

A hydrogen-bonded chain of rings in 5-amino-1-(4-methoxybenzoyl)-3-methylpyrazole and a three-dimensional hydrogen-bonded framework in 5-amino-3-methyl-1-(2-nitrobenzoyl)pyrazole

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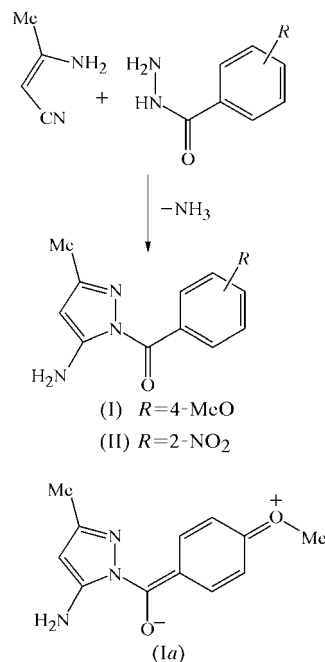
The molecules of 5-amino-1-(4-methoxybenzoyl)-3-methylpyrazole, C₁₂H₁₃N₃O₂, (I), and 5-amino-3-methyl-1-(2-nitrobenzoyl)pyrazole, C₁₁H₁₀N₄O₃, (II), both contain intramolecular N—H···O hydrogen bonds. The molecules of (I) are linked into a chain of rings by a combination of N—H···N and N—H···π(arene) hydrogen bonds, while those of (II) are linked into a three-dimensional framework structure by N—H···N and C—H···O hydrogen bonds.

Comment

5-Aminopyrazoles containing two or more functionalized substituent groups are versatile intermediates for the synthesis of polyheterocyclic systems (Bauer & Mahajanshetti, 1967; Tominaga *et al.*, 1995), which are themselves of interest because of their potential bioactivity. We describe here the structures of two new 5-amino-1-arylpazoles, 5-amino-1-(4-methoxybenzoyl)-3-methylpyrazole, (I) (Fig. 1), and 5-amino-3-methyl-1-(2-nitrobenzoyl)pyrazole, (II) (Fig. 2), which were both initially prepared for synthetic purposes using reactions between 3-aminocrotononitrile and an appropriately-substituted aroylhydrazide in the presence of sodium acetate.

The molecules of compounds (I) and (II) both contain an intramolecular N—H···O hydrogen bond (Tables 1 and 2), generating in each case an *S*(6) motif (Bernstein *et al.*, 1995). These interactions may have some influence in controlling the molecular conformations, where the carbonyl groups are nearly coplanar with the adjacent pyrazole rings, as shown by the key torsion angles (Table 1). On the other hand, the

benzene rings are twisted out of this plane; while the methoxy atom C141 in (I) is effectively coplanar with the benzene ring, the nitro group in (II) makes a dihedral angle of 23.8 (2)° with the adjacent benzene ring.



Two factors may contribute to the difference between the benzene ring conformations in (I) and (II). First, there is a short intramolecular C—H···N contact in (I) which, although probably not appropriately described as a hydrogen bond, may nonetheless be a weakly attractive interaction. Secondly, detailed comparison of the bond distances in the benzene rings of (I) and (II) (Table 3) shows that in (I) the C12—C13 and C15—C16 distances are slightly, but significantly, shorter than the remainder, indicative of a modest degree of quinoid character; the C1—C11 bond is significantly shorter in (I) than in (II), while C1—O1 is possibly longer in (I); and the C14—O14 bond is slightly short for its type [mean value (Allen *et al.*, 1987) = 1.370 Å and lower quartile value = 1.363 Å]. The resulting polarized form, (Ia), would enhance the barrier to rotation about the C1—C11 bond in compound (I). The remaining bond distances and inter-bond angles show no unusual features.

The molecules of (I) are linked by a combination of N—H···N and N—H···π(arene) hydrogen bonds into a chain of rings generated by translation along the [100] direction (Fig. 3). Within this chain, the N—H···N interaction generates a *C*(5) motif. The only direction-specific interaction of possible structural significance between adjacent chains is a rather long C—H···O contact between molecules in pairs of chains related by inversion.

By contrast, the molecules of (II) are linked by one N—H···N and three C—H···O hydrogen bonds, all involving nitro O atoms as the acceptors. It is sufficient to consider the framework formation in terms of just two hydrogen bonds, the N—H···N interaction and the shortest of the C—H···O interactions. Each of these two hydrogen bonds, acting inde-

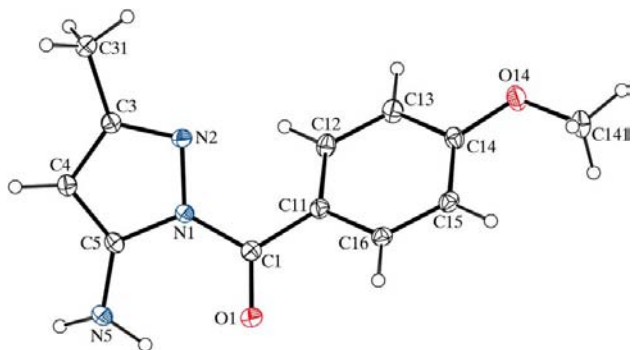


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

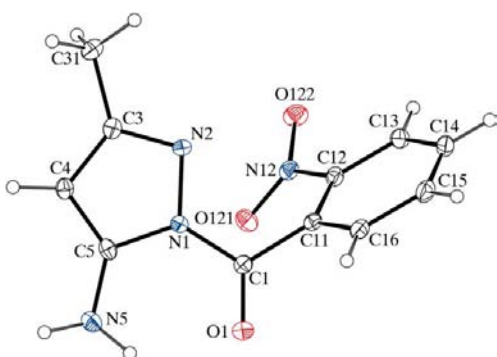


Figure 2
A molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

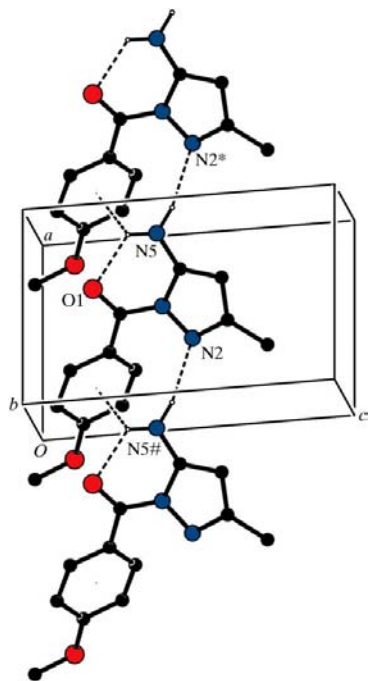


Figure 3
Part of the crystal structure of (I), showing the formation of a chain of rings along [100] built from N—H...O, N—H...N and N—H... π (arene) hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(-1 + x, y, z)$, respectively.

pendently, forms a simple chain, while the combination of the two interactions generates a third chain motif.

Amino atom N5 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H5B, to ring atom N2 in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, z)$, so forming a $C(5)$ chain running parallel to the [100] direction and consisting of molecules related by the a -glide plane at $y = \frac{3}{4}$ (Fig. 4). In the second chain motif, atom C16 at (x, y, z) acts as a hydrogen-bond donor to nitro atom O122 in the molecule at $(1 - x, 1 - y, -\frac{1}{2} + z)$, so forming a $C(6)$ chain running parallel to the [001] direction and consisting of molecules related by the 2_1 screw axis along $(\frac{1}{2}, \frac{1}{2}, z)$ (Fig. 5). Finally, the combination of these two hydrogen bonds, acting alternately, generates a $C_2^2(15)$ chain running parallel to the $[01\bar{1}]$ direction (Fig. 6). The combination of the chains along [100], $[01\bar{1}]$ and [001] is sufficient to generate a continuous three-dimensional framework structure. This framework may be modestly reinforced by the two hydrogen bonds involving C13 and C15, which generate, respectively, a $C(5)$ chain parallel to [100] and a $C(7)$ chain parallel to $[01\bar{1}]$.

Hence, in each of (I) and (II), an N—H...N hydrogen bond forms a $C(5)$ chain parallel to [100]. However, the hydrogen-bonded structure of (II) is much more complex than that of (I) by virtue of the presence of the nitro group with its two quite polar hydrogen-bond acceptors. It is noteworthy that the carbonyl O atom plays no significant role in the intermolecular hydrogen bonding in either compound, and that the resulting deficiency of hydrogen-bond acceptors in (I) leads to the formation of an N—H... π (arene) interaction.

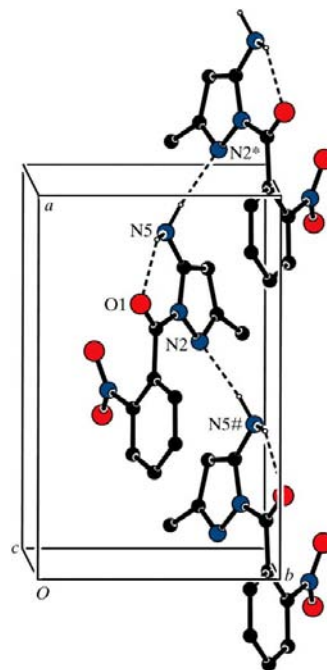


Figure 4
Part of the crystal structure of (II), showing the formation of a chain of rings along [100] containing N—H...O and N—H...N hydrogen bonds only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, z)$ and $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, respectively.

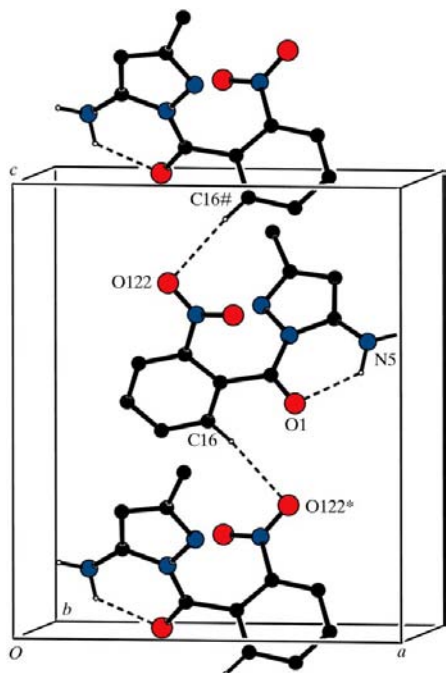


Figure 5
Part of the crystal structure of (II), showing the formation of a chain along [001] containing N—H...O and C—H...O hydrogen bonds only. For the sake of clarity, H atoms bonded to C atoms and not involved in the hydrogen bonding have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1-x, 1-y, -\frac{1}{2}+z)$ and $(1-x, 1-y, \frac{1}{2}+z)$, respectively.

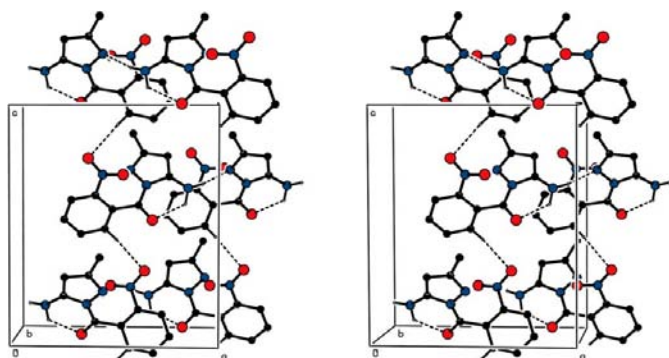


Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a chain along [011] containing N—H...O, N—H...N and C—H...O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms and not involved in the hydrogen bonding have been omitted.

Experimental

Mixtures containing equimolar quantities (2 mmol of each component) of 3-aminocrotononitrile, an aroylhydrazide, *viz.* 4-methoxybenzohydrazide for (I) and 2-nitrobenzohydrazide for (II), and sodium acetate trihydrate in ethanol (50 ml) were heated under reflux for 2 h. The reaction mixtures were allowed to cool to ambient temperature, and were then poured into water (50 ml) with vigorous stirring; stirring was continued for 20 min. The resulting solid products were collected by filtration and recrystallized from ethanol

to provide crystals of (I) and (II) suitable for single-crystal X-ray diffraction. For (I), colourless crystals, m.p. 354–355 K, yield 90%; MS (30 eV) m/z (%) 231 (16, M^+), 135 (100), 107 (13), 77 (20). For (II), yellow crystals, m.p. 490–491 K, yield 97%; MS (70 eV) m/z (%) 246 (34, M^+), 151 (66), 121 (70), 76 (85), 51 (91), 41 (100).

Compound (I)

Crystal data

$C_{12}H_{13}N_3O_2$	$\gamma = 82.83 (3)^\circ$
$M_r = 231.25$	$V = 571.1 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.1920 (15) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.192 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 10.546 (2) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\alpha = 73.69 (2)^\circ$	$0.50 \times 0.35 \times 0.27 \text{ mm}$
$\beta = 85.634 (17)^\circ$	

Data collection

Bruker–Nonius KappaCCD diffractometer	13948 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2614 independent reflections
$T_{\min} = 0.958, T_{\max} = 0.975$	1936 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	156 parameters
$wR(F^2) = 0.142$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
2614 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

Cg1 is the centroid of the C11–C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5A...O1	0.96	2.08	2.763 (2)	126
N5—H5A...Cg1 ⁱ	0.96	2.71	3.365 (2)	126
N5—H5B...N2 ⁱ	0.97	2.21	3.160 (2)	167
C12—H12...N2	0.95	2.49	2.889 (2)	105
C16—H16...O1 ⁱⁱ	0.95	2.58	3.317 (2)	135

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

Compound (II)

Crystal data

$C_{11}H_{10}N_4O_3$	$V = 1087.1 (3) \text{ \AA}^3$
$M_r = 246.23$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 11.4212 (15) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 7.1787 (14) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 13.2595 (10) \text{ \AA}$	$0.55 \times 0.51 \times 0.45 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD diffractometer	23596 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1309 independent reflections
$T_{\min} = 0.943, T_{\max} = 0.950$	1197 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	1 restraint
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
1309 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
165 parameters	

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N5—H5A...O1	0.94	2.12	2.788 (3)	127
N5—H5B...N2 ⁱ	0.95	2.10	3.033 (3)	169
C13—H13...O121 ⁱⁱ	0.95	2.54	3.457 (3)	161
C15—H15...O122 ⁱⁱⁱ	0.95	2.54	3.409 (4)	152
C16—H16...O122 ^{iv}	0.95	2.50	3.410 (3)	161

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

Table 3
Selected distances (Å) and torsion angles (°) for compounds (I) and (II).

	(I)	(II)
C1—O1	1.224 (2)	1.219 (3)
C1—C11	1.481 (2)	1.501 (4)
C11—C12	1.401 (2)	1.392 (4)
C12—C13	1.376 (2)	1.383 (4)
C13—C14	1.401 (2)	1.386 (4)
C14—C15	1.392 (2)	1.385 (4)
C15—C16	1.383 (2)	1.397 (4)
C16—C11	1.398 (2)	1.393 (4)
C14—O14	1.359 (2)	—
N2—N1—C1—O1	162.24 (14)	174.0 (2)
N2—N1—C1—C11	−17.6 (2)	−1.9 (3)
N1—C1—C11—C12	−34.3 (2)	−63.6 (3)
C13—C14—O14—C141	−179.22 (15)	—
C11—C12—N12—O121	—	−23.1 (3)

Crystals of (I) are triclinic; the space group $P\bar{1}$ was selected and confirmed by the structure analysis. For (II), the systematic absences permitted $Pna2_1$ or $Pnam$ ($= Pnma$) as possible space groups; $Pna2_1$ was selected and confirmed by the structure analysis. 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 distances of 0.95 (aromatic and pyrazole) or 0.98 Å (methyl) and $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for methyl groups and $k = 1.2$ for all other H atoms. The H atoms bonded to N atoms were permitted to ride at the positions deduced from the difference maps, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, giving N—H distances in the range 0.94–0.97 Å. In the absence of significant resonant scattering, it was not possible to determine the correct orientation of the structure of (II)

relative to the polar-axis direction; accordingly, the Friedel-equivalent reflections were merged prior to the final cycles of refinement.

For both compounds, data collection: *COLLECT* (Hooft, 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: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3064). Services for accessing these data are described at the back of the journal.

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