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5-Amino-3-anilino-1*H*-pyrazole-4-carbonitrile

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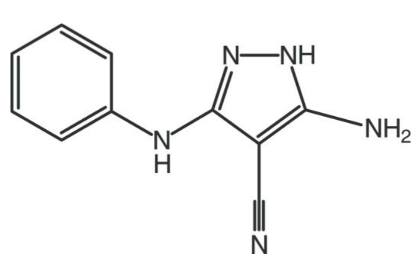
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.086; data-to-parameter ratio = 19.6.

In the title compound, $C_{10}H_9N_5$, the phenyl ring is twisted with respect to the pyrazole ring, forming a dihedral angle of 24.00 (6)°. In the crystal, molecules are linked by N—H···N hydrogen bonds into chains running parallel to [010] containing alternating $R_2^2(6)$ and $R_2^2(12)$ rings. Further interactions are found in the crystal, *viz*. N—H···π(phenyl) interactions and weak face-to-face π–π stacking interactions [centroid–centroid distance = 3.8890 (6) Å] between the centroids of the pyrazole and phenyl rings are observed.

Related literature

For biological activities of pyrazoles, see: Kaushik *et al.* (2010); Sheikh *et al.* (2009); Krishnamurthy *et al.* (2004); Grimmett (1970). For the use of related compounds as bridging ligands, see: Lynch & McClenaghan (2005). For the synthesis of the title compound, see: Soliman *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{10}H_9N_5$
M_r = 199.22
Orthorhombic, $P2_12_12_1$
a = 6.3441 (1) Å
b = 11.1354 (2) Å
c = 13.7754 (3) Å
V = 973.15 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 90 K
0.25 × 0.17 × 0.08 mm

Data collection

Bruker Kappa APEXII DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.978, T_{max} = 0.993
32878 measured reflections
2975 independent reflections
2767 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
Standard reflections: 0

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.086
S = 1.09
2975 reflections
152 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

*Cg*2 is the centroid of the C1–C6 phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···N5^{i}	0.84 (2)	2.15 (2)	2.9934 (13)	179 (2)
N3—H3*N*···N2^{ii}	0.87 (2)	2.09 (2)	2.8947 (13)	154 (2)
N4—H12···*Cg*2^{iii}	0.85 (2)	2.51 (2)	3.2011 (12)	140 (2)

Symmetry codes: (i) $x-\frac{1}{2}, -y-\frac{1}{2}, -z+2$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (iii) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5143).

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supporting information

Acta Cryst. (2012). E**68**, o2784 [doi:10.1107/S1600536812036045]

5-Amino-3-anilino-1*H*-pyrazole-4-carbonitrile

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S1. Comment

The interest in pyrazole compounds stems from their pharmaceutical and agricultural applications such as drugs, dyes and anaesthetics (Grimmett, 1970; Sheikh *et al.*, 2009; Kaushik *et al.*, 2010; Krishnamurthy *et al.*, 2004). In addition, such pyrazoles and related compounds are common molecules used in coordination or organometallic chemistry as bridging ligands, utilizing the ring positions of the two N atoms (Lynch & McClenaghan, 2005). We report herein the crystal structure of the title compound which was synthesized by our team as a precursor having two functional substituents (amino and nitrile groups) for the purposes of synthesis of multi-fused pyrazolo-heterocyclic compounds such as nitrogen bridgehead derivatives having potential biological activities (Soliman *et al.*, 2010).

In the molecule of the title compound, (Fig. 1), the phenyl and 1*H*-pyrazole ring makes a dihedral angle of 24.00 (6)° with each other.

The crystal structure is stabilized by N—H···N hydrogen bonds (Table 1, Fig. 2) which link the molecules into chains running parallel to [010] with alternating $R_2^2(6)$ and $R_2^2(12)$ motifs (Bernstein *et al.*, 1995). In addition, the crystal structure exhibits N—H···π(phenyl) interactions, Table 1, and weak face-to-face π—π stacking interactions [*Cg*1···*Cg*2 (1 + *x*, *y*, *z*) = 3.8890 (6) Å; where *Cg*1 and *Cg*2 are the centroid of the (N2/N3/C7–C9) 1*H*-pyrazole and (C1–C6) phenyl rings].

S2. Experimental

The title compound was prepared according to the literature procedure (Soliman *et al.*, 2010). Crystals were obtained from an ethanol solution of (I) by slow evaporation (*M*.pt: 481 K).

S3. Refinement

The hydrogen atoms bound to nitrogen were located from a difference Fourier map and were refined with a distance restraint of N—H = 0.86 (2) Å; their U_{iso} values were refined freely. The hydrogen atoms bound to carbon were positioned geometrically and refined using a riding model with C—H = 0.93 Å, and with $U_{iso} = 1.2U_{eq}$(C). The absolute structure could not be determined reliably; Friedel pairs were not merged.

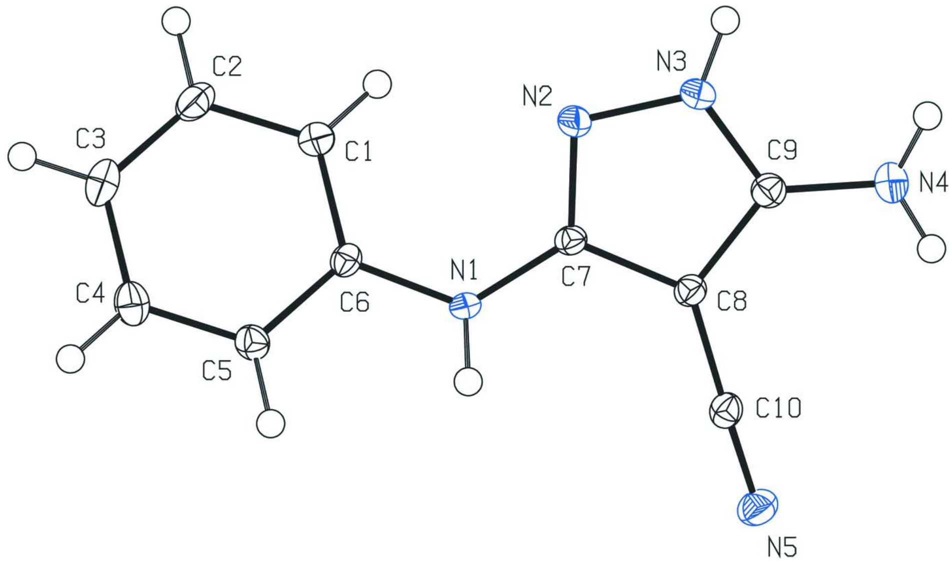

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

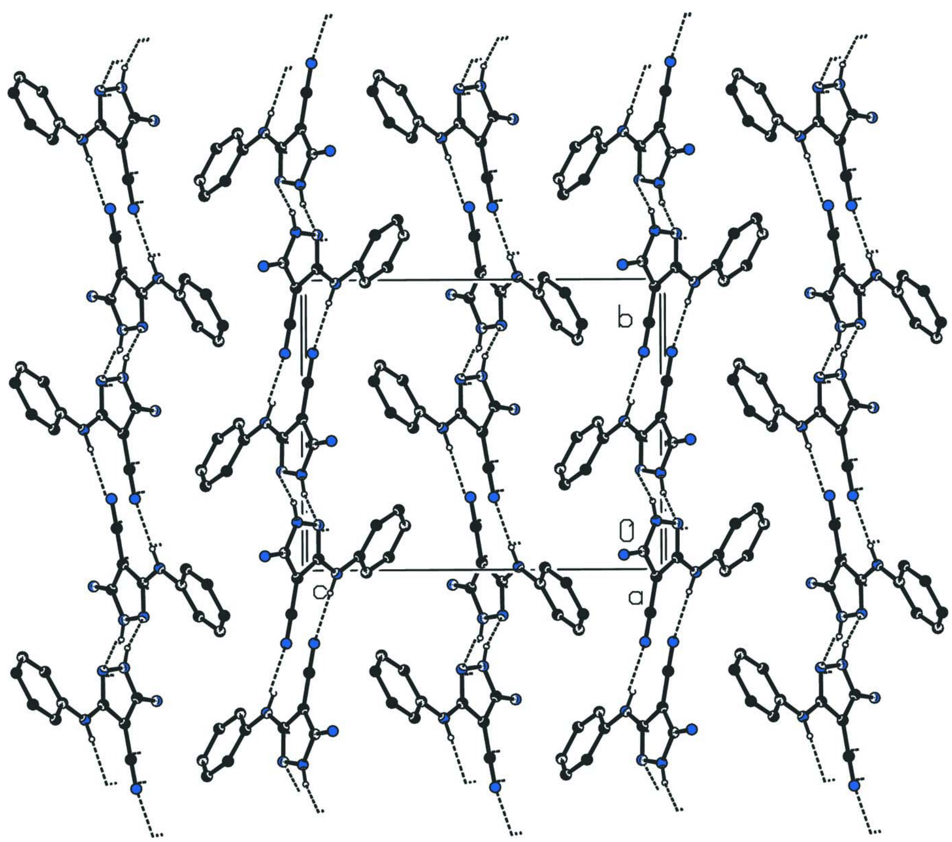

Figure 2

View of chains of the dimers formed by pairs of N—H···N hydrogen bonds, with the $R_2^2(12)$ and $R_2^2(6)$ motifs connected into a supramolecular chain. H atoms not involved in hydrogen bonds have been omitted for clarity.

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Crystal data

$C_{10}H_9N_5$
$M_r = 199.22$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.3441$ (1) Å
$b = 11.1354$ (2) Å
$c = 13.7754$ (3) Å
$V = 973.15$ (3) Å^3
$Z = 4$
$F(000) = 416$
$D_x = 1.360$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9908 reflections
$\theta = 2.4$–30.5°
$\mu = 0.09$ mm^{-1}
$T = 90$ K
Plate, colourless
0.25 × 0.17 × 0.08 mm

Data collection

Bruker Kappa APEXII DUO diffractometer
Radiation source: fine-focus sealed tube
TRIUMPH curved graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.978$, $T_{max} = 0.993$
32878 measured reflections
2975 independent reflections
2767 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 30.6°$, $\theta_{min} = 2.4°$
$h = -9\rightarrow9$
$k = -15\rightarrow15$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.086$
$S = 1.09$
2975 reflections
152 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1533P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Absolute structure: nd

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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}
N1	0.50345 (15)	−0.01004 (8)	0.89839 (7)	0.0142 (2)
N2	0.71282 (15)	0.15769 (8)	0.94613 (7)	0.0154 (2)
N3	0.89266 (15)	0.16812 (8)	1.00299 (7)	0.0168 (2)

N4	1.13973 (17)	0.05235 (10)	1.09010 (8)	0.0234 (3)
N5	0.84875 (15)	−0.24944 (9)	1.03572 (7)	0.0204 (3)
C1	0.40580 (18)	0.15607 (10)	0.78868 (8)	0.0173 (3)
C2	0.2548 (2)	0.20761 (11)	0.72811 (8)	0.0205 (3)
C3	0.06057 (19)	0.15345 (11)	0.71341 (8)	0.0213 (3)
C4	0.01783 (19)	0.04497 (11)	0.75945 (8)	0.0193 (3)
C5	0.16597 (18)	−0.00746 (10)	0.82040 (7)	0.0152 (3)
C6	0.36064 (16)	0.04854 (9)	0.83683 (7)	0.0130 (2)
C7	0.66942 (16)	0.04110 (9)	0.94711 (7)	0.0122 (2)
C8	0.81769 (17)	−0.02408 (9)	1.00460 (8)	0.0133 (2)
C9	0.96026 (17)	0.06332 (10)	1.03764 (8)	0.0153 (3)
C10	0.83277 (17)	−0.14847 (9)	1.02122 (7)	0.0145 (2)
H1	0.53600	0.19300	0.79700	0.0210*
H1N	0.459 (3)	−0.0771 (13)	0.9176 (12)	0.027 (4)*
H2	0.28480	0.27970	0.69700	0.0250*
H3	−0.03960	0.18910	0.67340	0.0260*
H3N	0.958 (3)	0.2358 (13)	1.0116 (14)	0.034 (5)*
H4	−0.11110	0.00720	0.74930	0.0230*
H5	0.13580	−0.08020	0.85050	0.0180*
H11	1.200 (3)	0.1170 (14)	1.1129 (13)	0.038 (5)*
H12	1.165 (3)	−0.0151 (14)	1.1162 (13)	0.036 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0145 (4)	0.0093 (4)	0.0189 (4)	−0.0012 (3)	−0.0034 (4)	0.0031 (3)
N2	0.0152 (4)	0.0112 (4)	0.0197 (4)	−0.0003 (3)	−0.0030 (3)	−0.0012 (3)
N3	0.0178 (4)	0.0117 (4)	0.0208 (4)	−0.0023 (3)	−0.0038 (3)	−0.0005 (3)
N4	0.0219 (5)	0.0230 (5)	0.0253 (5)	−0.0035 (4)	−0.0095 (4)	0.0041 (4)
N5	0.0189 (5)	0.0160 (4)	0.0262 (5)	0.0023 (4)	0.0001 (4)	0.0038 (4)
C1	0.0189 (5)	0.0150 (5)	0.0179 (5)	−0.0012 (4)	−0.0018 (4)	0.0018 (4)
C2	0.0260 (6)	0.0172 (5)	0.0183 (5)	0.0030 (4)	−0.0029 (4)	0.0044 (4)
C3	0.0206 (5)	0.0250 (6)	0.0182 (5)	0.0068 (5)	−0.0037 (4)	0.0018 (4)
C4	0.0144 (5)	0.0251 (5)	0.0184 (5)	0.0007 (4)	−0.0004 (4)	−0.0010 (4)
C5	0.0134 (5)	0.0170 (4)	0.0153 (4)	−0.0011 (4)	0.0010 (4)	0.0006 (4)
C6	0.0136 (4)	0.0126 (4)	0.0129 (4)	0.0025 (4)	−0.0004 (3)	−0.0002 (3)
C7	0.0124 (4)	0.0105 (4)	0.0137 (4)	0.0007 (4)	0.0005 (4)	0.0003 (3)
C8	0.0128 (4)	0.0126 (4)	0.0145 (4)	0.0008 (3)	0.0001 (4)	0.0011 (3)
C9	0.0157 (4)	0.0155 (5)	0.0147 (4)	−0.0005 (4)	0.0002 (3)	0.0004 (4)
C10	0.0125 (4)	0.0164 (4)	0.0147 (4)	0.0011 (4)	0.0008 (3)	0.0017 (3)

Geometric parameters (Å, º)

N1—C6	1.4020 (14)	C2—C3	1.3868 (17)
N1—C7	1.3724 (14)	C3—C4	1.3910 (17)
N2—N3	1.3888 (14)	C4—C5	1.3889 (16)
N2—C7	1.3272 (13)	C5—C6	1.4019 (15)
N3—C9	1.3318 (14)	C7—C8	1.4279 (15)

N4—C9	1.3541 (15)	C8—C9	1.4044 (15)
N5—C10	1.1464 (14)	C8—C10	1.4072 (14)
N1—H1N	0.841 (15)	C1—H1	0.9300
N3—H3N	0.868 (16)	C2—H2	0.9300
N4—H11	0.874 (17)	C3—H3	0.9300
N4—H12	0.848 (16)	C4—H4	0.9300
C1—C2	1.3940 (16)	C5—H5	0.9300
C1—C6	1.3985 (15)		

C6—N1—C7	126.77 (9)	N1—C7—N2	124.06 (9)
N3—N2—C7	104.27 (8)	N1—C7—C8	124.46 (9)
N2—N3—C9	113.17 (9)	C7—C8—C9	104.58 (9)
C6—N1—H1N	112.8 (13)	C7—C8—C10	129.45 (10)
C7—N1—H1N	118.2 (12)	C9—C8—C10	125.85 (10)
N2—N3—H3N	122.8 (12)	N3—C9—N4	122.76 (10)
C9—N3—H3N	123.9 (12)	N3—C9—C8	106.48 (9)
C9—N4—H12	117.7 (12)	N4—C9—C8	130.69 (11)
H11—N4—H12	119.7 (17)	N5—C10—C8	178.64 (11)
C9—N4—H11	119.1 (12)	C2—C1—H1	120.00
C2—C1—C6	119.71 (10)	C6—C1—H1	120.00
C1—C2—C3	121.26 (11)	C1—C2—H2	119.00
C2—C3—C4	118.97 (11)	C3—C2—H2	119.00
C3—C4—C5	120.58 (11)	C2—C3—H3	121.00
C4—C5—C6	120.45 (10)	C4—C3—H3	121.00
N1—C6—C1	123.57 (9)	C3—C4—H4	120.00
N1—C6—C5	117.39 (9)	C5—C4—H4	120.00
C1—C6—C5	119.00 (9)	C4—C5—H5	120.00
N2—C7—C8	111.48 (9)	C6—C5—H5	120.00

C7—N1—C6—C5	−159.01 (10)	C2—C3—C4—C5	0.99 (17)
C6—N1—C7—N2	3.39 (17)	C3—C4—C5—C6	0.32 (16)
C7—N1—C6—C1	23.65 (16)	C4—C5—C6—C1	−1.90 (15)
C6—N1—C7—C8	−176.20 (10)	C4—C5—C6—N1	−179.36 (10)
C7—N2—N3—C9	0.38 (12)	N1—C7—C8—C9	178.44 (10)
N3—N2—C7—C8	0.53 (12)	N2—C7—C8—C10	−177.26 (11)
N3—N2—C7—N1	−179.10 (10)	N1—C7—C8—C10	2.37 (18)
N2—N3—C9—N4	176.12 (10)	N2—C7—C8—C9	−1.19 (12)
N2—N3—C9—C8	−1.13 (13)	C7—C8—C9—N3	1.35 (12)
C6—C1—C2—C3	−0.88 (17)	C10—C8—C9—N4	0.7 (2)
C2—C1—C6—N1	179.46 (10)	C7—C8—C9—N4	−175.60 (12)
C2—C1—C6—C5	2.16 (16)	C10—C8—C9—N3	177.60 (10)
C1—C2—C3—C4	−0.71 (17)		

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C1–C6 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N5^{i}	0.84 (2)	2.15 (2)	2.9934 (13)	179 (2)

N3—H3*N*···N2[ii]	0.87 (2)	2.09 (2)	2.8947 (13)	154 (2)
C1—H1···N2	0.93	2.37	2.9152 (15)	117
N4—H12···*Cg*2[iii]	0.85 (2)	2.51 (2)	3.2011 (12)	140 (2)

Symmetry codes: (i) $x-1/2$, $-y-1/2$, $-z+2$; (ii) $x+1/2$, $-y+1/2$, $-z+2$; (iii) $-x+3/2$, $-y$, $z+1/2$.