C3—C11—C16 | 56.6 (3) | C5—C18—C25—C20 | -177.27 (16) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| N4—H4 \cdots N3 ⁱ | 0.86 | 2.23 | 3.066 (2) | 164 |
| C12—H12 \cdots Cg5 ⁱⁱ | 0.93 | 2.84 | 3.649 (3) | 146 |
| C23—H23 \cdots Cg4 ⁱⁱⁱ | 0.93 | 2.91 | 3.711 (3) | 145 |

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

Fig. 1

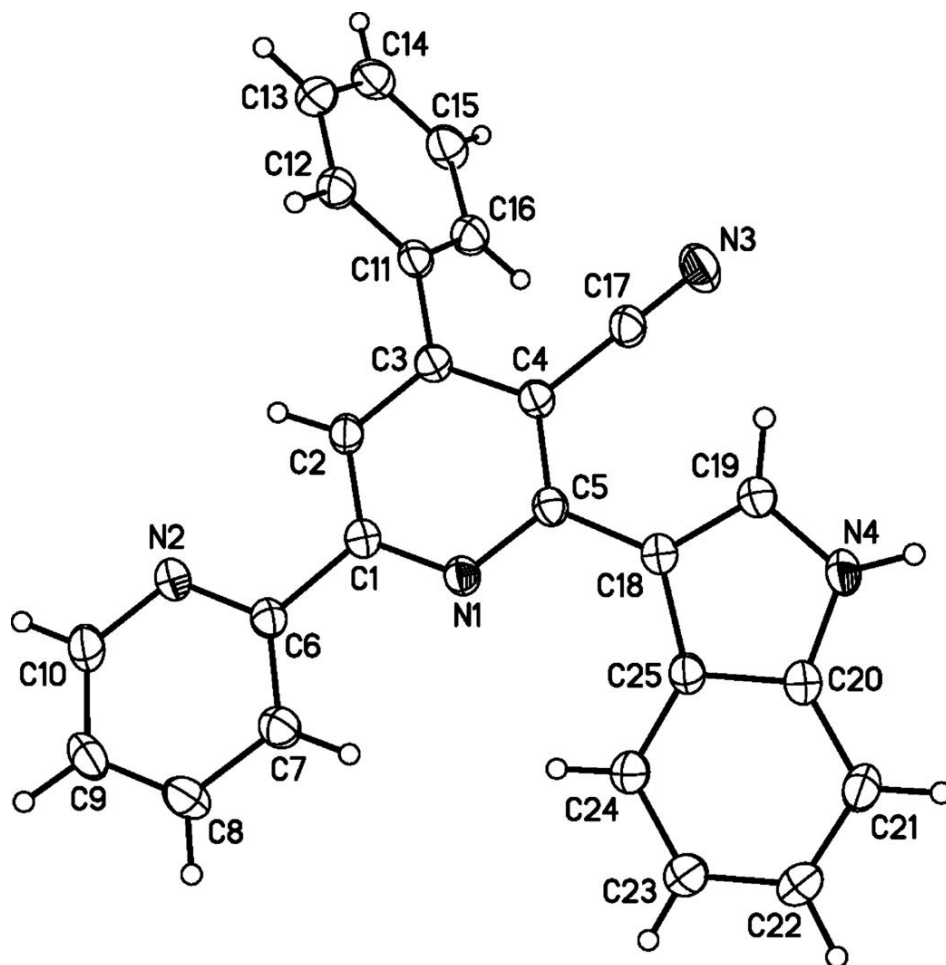


Fig. 2

