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π-Stacked chains in 3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-*b*,4′,3′-e]pyridine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.116
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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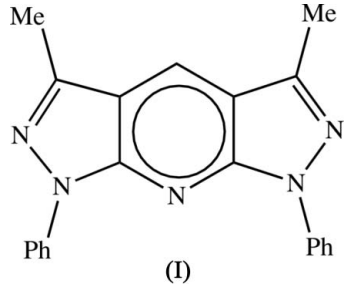
The title compound, $C_{21}H_{17}N_5$, was prepared using a microwave-induced condensation reaction between 5-amino-3-methyl-1-phenylpyrazole and formaldehyde. The molecules lie across twofold rotation axes in space group *C*2/*c* and are into chains by a π–π stacking interaction.

Comment

The title compound, (I), has been prepared using microwave irradiation in a solvent-free system and this provides an attractive alternative to the method recently reported (Abramos *et al.*, 2001), not only in eliminating the solvent, but also in reducing the reaction time from hours to minutes while considerably improving the yield, from 37% to 65%. The simplicity of the present procedure and its selectivity also contrast with the previous method which required two distinct azoles, an aminopyrazole and 5-chloro-4-formylpyrazole, to generate the product.



(I)

The molecules of the title compound (I) (Fig. 1) lie across twofold rotation axes in space group *C*2/*c*: the reference molecule was selected as that lying across the axis along $(\frac{1}{2}, y, \frac{1}{4})$.

The bond distances (Table 1) within the pyridine ring are consistent with aromatic delocalization, but there is very strong bond fixation within the pyrazole rings (see scheme). The dihedral angle between the phenyl ring and the adjacent pyrazole ring is 27.4 (2)°.

A single π···π stacking interaction links the molecules into chains. The reference molecule, which lies across $(\frac{1}{2}, y, \frac{1}{4})$, is related by inversion to the adjacent molecules lying across the axes along $(\frac{1}{2}, y, -\frac{1}{4})$ and $(\frac{1}{2}, y, \frac{3}{4})$; the heterocyclic systems in these three molecules are thus parallel with an interplanar spacing between adjacent rings of 3.363 (2) Å. The ring centroid separations between the pyridine ring of the reference molecule and the pyridine and pyrazole rings of an adjacent molecule are 3.772 (2) Å and 3.489 (2) Å, respectively. Propagation of this interaction by inversion thus generates a chain of π-stacked molecules along the [001]

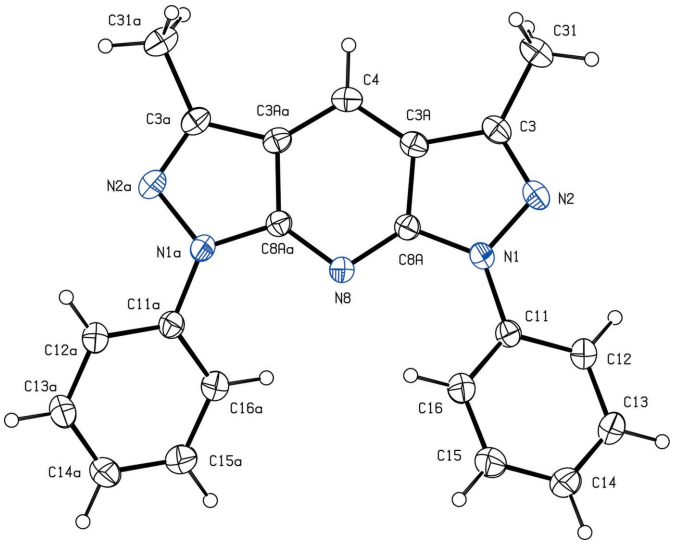


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level, and the atoms marked 'a' are at the symmetry position $(1-x, y, \frac{1}{2}-z)$.

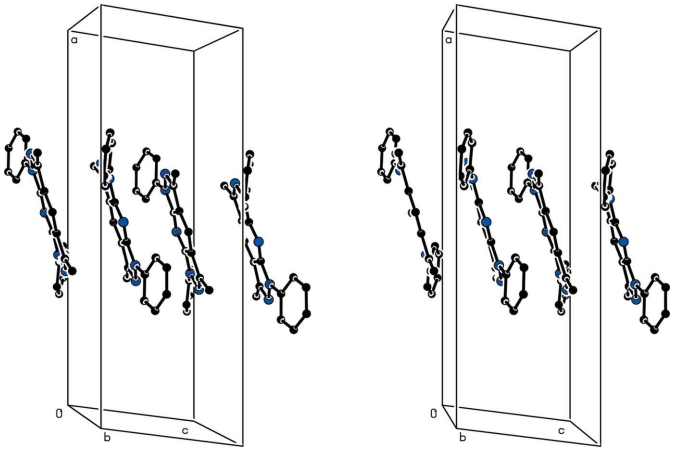


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a π-stacked chain along [001]. For the sake of clarity, H atoms have been omitted.

direction (Fig. 2). Two chains of this type, related to one another by the *C*-centring operation, pass through each unit cell, but there are no direction-specific interactions between adjacent chains: in particular C—H···N and C—H···π hydrogen bonds are absent from the structure of (I).

Experimental

Equimolar amounts of 5-amino-3-methyl-1-phenylpyrazole (1.0 mmol) and formaldehyde (1.0 mmol as 37% aqueous solution) were placed in open Pyrex vessels and irradiated in a domestic microwave oven for 1.5 min at 600 W. The reaction mixture was then extracted with ethanol. After the solvent had been removed under reduced pressure, the product was recrystallized from dimethylformamide to give crystals that were suitable for single-crystal X-ray diffraction. Yield 65%; m. p. 485–486 K, literature value 490–491 K (Abramos *et al.*, 2001),

Crystal data

$C_{21}H_{17}N_5$
$M_r = 339.40$
Monoclinic, $C2/c$
$a = 21.2976\ (4)$ Å
$b = 10.9267\ (3)$ Å
$c = 7.4201\ (2)$ Å
$\beta = 98.108\ (2)^\circ$
$V = 1709.49\ (7)$ Å^3
$Z = 4$
$D_x = 1.319$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1957 reflections
$\theta = 3.4$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 293\ (2)$ K
Lath, colourless
0.60 × 0.18 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.925$, $T_{max} = 0.990$
14999 measured reflections
1957 independent reflections
1703 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5^\circ$
$h = -27 \rightarrow 27$
$k = -14 \rightarrow 13$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 1.05$
1957 reflections
120 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.6017P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—N2	1.3900 (12)	N1—C8*A*	1.3686 (13)
N2—C3	1.3111 (15)	C3*A*—C8*A*	1.4195 (15)
C3—C3*A*	1.4320 (16)	N8—C8*A*	1.3375 (12)
C3*A*—C4	1.3860 (14)	N8—C8*A*	1.3375 (12)

All H atoms were located in difference maps, and then treated as riding atoms with C—H distances 0.93 Å (aromatic) or 0.96 Å (methyl), and with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl group.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2004) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, UK. JC and JT thank the Consejería de Innovación, Ciencia *y* Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JT also thanks the Universidad de Jaén for a research scholarship supporting a short stay at the EPSRC X-ray Crystallographic Service, University of Southampton, UK. JP thanks COLCIENCIAS and UNIVALLE (Universidad del Valle, Colombia) for financial support.

References

Abramos, M. A., Ceulemans, E., Jackers, C., der Auweraer, M. & Dehaen, W. (2001). *Tetrahedron*, **57**, 9123–9129.

Burla, M. C., Caliandro, R., Camalli, M., Carrazzini, B., Cascarano, G. L.,De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10, Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

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$Z = 4$
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$D_x = 1.319$ Mg m^{-3}
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Cell parameters from 1957 reflections
$\theta = 3.4$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Lath, colourless
0.60 × 0.18 × 0.12 mm

Data collection

Bruker-Nonius KappaCCD diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.925$, $T_{max} = 0.990$
14999 measured reflections
1957 independent reflections
1703 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -27\rightarrow27$
$k = -14\rightarrow13$
$l = -8\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 1.05$
1957 reflections
120 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
$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.6017P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.39729 (4)	0.63736 (8)	0.34529 (13)	0.0370 (2)

C11	0.37789 (5)	0.75836 (10)	0.37869 (14)	0.0369 (3)
C12	0.31364 (6)	0.78442 (12)	0.36680 (18)	0.0470 (3)
C13	0.29433 (7)	0.90036 (13)	0.4097 (2)	0.0571 (4)
C14	0.33815 (8)	0.99045 (14)	0.4626 (2)	0.0617 (4)
C15	0.40171 (8)	0.96455 (13)	0.4712 (2)	0.0613 (4)
C16	0.42225 (6)	0.84907 (12)	0.4299 (2)	0.0495 (3)
N2	0.35836 (5)	0.54010 (9)	0.37799 (14)	0.0411 (3)
C3	0.38888 (6)	0.43936 (11)	0.34922 (15)	0.0390 (3)
C31	0.36138 (7)	0.31626 (12)	0.37483 (18)	0.0512 (3)
C3A	0.44940 (5)	0.46605 (9)	0.29545 (14)	0.0354 (3)
C4	0.5000	0.39861 (14)	0.2500	0.0374 (4)
N8	0.5000	0.66527 (11)	0.2500	0.0346 (3)
C8A	0.45281 (5)	0.59578 (10)	0.29447 (14)	0.0331 (3)
H12	0.2837	0.7242	0.3301	0.056*
H13	0.2513	0.9176	0.4028	0.069*
H14	0.3249	1.0681	0.4923	0.074*
H15	0.4314	1.0257	0.5052	0.074*
H16	0.4654	0.8326	0.4366	0.059*
H31A	0.3220	0.3253	0.4222	0.077*
H31B	0.3904	0.2696	0.4588	0.077*
H31C	0.3541	0.2745	0.2599	0.077*
H4	0.5000	0.3135	0.2500	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0323 (5)	0.0356 (5)	0.0439 (5)	−0.0034 (4)	0.0084 (4)	0.0034 (4)
C11	0.0380 (6)	0.0375 (6)	0.0368 (5)	0.0002 (4)	0.0111 (4)	0.0030 (4)
C12	0.0375 (6)	0.0473 (7)	0.0581 (7)	0.0005 (5)	0.0132 (5)	0.0025 (6)
C13	0.0460 (7)	0.0534 (8)	0.0768 (9)	0.0099 (6)	0.0252 (6)	0.0048 (7)
C14	0.0665 (9)	0.0442 (7)	0.0815 (10)	0.0052 (7)	0.0348 (8)	−0.0039 (7)
C15	0.0593 (9)	0.0443 (8)	0.0847 (11)	−0.0094 (6)	0.0249 (8)	−0.0126 (7)
C16	0.0407 (6)	0.0452 (7)	0.0643 (8)	−0.0029 (5)	0.0135 (6)	−0.0053 (6)
N2	0.0375 (5)	0.0417 (6)	0.0445 (6)	−0.0093 (4)	0.0068 (4)	0.0035 (4)
C3	0.0401 (6)	0.0393 (6)	0.0361 (6)	−0.0083 (5)	0.0006 (4)	0.0030 (4)
C31	0.0571 (8)	0.0440 (7)	0.0523 (7)	−0.0161 (6)	0.0071 (6)	0.0012 (5)
C3A	0.0374 (6)	0.0340 (6)	0.0333 (5)	−0.0039 (4)	−0.0005 (4)	0.0014 (4)
C4	0.0442 (8)	0.0300 (7)	0.0359 (7)	0.000	−0.0019 (6)	0.000
N8	0.0310 (6)	0.0333 (6)	0.0397 (7)	0.000	0.0059 (5)	0.000
C8A	0.0314 (5)	0.0335 (5)	0.0335 (5)	−0.0006 (4)	0.0015 (4)	0.0015 (4)

Geometric parameters (Å, º)

N1—N2	1.3900 (12)	C13—H13	0.93
N2—C3	1.3111 (15)	C14—C15	1.376 (2)
C3—C3A	1.4320 (16)	C14—H14	0.93
C3A—C4	1.3860 (14)	C15—C16	1.3838 (18)
N1—C8A	1.3686 (13)	C15—H15	0.93

C3A—C8A	1.4195 (15)	C16—H16	0.93
N8—C8A	1.3375 (12)	C3—C31	1.4899 (16)
N1—C11	1.4174 (14)	C31—H31A	0.96
C11—C16	1.3850 (16)	C31—H31B	0.96
C11—C12	1.3883 (16)	C31—H31C	0.96
C12—C13	1.3829 (19)	C4—H4	0.93
C12—H12	0.93	N8—C8A	1.3375 (12)
C13—C14	1.375 (2)		

C8A—N1—N2	110.74 (9)	C3—N2—N1	106.97 (10)
C8A—N1—C11	129.96 (9)	N2—C3—C3A	111.14 (10)
N2—N1—C11	119.14 (9)	N2—C3—C31	121.63 (11)
C16—C11—C12	119.91 (11)	C3A—C3—C31	127.22 (11)
C16—C11—N1	120.75 (10)	C3—C31—H31A	109.5
C12—C11—N1	119.28 (10)	C3—C31—H31B	109.5
C13—C12—C11	119.72 (12)	H31A—C31—H31B	109.5
C13—C12—H12	120.1	C3—C31—H31C	109.5
C11—C12—H12	120.1	H31A—C31—H31C	109.5
C14—C13—C12	120.65 (13)	H31B—C31—H31C	109.5
C14—C13—H13	119.7	C4—C3A—C8A	119.18 (10)
C12—C13—H13	119.7	C4—C3A—C3	136.13 (11)
C13—C14—C15	119.32 (13)	C8A—C3A—C3	104.69 (10)
C13—C14—H14	120.3	C3A^{i}—C4—C3A	115.75 (14)
C15—C14—H14	120.3	C3A^{i}—C4—H4	122.1
C14—C15—C16	121.13 (14)	C3A—C4—H4	122.1
C14—C15—H15	119.4	C8A^{i}—N8—C8A	110.82 (13)
C16—C15—H15	119.4	N8—C8A—N1	126.02 (10)
C15—C16—C11	119.25 (12)	N8—C8A—C3A	127.52 (10)
C15—C16—H16	120.4	N1—C8A—C3A	106.45 (9)
C11—C16—H16	120.4		

C8A—N1—C11—C16	−24.88 (18)	N2—C3—C3A—C4	179.68 (10)
N2—N1—C11—C16	150.10 (11)	C31—C3—C3A—C4	0.6 (2)
C8A—N1—C11—C12	157.75 (11)	N2—C3—C3A—C8A	0.06 (12)
N2—N1—C11—C12	−27.28 (15)	C31—C3—C3A—C8A	−179.04 (11)
C16—C11—C12—C13	−1.26 (19)	C8A—C3A—C4—C3A^{i}	−0.65 (6)
N1—C11—C12—C13	176.14 (12)	C3—C3A—C4—C3A^{i}	179.77 (14)
C11—C12—C13—C14	0.6 (2)	C8A^{i}—N8—C8A—N1	−179.48 (12)
C12—C13—C14—C15	0.5 (2)	C8A^{i}—N8—C8A—C3A	−0.76 (7)
C13—C14—C15—C16	−0.9 (3)	N2—N1—C8A—N8	178.68 (8)
C14—C15—C16—C11	0.2 (2)	C11—N1—C8A—N8	−6.02 (17)
C12—C11—C16—C15	0.87 (19)	N2—N1—C8A—C3A	−0.26 (11)
N1—C11—C16—C15	−176.49 (12)	C11—N1—C8A—C3A	175.05 (10)
C8A—N1—N2—C3	0.30 (12)	C4—C3A—C8A—N8	1.51 (14)
C11—N1—N2—C3	−175.58 (9)	C3—C3A—C8A—N8	−178.79 (9)

N1—N2—C3—C3A	−0.21 (13)	C4—C3A—C8A—N1	−179.57 (8)
N1—N2—C3—C31	178.94 (10)	C3—C3A—C8A—N1	0.13 (11)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.