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5-Amino-1-(5-methyl-1-phenylpyrazol-4-ylcarbonyl)pyrazole-4-carbonitrile

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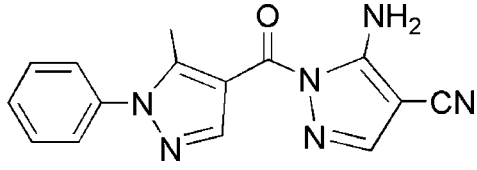
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.115; data-to-parameter ratio = 14.2.

In the molecule of the title compound, $C_{15}H_{12}N_6O$, the central pyrazole ring forms dihedral angles of 25.10 (7) and 40.22 (7)° with the outer pyrazole and phenyl rings, respectively. In the crystal structure, centrosymmetrically related molecules are linked into dimers by intermolecular N—H···N hydrogen bonds. The dimers interact along the b axis through intermolecular C—H···O hydrogen bonds to form chains. There is an intramolecular N—H···O hydrogen bond.

Related literature

For related literature, see: Chen *et al.* (2000); Elgemeie *et al.* (2002); Wen *et al.* (2006).



Experimental

Crystal data

$C_{15}H_{12}N_6O$
M_r = 292.31
Monoclinic, $P2_1/n$
a = 7.496 (2) Å
b = 12.345 (4) Å
c = 15.426 (5) Å
β = 102.052 (6)°
V = 1396.0 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.36 × 0.22 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.958, T_{max} = 0.983
7890 measured reflections
2852 independent reflections
1877 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.115
S = 1.00
2852 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O1	0.94	1.99	2.676 (2)	128
N5—H5B···N6^{i}	0.99	2.03	2.971 (2)	159
C5—H5···O1^{ii}	0.93	2.51	3.409 (3)	164

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2149).

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supplementary materials

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5-Amino-1-(5-methyl-1-phenylpyrazol-4-ylcarbonyl)pyrazole-4-carbonitrile

J.-C. Li, Y.-H. Feng, Q. Lin and D.-L. Zhang

Comment

Pyrazole and its derivatives possess a wide spectrum of biological activities, such as antibacterial, fungicidal, herbicidal and insecticidal activities (Chen *et al.*, 2000). In the course of our systematic studies aimed at the synthesis of new bioactive compounds, we synthesized the title compound and its structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The molecule consists of two planar five-membered pyrazole rings (maximum displacement 0.002 (2)° for atoms C10, C13 and C15) forming a dihedral angle 25.10 (7)°, which is close to the value of 28.96° observed in 5-amino-4-cyano-1-[(5-methyl-1-*tert*-butyl-4-pyrazolyl)carbonyl]-3-methylthio −1*H*-pyrazole (Wen *et al.*, 2006). The benzene ring forms a dihedral angle of 40.22 (7)° with the linked pyrazole ring. Bond distances and angles are as expected for this type of compound. The molecular conformation is stabilized by an intramolecular N—H···O hydrogen bonding interaction (Table 1). In the crystal structure, centrosymmetrically related molecules are linked into dimers by intermolecular N—H···N hydrogen bonds. The dimers interact through intermolecular N—H···N and C—H···O hydrogen bonds to form chains along the *b* axis (Fig. 2).

Experimental

To 10 ml anhydrous ethanol,a mixture of 1-phenyl-5-methyl-1*H*-4-pyrazolaldehyde (3 mmol, 0.65 g) and 2-cyano-3, 3-ethyloxy-acrylonitrile(3 mmol, 0.48 g) synthesized according to the literature method (Elgemeie *et al.*, 2002) was added and refluxed at room temperature for about 6 h. The solvent was removed under reduced pressure and the residue was recrystallized from anhydrous ethanol. Single crystals suitable for X-ray analysis were obtained as colourless blocks by slow evaporation of the solvent (m.p. 486 K).

Refinement

All H atoms were placed in calculated positions, with C—H = 0.93–0.96 Å, N—H = 0.94–0.98 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) set at 1.2U_{eq}(C,*N*) or 1.5U_{eq}(C) for methyl H atoms.

Figures

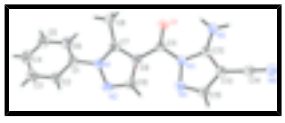

Fig. 1. View of the title compound with 35% probability ellipsoids.

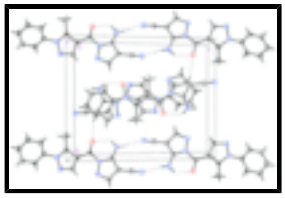

Fig. 2. Perspective view of the molecular packing of the title compound viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

5-Amino-1-(5-methyl-1-phenylpyrazol-4-ylcarbonyl)pyrazole-4-carbonitrile

Crystal data

$C_{15}H_{12}N_6O$	F_{000} = 608
M_r = 292.31	D_x = 1.391 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 701 reflections
a = 7.496 (2) Å	θ = 3.2–24.3º
b = 12.345 (4) Å	μ = 0.10 mm^{-1}
c = 15.426 (5) Å	T = 293 (2) K
β = 102.052 (6)º	Block, colourless
V = 1396.0 (7) Å^3	0.36 × 0.22 × 0.18 mm
Z = 4	

Data collection

Bruker APEX area-detector diffractometer	2852 independent reflections
Radiation source: fine-focus sealed tube	1877 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.035
T = 293(2) K	θ_{max} = 26.4º
φ and ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −9→4
T_{min} = 0.958, T_{max} = 0.983	k = −15→15
7890 measured reflections	l = −18→19

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.046	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.204P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.115	$(\Delta/\sigma)_{max} < 0.001$
S = 1.00	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
2852 reflections	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
201 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Extinction coefficient: 0.0059 (11)

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 $F^2 > 2\text{sigma}(F^2)$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1960 (2)	0.37490 (9)	0.35855 (8)	0.0561 (4)
N1	0.3081 (2)	0.50869 (11)	0.61167 (9)	0.0418 (4)
N2	0.3372 (2)	0.61420 (11)	0.58900 (10)	0.0510 (5)
N3	0.1562 (2)	0.54513 (11)	0.30584 (9)	0.0403 (4)
N4	0.1234 (2)	0.65456 (11)	0.31914 (10)	0.0465 (4)
N5	0.1473 (2)	0.42064 (12)	0.18564 (10)	0.0574 (5)
H5A	0.1731	0.3647	0.2279	0.069*
H5B	0.1326	0.4113	0.1208	0.069*
N6	−0.0183 (3)	0.63464 (13)	0.00460 (12)	0.0717 (6)
C1	0.3436 (2)	0.48244 (14)	0.70408 (11)	0.0408 (4)
C2	0.2944 (3)	0.55511 (15)	0.76258 (12)	0.0482 (5)
H2	0.2362	0.6195	0.7420	0.058*
C3	0.3319 (3)	0.53180 (17)	0.85192 (13)	0.0599 (6)
H3	0.3004	0.5813	0.8917	0.072*
C4	0.4151 (3)	0.43640 (18)	0.88279 (14)	0.0629 (6)
H4	0.4384	0.4207	0.9431	0.075*
C5	0.4639 (3)	0.36406 (17)	0.82421 (13)	0.0599 (6)
H5	0.5198	0.2991	0.8450	0.072*
C6	0.4307 (3)	0.38715 (15)	0.73466 (13)	0.0506 (5)
H6	0.4667	0.3389	0.6953	0.061*
C7	0.2505 (2)	0.44502 (13)	0.54006 (11)	0.0388 (4)
C8	0.1977 (3)	0.32966 (14)	0.54553 (12)	0.0513 (5)
H8A	0.3005	0.2842	0.5432	0.077*
H8B	0.0994	0.3128	0.4967	0.077*
H8C	0.1591	0.3175	0.6003	0.077*
C9	0.2420 (2)	0.51173 (13)	0.46691 (11)	0.0389 (4)
C10	0.2967 (3)	0.61456 (13)	0.50210 (12)	0.0476 (5)
H10	0.3033	0.6757	0.4677	0.057*
C11	0.1981 (2)	0.47117 (13)	0.37665 (11)	0.0398 (4)
C12	0.1246 (2)	0.51948 (14)	0.21706 (11)	0.0416 (4)

C13	0.0704 (3)	0.61514 (14)	0.17264 (11)	0.0435 (5)
C14	0.0218 (3)	0.62706 (14)	0.07981 (13)	0.0511 (5)
C15	0.0725 (3)	0.69317 (14)	0.23900 (12)	0.0468 (5)
H15	0.0408	0.7653	0.2271	0.056*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0872 (11)	0.0354 (7)	0.0427 (8)	−0.0006 (6)	0.0067 (7)	−0.0013 (6)
N1	0.0487 (9)	0.0368 (8)	0.0381 (9)	−0.0019 (7)	0.0047 (7)	−0.0011 (6)
N2	0.0674 (11)	0.0373 (9)	0.0429 (9)	−0.0072 (7)	−0.0005 (8)	0.0000 (7)
N3	0.0507 (9)	0.0345 (8)	0.0339 (8)	0.0017 (7)	0.0049 (7)	0.0011 (6)
N4	0.0592 (10)	0.0353 (8)	0.0433 (9)	0.0032 (7)	0.0070 (7)	−0.0009 (7)
N5	0.0882 (13)	0.0446 (9)	0.0366 (9)	0.0111 (9)	0.0067 (8)	−0.0033 (7)
N6	0.1221 (17)	0.0467 (10)	0.0413 (10)	0.0064 (10)	0.0057 (10)	0.0022 (8)
C1	0.0401 (10)	0.0434 (10)	0.0362 (10)	−0.0023 (8)	0.0017 (8)	0.0011 (8)
C2	0.0509 (12)	0.0464 (11)	0.0449 (11)	0.0021 (9)	0.0046 (9)	−0.0027 (9)
C3	0.0720 (15)	0.0644 (14)	0.0418 (12)	−0.0012 (11)	0.0083 (10)	−0.0108 (10)
C4	0.0701 (15)	0.0724 (15)	0.0409 (12)	−0.0051 (12)	−0.0003 (10)	0.0060 (11)
C5	0.0616 (14)	0.0584 (13)	0.0539 (13)	0.0057 (10)	−0.0012 (11)	0.0124 (10)
C6	0.0514 (12)	0.0496 (11)	0.0492 (12)	0.0084 (9)	0.0071 (9)	0.0007 (9)
C7	0.0388 (10)	0.0361 (9)	0.0408 (10)	0.0018 (7)	0.0068 (8)	−0.0027 (8)
C8	0.0674 (14)	0.0408 (10)	0.0465 (11)	−0.0069 (9)	0.0139 (10)	0.0005 (8)
C9	0.0409 (11)	0.0360 (9)	0.0382 (10)	−0.0004 (7)	0.0042 (8)	0.0009 (7)
C10	0.0599 (13)	0.0385 (10)	0.0403 (11)	−0.0052 (9)	0.0011 (9)	0.0036 (8)
C11	0.0429 (11)	0.0367 (10)	0.0384 (10)	−0.0015 (8)	0.0049 (8)	0.0004 (8)
C12	0.0447 (11)	0.0438 (10)	0.0350 (10)	−0.0013 (8)	0.0056 (8)	−0.0017 (8)
C13	0.0494 (12)	0.0423 (10)	0.0373 (10)	−0.0010 (8)	0.0052 (8)	0.0027 (8)
C14	0.0694 (15)	0.0378 (10)	0.0436 (12)	0.0015 (9)	0.0061 (10)	0.0034 (9)
C15	0.0562 (13)	0.0370 (10)	0.0449 (11)	0.0033 (8)	0.0053 (9)	0.0051 (8)

Geometric parameters (Å, °)

O1—C11	1.2201 (19)	C4—C5	1.373 (3)
N1—C7	1.351 (2)	C4—H4	0.9300
N1—N2	1.3779 (19)	C5—C6	1.381 (3)
N1—C1	1.431 (2)	C5—H5	0.9300
N2—C10	1.311 (2)	C6—H6	0.9300
N3—C12	1.377 (2)	C7—C9	1.388 (2)
N3—N4	1.3959 (19)	C7—C8	1.485 (2)
N3—C11	1.408 (2)	C8—H8A	0.9600
N4—C15	1.305 (2)	C8—H8B	0.9600
N5—C12	1.337 (2)	C8—H8C	0.9600
N5—H5A	0.9418	C9—C10	1.408 (2)
N5—H5B	0.9892	C9—C11	1.451 (2)
N6—C14	1.140 (2)	C10—H10	0.9300
C1—C2	1.376 (3)	C11—O1	1.2201 (19)
C1—C6	1.380 (2)	C12—C13	1.383 (2)
C2—C3	1.378 (3)	C13—C15	1.403 (2)

C2—H2	0.9300	C13—C14	1.410 (3)
C3—C4	1.371 (3)	C15—H15	0.9300
C3—H3	0.9300		
C7—N1—N2	112.51 (14)	N1—C7—C8	123.70 (15)
C7—N1—C1	130.07 (15)	C9—C7—C8	130.37 (15)
N2—N1—C1	117.42 (13)	C7—C8—H8A	109.5
C10—N2—N1	104.34 (13)	C7—C8—H8B	109.5
C12—N3—N4	111.69 (13)	H8A—C8—H8B	109.5
C12—N3—C11	125.91 (14)	C7—C8—H8C	109.5
N4—N3—C11	122.10 (14)	H8A—C8—H8C	109.5
C15—N4—N3	103.88 (14)	H8B—C8—H8C	109.5
C12—N5—H5A	116.2	C7—C9—C10	105.15 (15)
C12—N5—H5B	118.5	C7—C9—C11	122.55 (15)
H5A—N5—H5B	125.3	C10—C9—C11	132.12 (16)
C2—C1—C6	120.26 (17)	N2—C10—C9	112.20 (15)
C2—C1—N1	119.07 (16)	N2—C10—H10	123.9
C6—C1—N1	120.65 (17)	C9—C10—H10	123.9
C1—C2—C3	119.53 (18)	O1—C11—N3	117.65 (15)
C1—C2—H2	120.2	O1—C11—N3	117.65 (15)
C3—C2—H2	120.2	O1—C11—C9	123.03 (15)
C4—C3—C2	120.6 (2)	O1—C11—C9	123.03 (15)
C4—C3—H3	119.7	N3—C11—C9	119.32 (15)
C2—C3—H3	119.7	N5—C12—N3	124.19 (15)
C3—C4—C5	119.6 (2)	N5—C12—C13	130.26 (17)
C3—C4—H4	120.2	N3—C12—C13	105.54 (15)
C5—C4—H4	120.2	C12—C13—C15	105.51 (16)
C4—C5—C6	120.44 (19)	C12—C13—C14	125.39 (16)
C4—C5—H5	119.8	C15—C13—C14	129.09 (16)
C6—C5—H5	119.8	N6—C14—C13	178.7 (2)
C1—C6—C5	119.45 (19)	N4—C15—C13	113.37 (16)
C1—C6—H6	120.3	N4—C15—H15	123.3
C5—C6—H6	120.3	C13—C15—H15	123.3
N1—C7—C9	105.79 (15)		
C7—N1—N2—C10	0.0 (2)	C11—C9—C10—N2	−174.81 (19)
C1—N1—N2—C10	179.30 (16)	O1—O1—C11—N3	0.0 (3)
C12—N3—N4—C15	0.2 (2)	O1—O1—C11—C9	0.0 (3)
C11—N3—N4—C15	−173.90 (17)	C12—N3—C11—O1	−4.7 (3)
C7—N1—C1—C2	−140.9 (2)	N4—N3—C11—O1	168.54 (17)
N2—N1—C1—C2	39.9 (2)	C12—N3—C11—O1	−4.7 (3)
C7—N1—C1—C6	41.0 (3)	N4—N3—C11—O1	168.54 (17)
N2—N1—C1—C6	−138.21 (18)	C12—N3—C11—C9	175.11 (17)
C6—C1—C2—C3	−0.3 (3)	N4—N3—C11—C9	−11.7 (3)
N1—C1—C2—C3	−178.45 (17)	C7—C9—C11—O1	−12.8 (3)
C1—C2—C3—C4	−1.0 (3)	C10—C9—C11—O1	161.6 (2)
C2—C3—C4—C5	0.9 (3)	C7—C9—C11—O1	−12.8 (3)
C3—C4—C5—C6	0.4 (3)	C10—C9—C11—O1	161.6 (2)
C2—C1—C6—C5	1.6 (3)	C7—C9—C11—N3	167.39 (16)
N1—C1—C6—C5	179.71 (17)	C10—C9—C11—N3	−18.2 (3)

C4—C5—C6—C1	−1.6 (3)	N4—N3—C12—N5	179.26 (17)
N2—N1—C7—C9	0.2 (2)	C11—N3—C12—N5	−6.9 (3)
C1—N1—C7—C9	−179.00 (17)	N4—N3—C12—C13	0.0 (2)
N2—N1—C7—C8	−175.96 (16)	C11—N3—C12—C13	173.81 (17)
C1—N1—C7—C8	4.8 (3)	N5—C12—C13—C15	−179.4 (2)
N1—C7—C9—C10	−0.3 (2)	N3—C12—C13—C15	−0.2 (2)
C8—C7—C9—C10	175.53 (19)	N5—C12—C13—C14	1.4 (4)
N1—C7—C9—C11	175.40 (16)	N3—C12—C13—C14	−179.35 (19)
C8—C7—C9—C11	−8.8 (3)	N3—N4—C15—C13	−0.3 (2)
N1—N2—C10—C9	−0.2 (2)	C12—C13—C15—N4	0.3 (2)
C7—C9—C10—N2	0.3 (2)	C14—C13—C15—N4	179.4 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5A···O1	0.94	1.99	2.676 (2)	128
N5—H5B···N6^{i}	0.99	2.03	2.971 (2)	159
C5—H5···O1^{ii}	0.93	2.51	3.409 (3)	164

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

Fig. 1

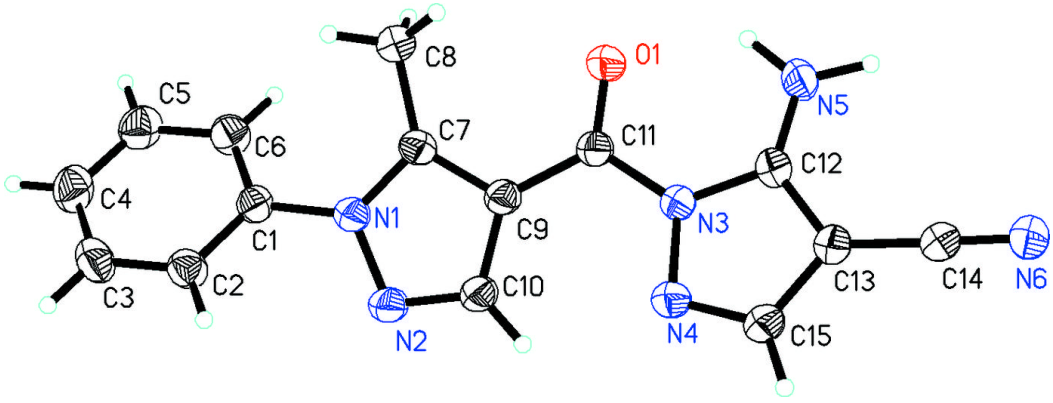
C8
O1
C5
N5
C7
C11
C6
C12
C4
N1
C9
N3
C1
C13
C14
N6
C3
C2
C10
N2
N4
C15

Fig. 2