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3-Amino-1-phenyl-1*H*-pyrazole

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.097
Data-to-parameter ratio = 9.3

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

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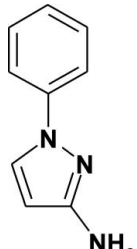
In the crystal structure of the title compound, $C_9H_9N_3$, the asymmetric unit contains two independent molecules. In the crystal structure, the molecules are involved in networks of N—H···N hydrogen-bond interactions linking the N atoms from both the amino and the imino groups. The compound also demonstrates an interesting stacking formation of a secondary structure. Two crystallographically independent molecules are connected in helical chains, with four molecules per helical turn.

Comment

N-Phenylpyrazole derivatives find application in many branches of chemistry, such as components of colorants (Folli *et al.*, 1980), or as inhibitors or activators of receptors and enzymes in medicinal chemistry, for example, in the selective binding activity of the compound SR141716A to brain cannabinoid receptors (CB1) without producing cannabimimetic activity *in vivo* (Wiley *et al.*, 2001).

1-Phenyl-3-aminopyrazole, (I), is a structurally important part of new fentanyl analogues with interesting analgesic properties (Jagerovic *et al.*, 2002), being more potent than morphine and less than fentanyl but with longer duration of action. The 1-phenyl-3-aminopyrazole molecule was also applied to activators of guanylate cyclase (Selwood *et al.*, 2001) and to some non-peptidic inhibitors of the apoptosis family of proteins (XIAP) (Park *et al.*, 2005).



(I)

In the crystal structure of (I), the asymmetric unit contains two independent molecules. The phenyl and pyrazole rings in each independent molecule of (I) are essentially coplanar (Fig. 1). The dihedral angle between the mean planes through the phenyl and pyrazole rings is 9.96 (9) and 7.34 (9)° for the two molecules of the asymmetric unit. A least-squares overlay of the two independent molecules of (I) calculated for the atoms of the pyrazole rings is depicted in Fig. 2.

The molecular packing in (I) is stabilized by intermolecular N—H···N hydrogen bonds involving the N atoms of the amino and imino groups (Table 2). The crystal structure is also

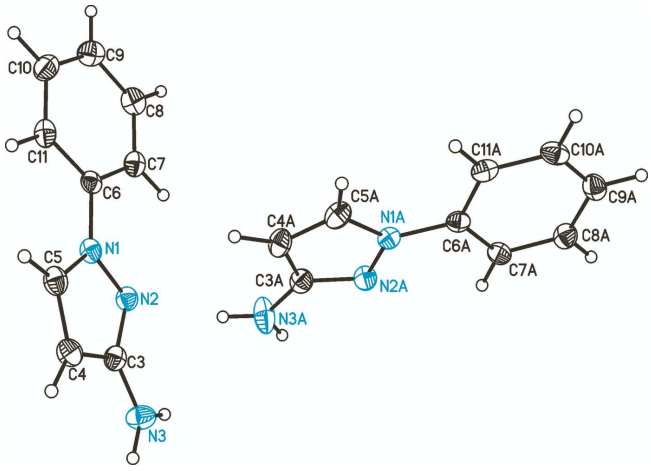


Figure 1
An *ORTEPIII* (Johnson & Burnett, 1996) plot of the asymmetric unit of (I). Non-H atoms are drawn with 50% probability displacement ellipsoids and H atoms as small spheres of arbitrary radii.

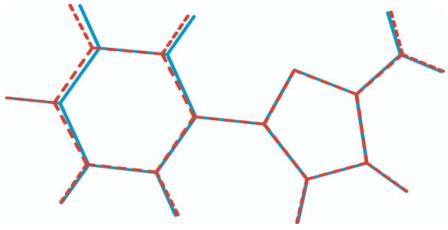


Figure 2
A least-squares overlay of the two independently refined molecules of (I), fitting the atoms of the pyrazole rings.

stabilized by a number of weak interactions of the type N—H···C and π-stacking interactions of the type C—H···C. The two crystallographically independent molecules are connected in helical chains with four molecules per helical turn in the [010] direction (Fig. 3).

Experimental

1-Phenyl-3-aminopyrazole, (I), was prepared by a multiple-step synthesis based on the cycloaddition reaction of phenylhydrazine and acrylonitrile as described by Grandberg *et al.* (1972). The final product was purified by flash chromatography. To obtain crystals suitable for single-crystal X-ray analysis the solid compound was sublimed in a test-tube with a cooling finger in a vacuum [393 K (oil bath), 1.3 h Pa].

Crystal data

$C_9H_9N_3$
M_r = 159.19
Monoclinic, $P2_1$
a = 11.9730 (10) Å
b = 5.5395 (4) Å
c = 11.9869 (10) Å
β = 90.158 (8)°
V = 795.02 (11) Å^3
Z = 4
D_x = 1.330 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3218 reflections
θ = 1.7–27.9°
μ = 0.08 mm^{-1}
T = 105 (2) K
Prism, colorless
0.35 × 0.30 × 0.25 mm

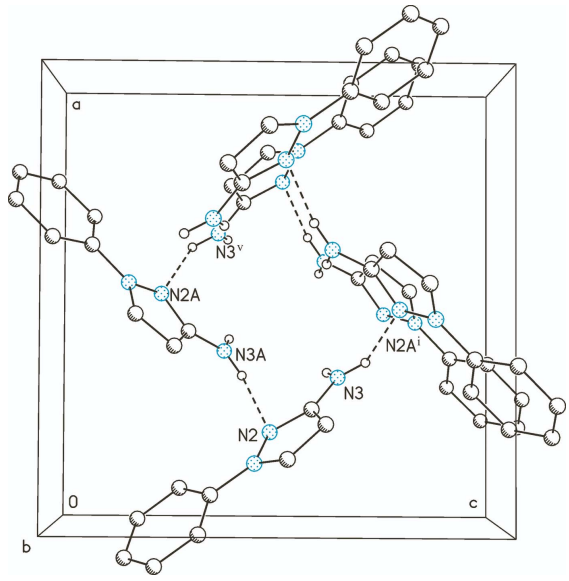


Figure 3
Part of the crystal structure of (I), showing the formation of a helical chain of hydrogen-bonded (dashed lines) molecules in the direction [101]. [Symmetry codes: (i) $1-x, y+\frac{1}{2}, 1-z$; (v) $1-x, y-\frac{1}{2}, 1-z$]. The view direction is parallel to an axis of the helix. C-bound H atoms have been omitted.

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: none
7425 measured reflections
2012 independent reflections
1795 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 7$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.097
S = 1.21
2012 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.25P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1*A*—C5*A*	1.350 (3)	N1—C5	1.352 (4)
N1*A*—N2*A*	1.379 (3)	N1—N2	1.386 (3)
N1*A*—C6*A*	1.418 (3)	N1—C6	1.415 (3)
N2*A*—C3*A*	1.334 (4)	N2—C3	1.328 (4)
N3*A*—C3*A*	1.371 (4)	N3—C3	1.387 (4)
C3*A*—C4*A*	1.415 (4)	C3—C4	1.417 (4)
C4*A*—C5*A*	1.363 (4)	C4—C5	1.367 (4)
C5*A*—N1*A*—N2*A*	111.1 (2)	C5—N1—N2	111.0 (2)
C5*A*—N1*A*—C6*A*	128.8 (2)	C5—N1—C6	128.6 (2)
N2*A*—N1*A*—C6*A*	120.0 (2)	N2—N1—C6	120.4 (2)
C3*A*—N2*A*—N1*A*	104.8 (2)	C3—N2—N1	104.3 (2)
N2*A*—C3*A*—N3*A*	121.5 (3)	N2—C3—N3	121.3 (3)
N2*A*—C3*A*—C4*A*	111.1 (3)	N2—C3—C4	112.1 (3)
N3*A*—C3*A*—C4*A*	127.4 (3)	N3—C3—C4	126.6 (3)
C5*A*—C4*A*—C3*A*	105.1 (3)	C5—C4—C3	104.3 (3)
N1*A*—C5*A*—C4*A*	108.0 (3)	N1—C5—C4	108.3 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···N2A^{i}	0.88	2.27	3.021 (3)	143
N3A—H3AB···N2	0.88	2.19	3.016 (3)	156
C9—H9···C9A^{ii}	0.95	2.81	3.704 (4)	157
C10A—H10A···C3A^{iii}	0.95	2.89	3.513 (4)	124
N3—H3A···C4^{iv}	0.88	2.83	3.574 (4)	143

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

All H atoms were located in a difference map and refined using a riding model with C—H distances of 0.95 Å and N—H distances of 0.88 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N). We also tried to refine the H atoms of the amino groups freely. However, the best result was achieved by using the riding-model approximation.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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