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1-Methyl-4-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine

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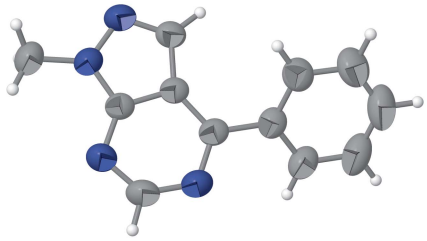
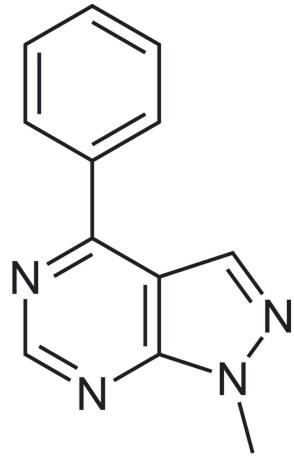
Structural data: full structural data are available from iucrdata.iucr.org

In the crystal, molecules of the title compound, $C_{12}H_{10}N_4$, stack in a head-to-tail manner along the *b* direction through π–π stacking interactions between both portions of the pyrazolopyrimidine ring system.

3D view



Chemical scheme



Structure description

During the last decade, considerable interest has been paid to the chemistry of pyrazolo[3,4-*d*]pyrimidines. This is undoubtedly due to a broad variety of biological activities of pyrazolo[3,4-*d*]pyrimidine derivatives, such as their action as antitubercular (Trivedi *et al.*, 2012), antibacterial (Rostamizadeh *et al.*, 2013) and antitumor agents (Intori *et al.*, 2015). The present work is a continuation of the investigation of pyrazolo[3,4-*d*]pyrimidine derivatives reported by our team (Alsubari *et al.*, 2011).

The fused heterobicyclic ring system (Fig. 1) shows maximum deviations of 0.0257 (1) and −0.0270 (1) Å from the least-squares plane through the nine atoms (r.m.s. deviation = 0.0209 Å). The dihedral angle between this plane and that of the phenyl ring is 33.43 (4)°. In the crystal, molecules stack along the *b*-axis direction in a head-to-tail fashion through π–π stacking interactions of the bicyclic core (Fig. 2). The dihedral angle between the five- and six-membered rings in each interaction is 2.30 (7)°, while the centroid–centroid distances alternate between 3.509 (1) and 3.645 (1) Å along the stack. In addition, there are C8—H8···π(ring) (ring = C7–C12, H···centroid = 2.93 Å and C—H···centroid = 148°) interactions on the outside of the stacks which are responsible in part for the orientation of the phenyl ring relative to the bicyclic core (Fig. 3).

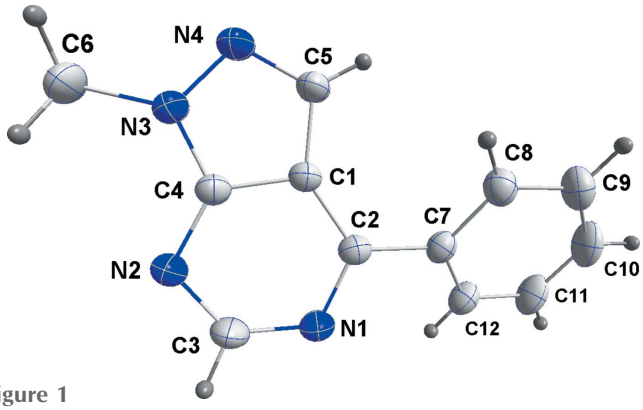


Figure 1
The title molecule, with the atom-labelling scheme and 25% probability ellipsoids.

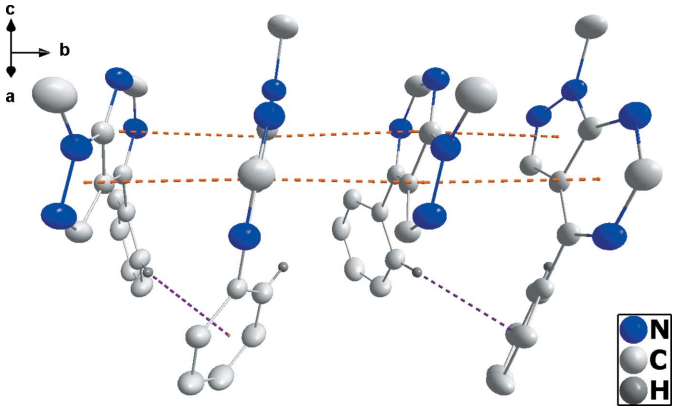


Figure 2
Detail of the π–π stacking (orange dotted lines) and the C—H$\cdots\pi$(ring) (purple dotted lines) interactions forming stacks along the *b* direction. H atoms not involved in the interactions have been omitted for clarity.

Synthesis and crystallization

To a microwave vial was added 1-methyl-4-chloro-1*H*-pyrazolo[3,4-*d*]pyrimidine (50 mg, 0.3 mmol), phenylboronic acid (40.23 mg, 0.33 mmol), K_2CO_3 (124.38 mg, 0.9 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) or $PdCl_2$(dppf) (22 mg, 0.03 mmol), THF (3 ml) and H_2O (10 µl). The reaction mixture was heated with stirring in a microwave reactor at 443 K for 10 min. The crude reaction mixture was passed through a small silica-gel plug, eluting with EtOAc, and the crude material was purified by silica-gel chromatography (0 to 10% EtOAc gradient in hexanes). The title compound was recrystallized from ethanol, at room temperature, giving colourless crystals (yield 80%; m.p. 388–390 K).

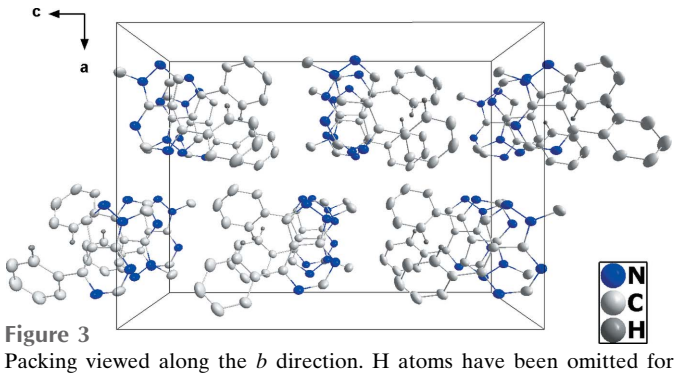


Figure 3
Packing viewed along the *b* direction. H atoms have been omitted for clarity.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}N_4$
M_r	210.24
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, *b*, *c* (Å)	14.6205 (10), 7.1497 (5), 20.3532 (15)
V (Å^3)	2127.6 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.29 × 0.20 × 0.16
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.86, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18616, 2639, 1725
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.139, 1.06
No. of reflections	2639
No. of parameters	147
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.14

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal and refinement data are presented in Table 1.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171238 [https://doi.org/10.1107/S241431461701238X]

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1-Methyl-4-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine

Crystal data

$C_{12}H_{10}N_4$
M_r = 210.24
Orthorhombic, *Pbca*
a = 14.6205 (10) Å
b = 7.1497 (5) Å
c = 20.3532 (15) Å
V = 2127.6 (3) Å^3
Z = 8
F(000) = 880
D_x = 1.313 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 4337 reflections
θ = 2.4–24.3°
μ = 0.08 mm^{-1}
T = 296 K
Column, colourless
0.29 × 0.20 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.86, T_{max} = 0.99
18616 measured reflections
2639 independent reflections
1725 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 28.3°, θ_{min} = 2.0°
h = −19→19
k = −9→9
l = −27→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.139
S = 1.06
2639 reflections
147 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.1279P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0053 (13)

Special details

Experimental. The diffraction data were collected in three sets of 363 frames (0.5° width in ω) at φ = 0, 120 and 240°. 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 $F^2 > 2\text{sigma}(F^2)$ 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 = 0.93 - 0.97 Å). All were included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.40768 (7)	0.80901 (19)	0.41811 (6)	0.0650 (4)
N2	0.31476 (8)	0.87710 (17)	0.51276 (6)	0.0621 (3)
N3	0.15455 (7)	0.85635 (16)	0.49050 (6)	0.0582 (3)
N4	0.09970 (8)	0.8116 (2)	0.43846 (6)	0.0670 (4)
C1	0.24717 (8)	0.80131 (17)	0.40626 (6)	0.0475 (3)
C2	0.33514 (9)	0.78419 (17)	0.37892 (7)	0.0505 (3)
C3	0.39276 (10)	0.8529 (2)	0.48141 (8)	0.0704 (4)
H3	0.4451	0.8685	0.5068	0.084*
C4	0.24321 (8)	0.84873 (17)	0.47294 (7)	0.0493 (3)
C5	0.15443 (9)	0.77896 (19)	0.38832 (7)	0.0574 (4)
H5	0.1346	0.7455	0.3465	0.069*
C6	0.11689 (12)	0.8901 (3)	0.55525 (7)	0.0776 (5)
H6A	0.0636	0.9678	0.5515	0.116*
H6B	0.1617	0.9519	0.5820	0.116*
H6C	0.1004	0.7731	0.5751	0.116*
C7	0.35299 (10)	0.73913 (17)	0.30951 (6)	0.0546 (4)
C8	0.29471 (11)	0.7977 (2)	0.26000 (7)	0.0671 (4)
H8	0.2427	0.8664	0.2705	0.081*
C9	0.31320 (15)	0.7549 (3)	0.19521 (8)	0.0852 (6)
H9	0.2741	0.7961	0.1622	0.102*
C10	0.38869 (16)	0.6522 (3)	0.17949 (9)	0.0936 (6)
H10	0.4003	0.6219	0.1358	0.112*
C11	0.44746 (14)	0.5936 (2)	0.22764 (9)	0.0861 (5)
H11	0.4990	0.5242	0.2166	0.103*
C12	0.43046 (10)	0.6371 (2)	0.29249 (7)	0.0665 (4)
H12	0.4709	0.5981	0.3250	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0461 (7)	0.0821 (9)	0.0667 (7)	0.0000 (5)	−0.0014 (5)	−0.0019 (6)
N2	0.0523 (7)	0.0758 (8)	0.0583 (7)	−0.0049 (5)	−0.0055 (5)	−0.0033 (6)

N3	0.0458 (6)	0.0708 (7)	0.0580 (7)	−0.0006 (5)	0.0031 (5)	−0.0006 (5)
N4	0.0459 (7)	0.0877 (9)	0.0675 (8)	−0.0034 (6)	−0.0042 (5)	0.0008 (6)
C1	0.0454 (7)	0.0433 (6)	0.0538 (7)	−0.0003 (5)	−0.0030 (5)	0.0033 (5)
C2	0.0474 (7)	0.0452 (7)	0.0588 (7)	0.0016 (5)	−0.0006 (6)	0.0041 (5)
C3	0.0483 (8)	0.0932 (11)	0.0697 (9)	−0.0054 (7)	−0.0108 (7)	−0.0041 (8)
C4	0.0459 (7)	0.0468 (7)	0.0553 (7)	−0.0011 (5)	−0.0017 (6)	0.0032 (5)
C5	0.0494 (7)	0.0650 (9)	0.0578 (8)	−0.0032 (6)	−0.0061 (6)	0.0011 (6)
C6	0.0628 (9)	0.1040 (13)	0.0661 (10)	0.0007 (9)	0.0138 (7)	−0.0065 (8)
C7	0.0588 (8)	0.0477 (7)	0.0573 (8)	−0.0024 (5)	0.0073 (6)	0.0046 (6)
C8	0.0747 (10)	0.0648 (9)	0.0619 (9)	0.0045 (7)	0.0022 (7)	0.0096 (7)
C9	0.1075 (15)	0.0887 (13)	0.0592 (10)	−0.0010 (10)	0.0010 (9)	0.0129 (9)
C10	0.1308 (17)	0.0880 (12)	0.0620 (10)	−0.0013 (12)	0.0268 (11)	0.0010 (9)
C11	0.1003 (13)	0.0744 (11)	0.0835 (11)	0.0083 (9)	0.0372 (10)	0.0005 (9)
C12	0.0638 (9)	0.0646 (9)	0.0712 (10)	0.0051 (7)	0.0152 (7)	0.0054 (7)

Geometric parameters (Å, º)

N1—C2	1.3388 (17)	C6—H6A	0.9600
N1—C3	1.344 (2)	C6—H6B	0.9600
N2—C3	1.3181 (18)	C6—H6C	0.9600
N2—C4	1.3387 (17)	C7—C8	1.385 (2)
N3—C4	1.3458 (16)	C7—C12	1.391 (2)
N3—N4	1.3665 (16)	C8—C9	1.380 (2)
N3—C6	1.4486 (18)	C8—H8	0.9300
N4—C5	1.3176 (18)	C9—C10	1.363 (3)
C1—C4	1.4001 (19)	C9—H9	0.9300
C1—C2	1.4068 (18)	C10—C11	1.369 (3)
C1—C5	1.4132 (18)	C10—H10	0.9300
C2—C7	1.4722 (19)	C11—C12	1.379 (2)
C3—H3	0.9300	C11—H11	0.9300
C5—H5	0.9300	C12—H12	0.9300
C2—N1—C3	118.27 (11)	H6A—C6—H6B	109.5
C3—N2—C4	111.29 (12)	N3—C6—H6C	109.5
C4—N3—N4	110.49 (11)	H6A—C6—H6C	109.5
C4—N3—C6	127.91 (12)	H6B—C6—H6C	109.5
N4—N3—C6	121.42 (12)	C8—C7—C12	118.58 (13)
C5—N4—N3	106.58 (11)	C8—C7—C2	121.55 (13)
C4—C1—C2	116.25 (11)	C12—C7—C2	119.87 (13)
C4—C1—C5	103.78 (11)	C9—C8—C7	120.51 (16)
C2—C1—C5	139.92 (13)	C9—C8—H8	119.7
N1—C2—C1	118.49 (12)	C7—C8—H8	119.7
N1—C2—C7	117.41 (12)	C10—C9—C8	120.14 (18)
C1—C2—C7	124.10 (12)	C10—C9—H9	119.9
N2—C3—N1	129.43 (13)	C8—C9—H9	119.9
N2—C3—H3	115.3	C9—C10—C11	120.32 (17)
N1—C3—H3	115.3	C9—C10—H10	119.8
N2—C4—N3	125.86 (12)	C11—C10—H10	119.8

N2—C4—C1	126.24 (12)	C10—C11—C12	120.20 (17)
N3—C4—C1	107.88 (11)	C10—C11—H11	119.9
N4—C5—C1	111.26 (12)	C12—C11—H11	119.9
N4—C5—H5	124.4	C11—C12—C7	120.24 (16)
C1—C5—H5	124.4	C11—C12—H12	119.9
N3—C6—H6A	109.5	C7—C12—H12	119.9
N3—C6—H6B	109.5		

C4—N3—N4—C5	−0.93 (16)	C2—C1—C4—N3	−179.22 (11)
C6—N3—N4—C5	−176.30 (14)	C5—C1—C4—N3	−1.27 (13)
C3—N1—C2—C1	−1.3 (2)	N3—N4—C5—C1	0.09 (16)
C3—N1—C2—C7	179.06 (13)	C4—C1—C5—N4	0.73 (15)
C4—C1—C2—N1	1.71 (18)	C2—C1—C5—N4	177.88 (15)
C5—C1—C2—N1	−175.20 (15)	N1—C2—C7—C8	−147.81 (14)
C4—C1—C2—C7	−178.72 (11)	C1—C2—C7—C8	32.62 (19)
C5—C1—C2—C7	4.4 (2)	N1—C2—C7—C12	31.51 (18)
C4—N2—C3—N1	1.1 (2)	C1—C2—C7—C12	−148.06 (13)
C2—N1—C3—N2	−0.2 (3)	C12—C7—C8—C9	0.2 (2)
C3—N2—C4—N3	177.61 (13)	C2—C7—C8—C9	179.54 (14)
C3—N2—C4—C1	−0.6 (2)	C7—C8—C9—C10	0.8 (3)
N4—N3—C4—N2	−177.11 (13)	C8—C9—C10—C11	−1.1 (3)
C6—N3—C4—N2	−2.1 (2)	C9—C10—C11—C12	0.4 (3)
N4—N3—C4—C1	1.41 (14)	C10—C11—C12—C7	0.7 (3)
C6—N3—C4—C1	176.39 (14)	C8—C7—C12—C11	−1.0 (2)
C2—C1—C4—N2	−0.72 (19)	C2—C7—C12—C11	179.70 (14)
C5—C1—C4—N2	177.24 (13)		