

5-Amino-1-benzoyl-3-methylpyrazole: complex sheets built from N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds

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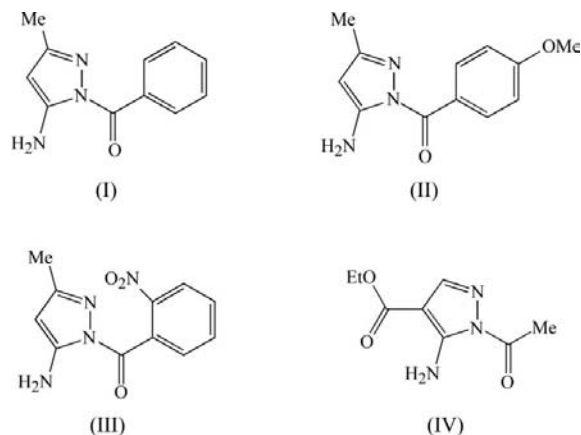
Molecules of the title compound [systematic name: (5-amino-3-methylpyrazol-1-yl)(phenyl)methanone], C₁₁H₁₁N₃O, contain an intramolecular hydrogen bond. The molecules are linked into sheets by a combination of N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds. Comparisons are made with the hydrogen-bonded structures of some related compounds.

Comment

We report here the structure and supramolecular aggregation of the title compound, (I) (Fig. 1), a member of the class of 5-aminopyrazoles containing an aroyl substituent, which are useful and versatile intermediates in the synthesis of polyaza heterocycles (Bauer & Mahajanshetti, 1967; Tominaga *et al.*, 1995), in particular fused pyrazole derivatives, which exhibit a wide range of potential applications (Elguero, 1984, 1996). We have recently reported (Quiroga *et al.*, 2008) the structures of two aryl-substituted analogues, (II) and (III) (see scheme), which exhibit very different hydrogen-bonding arrangements, and we have therefore now investigated the unsubstituted parent compound, (I), the structure of which is reported here. Compound (I) was prepared using the same procedure as previously employed for (II) and (III), namely a deaminative condensation between 3-aminocrotononitrile and, in this case, benzohydrazide PhCONHNH₂, in the presence of sodium acetate.

The molecule of (I) contains an intramolecular N—H···O hydrogen bond (Table 2), forming an *S*(6) motif (Bernstein *et al.*, 1995), and this may assist in controlling the molecular

conformation, since the carbonyl group is nearly coplanar with the pyrazole ring, as shown by the leading torsion angles (Table 1). The phenyl group, on the other hand, is markedly twisted out of this plane; the orientation of the phenyl ring may be dominated by the intermolecular hydrogen bonds (Table 2). The bond distances in (I) show no unexpected or unusual features.



The molecules of compound (I) are linked into sheets by a combination of N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds (Table 2). The H···O distance for the C—H···O interaction is quite long, but the formation of the sheet does not depend upon this interaction, as the sheet could, in fact, be envisaged as constructed solely from the N—H···N and C—H··· π (arene) hydrogen bonds. The N—H···N hydrogen bond links molecules related by the *c*-glide plane at $y = \frac{3}{4}$ into a *C*(5) chain running parallel to the [001] direction (Fig. 2), while the C—H··· π (arene) hydrogen bond links molecules related by the 2₁ screw axis along ($\frac{1}{2}$, y , $\frac{3}{4}$) into a chain running parallel to the [010] direction (Fig. 3). In addition to these two chains, the combination of which is sufficient to form a sheet lying parallel to (100), the rather long C—H···O hydrogen bond links molecules related by the *c*-glide plane at $y = \frac{3}{4}$ into a *C*(6) chain running parallel to the [001]. Combination of the *C*(5) and *C*(6) chains parallel to [001] is itself sufficient to form a sheet parallel to (100) (Fig. 4) and, in

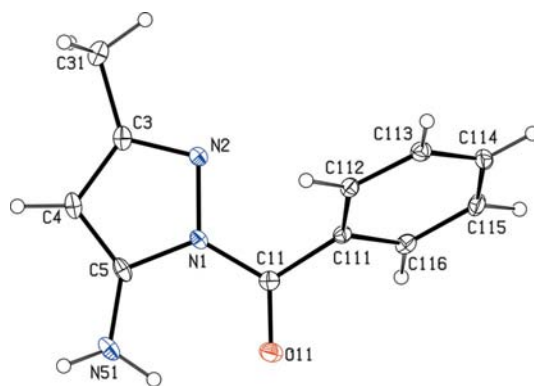
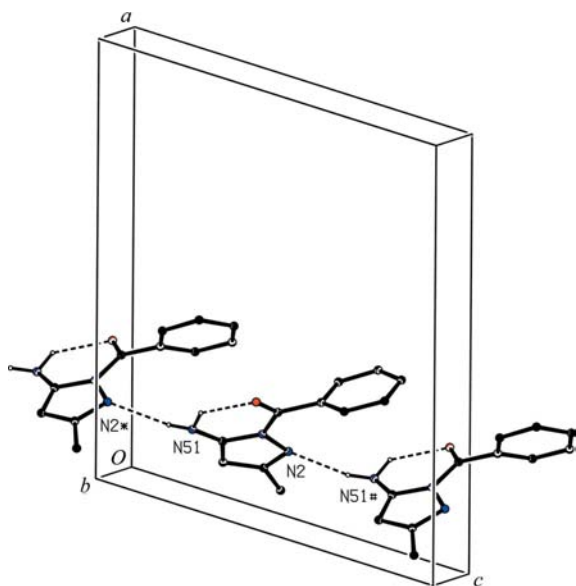
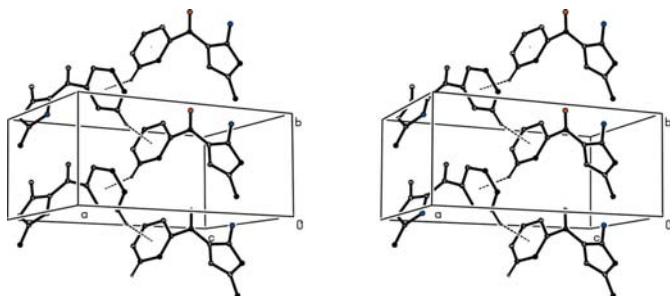


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

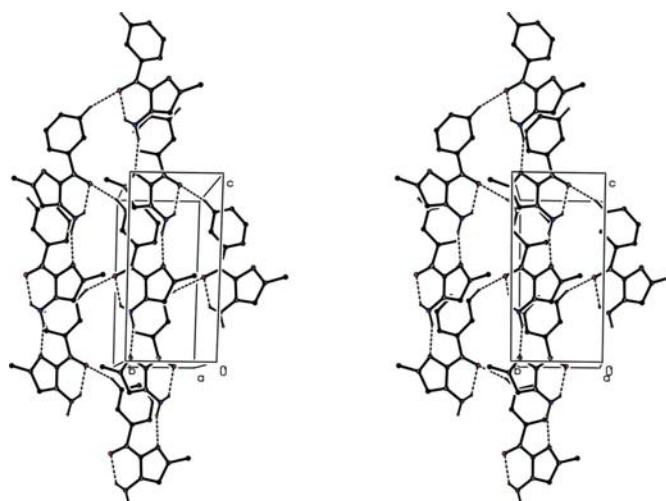
Part of the crystal structure of (I), showing the intramolecular N—H...O hydrogen bond and the formation of a C(5) chain along [001] built from N—H...N hydrogen bonds. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively.


Figure 3

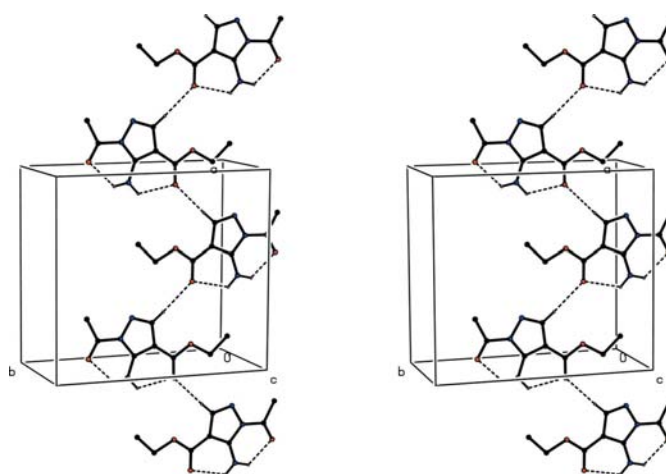
A stereoview of part of the crystal structure of (I), showing the formation of a chain along [010] built from C—H... π (arene) hydrogen bonds (dashed lines). For the sake of clarity, H atoms not involved in the motif shown have been omitted.

fact, any pairwise combination of the chains generated by, respectively, the N—H...N, C—H...O and C—H... π (arene) hydrogen bonds will generate a sheet parallel to (100). A single sheet passes through each unit cell, but there are no direction-specific interactions between adjacent sheets. In particular, aromatic π - π stacking interactions are absent from the crystal structure of (I).

The two-dimensional hydrogen-bonded structure of (I) may be contrasted with the hydrogen-bonded structures of the singly-substituted analogues (II) and (III) (Quiroga *et al.*, 2008). In the crystal structure of the 4-methoxyphenyl analogue, (II), which crystallizes in the space group $P\bar{1}$, a combination of N—H...N and N—H... π (arene) hydrogen bonds links molecules related by translation into a chain of rings, while a C—H...O interaction, which is probably weaker than the analogous interaction in (I), links pairs of chains


Figure 4

A stereoview of part of the crystal structure of (I), showing the formation of a sheet parallel to (100) built from N—H...N and C—H...O hydrogen bonds (dashed lines). For the sake of clarity, H atoms bonded to C atoms but not involved in the motifs shown have been omitted.


Figure 5

A stereoview of part of the crystal structure of (IV) (Kusakiewicz-Dawid *et al.*, 2007), showing the formation of two intramolecular N—H...O hydrogen bonds and a C(5) chain running parallel to [100] and built from a single C—H...O hydrogen bond. Hydrogen bonds are shown as dashed lines. The deposited atom coordinates (CSD refcode HIVTAI) were used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

which are related by inversion and thus antiparallel. Hence, the hydrogen-bonded structure of (II) is strictly one-dimensional. In the 2-nitrophenyl analogue, (III), which crystallizes in the space group $Pna2_1$, a combination of one N—H...N hydrogen bond and three independent C—H...O hydrogen bonds, all of them utilizing nitro O atoms as hydrogen-bond acceptors, links the molecules into a fairly complex three-dimensional structure. Hence, compounds (I)–(III) all crystallize in different space groups with very different unit-cell metrics, all exhibit different selections of intermolecular hydrogen bonds, and their hydrogen-bonded structures are, respectively, two-, one- and three-dimensional.

Rather closely related to the series of compounds (I)–(III) is compound (IV) (see scheme). This was reported (Kusakiewicz-Dawid *et al.*, 2007) on a proof-of-constitution basis, with no description of the intermolecular aggregation. Compound (IV) crystallizes in space group No. 62, for which the authors employed the nonstandard setting *Pnam*, with all of the non-H atoms lying on the mirror plane at $z = \frac{1}{4}$. Analysis of the structure using the deposited atomic coordinates [Cambridge Structural Database (CSD; Allen, 2002) refcode HIVTAI] shows that the molecular conformation is associated with the occurrence of two intramolecular N–H···O hydrogen bonds, each forming an *S*(6) ring, while a single intermolecular C–H···O hydrogen bond links molecules related by the 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{4})$ into *C*(5) chains (Fig. 5).

Experimental

A mixture of 3-aminocrotononitrile (2 mmol), benzohydrazide (2 mmol) and sodium acetate trihydrate (2 mmol) in ethanol (50 ml) was heated under reflux for 2 h. The mixture was allowed to cool to ambient temperature and was then poured into water (50 ml) with vigorous stirring. Stirring was continued for 20 min. The resulting solid product, (I), was collected by filtration and recrystallized from ethanol to give colourless crystals suitable for single-crystal X-ray diffraction (yield 94%, m.p. 369–370 K). MS (70 eV) *m/z* (%): 201 (15, M^+), 10 (100), 77 (55).

Crystal data

$C_{11}H_{11}N_3O$	$V = 980.90 (6) \text{ \AA}^3$
$M_r = 201.23$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.7443 (6) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 5.7669 (2) \text{ \AA}$	$T = 120 \text{ K}$
$c = 12.0082 (3) \text{ \AA}$	$0.20 \times 0.14 \times 0.08 \text{ mm}$
$\beta = 106.119 (2)^\circ$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	1919 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1919 independent reflections
$T_{\min} = 0.982$, $T_{\max} = 0.993$	1673 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	
$S = 1.20$	$\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
1919 reflections	$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$
144 parameters	

All H atoms were located in difference maps. H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic and pyrazole) or 0.98 Å (methyl), and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl group, which was permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. The coordinates of H atoms bonded to N atoms were freely refined, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, giving N–H distances of 0.89 (3) and 0.92 (3) Å. Data validation after the initial refinements appeared to be complete indicated that the refinement should be handled as a nonmerohedral twin, with twinning matrix (1.000, 0.000, 0.682/0.000, –1.000, 0.000/0.000, 0.000,

Table 1

Selected torsion angles ($^\circ$).

N2–N1–C11–O11	–169.68 (18)	N1–C11–C111–C112	56.0 (3)
N2–N1–C11–C111	10.0 (3)		

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

C_g is the centroid of the C111–C116 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N51–H51A···N2 ⁱ	0.89 (2)	2.20 (2)	3.048 (2)	158 (2)
N51–H51B···O11	0.92 (3)	2.05 (2)	2.749 (3)	132 (2)
C115–H115···O11 ⁱⁱ	0.95	2.55	3.387 (3)	147
C113–H113··· C_g^{iii}	0.95	2.84	3.514 (2)	128

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{5}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

–1.000). From the original data set (12071 measured reflections, $R_{\text{int}} = 0.0534$), a modified data set was prepared using the TwinRotMat option in *PLATON* (Spek, 2009), and this was used in conjunction with the HKLF5 option in *SHELXL97* (Sheldrick, 2008), giving twin fractions of 0.175 (3) and 0.825 (3).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3230). Services for accessing these data are described at the back of the journal.

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