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Hydrogen-bonded chains of rings in methyl 4-[(5-methyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate and hydrogen-bonded sheets in methyl 1-(5-methyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole-5-carboxylate

Jaime Portilla,[a] Ernesto G. Mata,[b] Manuel Nogueras,[c] Justo Cobo,[c] John N. Low[d] and Christopher Glidewell[e]*

[a]Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]CONICET–Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Rosario, Suipacha 531, S2002LRK, Argentina, [c]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [d]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [e]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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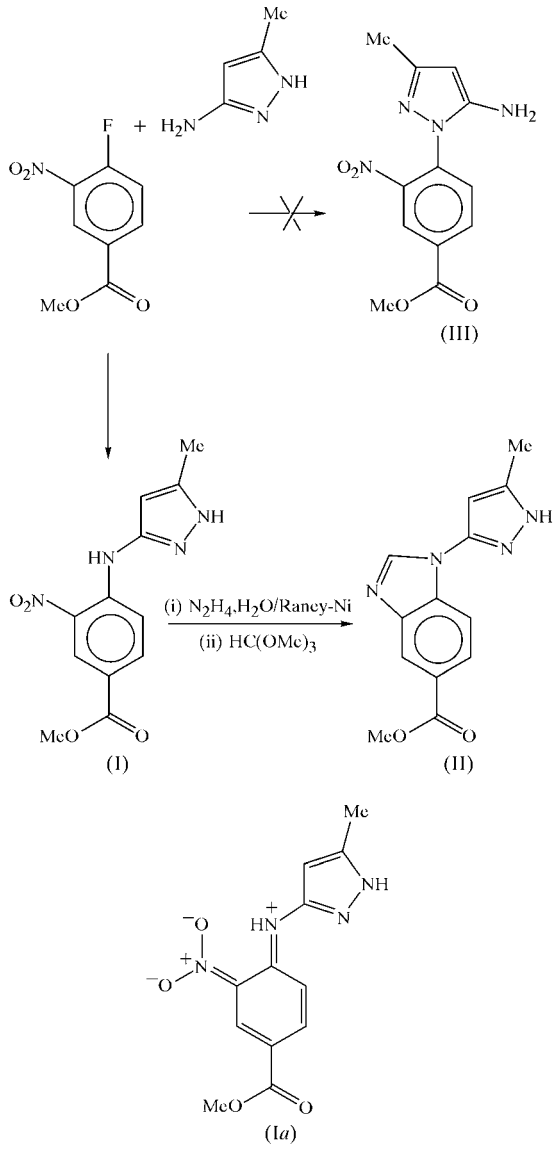
Molecules of methyl 4-[(5-methyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate, $C_{12}H_{12}N_4O_4$, (I), exhibit a polarized (charge-separated) structure in the nitroaniline portion. The molecules are linked into chains of edge-fused $R_2^2(16)$ and $R_2^2(22)$ rings by a combination of N—H···O(carbonyl) and C—H···O(nitro) hydrogen bonds. Methyl 1-(5-methyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole-5-carboxylate, $C_{13}H_{12}N_4O_2$, (II), which is readily formed from (I) by reduction followed by ring formation, crystallizes with $Z' = 2$ in the space group $P\overline{1}$. Each of the two independent molecular types is linked into sheets of $R_4^4(28)$ rings by a combination of N—H···N and C—H···O(carbonyl) hydrogen bonds.

Comment

As part of our continuing study of biologically active molecules containing fused pyrazole systems, we have attempted the preparation of pyrazolo[1,5-*a*][1,3,5]benzotriazepine, which is useful for drug, agrochemical or dye intermediates (Tachibana & Kaneko, 1989), by means of a simple three-step procedure from 3-amino-5-methyl-1*H*-pyrazole and methyl 4-fluoro-3-nitrobenzoate. However, the first step of that procedure in fact provided not the anticipated compound, (III) (see scheme), but instead the isomeric compound, methyl 4-[(5-methyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate, (I), which afforded methyl 1-(5-methyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole-5-carboxylate, (II), as the final product instead of the expected pyrazolo[1,5-*a*][1,3,5]benzotriazepine. We report here the molecular and supramolecular structures of compounds (I) and (II).



The molecule of compound (I) (Fig. 1) is almost planar, as shown by the key torsion angles (Table 1), and this is possibly influenced by the intramolecular hydrogen bond (Table 2). Within the aryl ring, the C1—C2 and C5—C6 bonds are significantly shorter than the remainder. In addition, the C3—N3 bond is short for its type (Allen *et al.*, 1987), while the N—O bonds are both long, and the C4—N45 bond is significantly shorter than N45—C45. These observations indicate that the charge-separated form (I*a*) (see scheme) is a significant contributor to the overall molecular electronic structure.

Compound (II) crystallizes with $Z' = 2$, and the molecular geometries of the two independent molecules (Fig. 2) are very similar. As for compound (I), the molecules of (II) are almost planar. The dihedral angle between the pyrazole and imidazole rings is 5.5 (2)° in molecule *A* (containing N11) and 5.9 (2)° in molecule *B* (containing N31). There is marked bond fixation in the imidazole rings (Table 3), with only a modest variation in the C—C distances in the aryl rings, indicating that

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the form shown in the scheme is the appropriate representation for this compound.

The molecules of compound (I) are linked into chains of edge-fused rings by a combination of N—H···O(carbonyl) and C—H···O(nitro) hydrogen bonds (Table 2). Pyrazole atom N42 in the molecule at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O11 in the molecule at ($1-x$, $1-y$, $1-z$), so generating by inversion an $R_2^2(22)$ (Bernstein *et al.*, 1995) ring centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and atom C44 at (x, y, z) acts as hydrogen-bond donor to nitro atom O31 in the molecule at

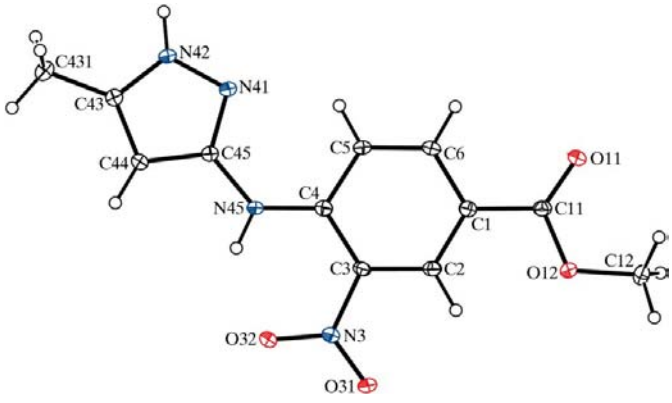

Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

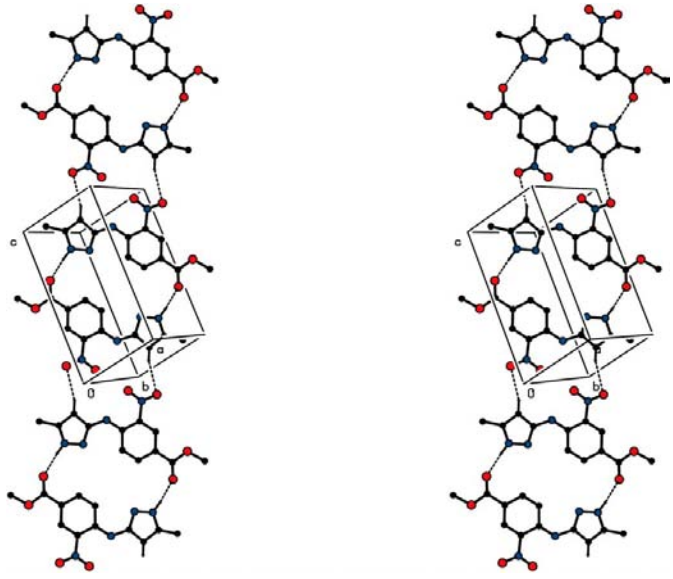

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of edge-fused $R_2^2(16)$ and $R_2^2(22)$ rings along [101]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

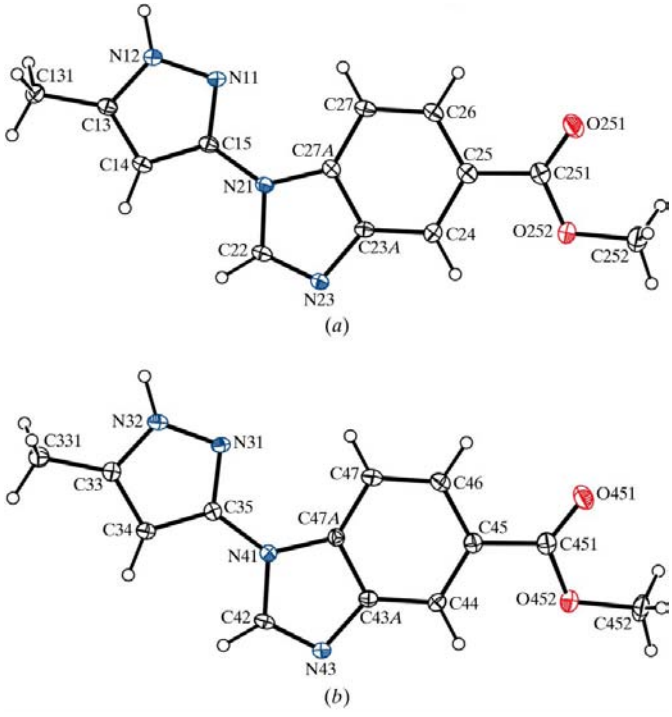

Figure 2
The two independent molecules in compound (II), *viz*. (*a*) a type *A* molecule and (*b*) a type *B* molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

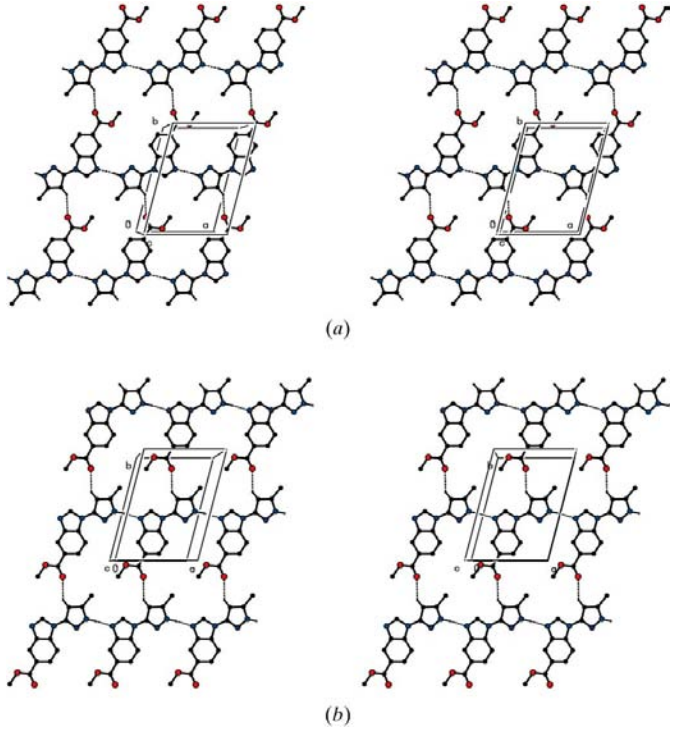

Figure 4
Stereoviews of parts of the crystal structure of compound (II), showing the formation of sheets of $R_4^4(28)$ rings parallel to (001) for (*a*) a sheet of type *A* molecules and (*b*) a sheet of type *B* molecules. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

$(-x, 1-y, -z)$, so generating a second centrosymmetric ring, this time of $R_2^2(16)$ type and centred at $(0, \frac{1}{2}, 0)$. The combination of these two motifs generates a chain of edge-fused rings running parallel to the [101] direction, with $R_2^2(16)$ rings centred at $(n, \frac{1}{2}, n)$ (n = zero or integer) alternating with $R_2^2(22)$ rings centred at $(n+\frac{1}{2}, \frac{1}{2}, n+\frac{1}{2})$ (n = zero or integer) (Fig. 3). Within the $R_2^2(16)$ ring, there is a short contact between the two atoms of type O32, separated by only 2.875 (2) Å.

In the crystal structure of compound (II), there are two virtually identical substructures, each containing only one of the two independent molecules and each built from a combination of N—H···N and C—H···O(carbonyl) hydrogen bonds (Table 4). Atoms N12 and C14 in the type *A* molecule at (x, y, z) act as hydrogen-bond donors to, respectively, imidazole atom N23 in the type *A* molecule at $(-1+x, y, z)$ and carbonyl atom O251 in the type *A* molecule at $(x, -1+y, z)$, so generating by translation an almost planar sheet parallel to (001) in the domain $0.05 < z < 0.20$ and containing a single $R_4^4(28)$ ring (Fig. 4*a*). This sheet lies in the domain $0.05 < z < 0.20$, with an inversion-related sheet of type *A* molecules in the domain $0.80 < z < 0.95$. A very similar sheet is built from type *B* molecules (Fig. 4*b* and Table 4), and inversion-related pairs of type *B* sheets lie in the domains $0.36 < z < 0.43$ and $0.57 < z < 0.64$. Thus, the overall structure consists of a millefeuille-style stack of almost planar sheets, with pairs of sheets of type *A* molecules alternating with pairs of type *B* molecules. However, there are no direction-specific interactions between adjacent sheets. The only stacking contacts between adjacent sheets all involve the imidazole rings. They exhibit very strong bond fixation and hence are non-aromatic, so that such contacts are unlikely to be energetically and hence structurally significant.

Experimental

For the synthesis of compound (I), a solution of 3-amino-5-methyl-1*H*-pyrazole (2 mmol) and methyl 4-fluoro-3-nitrobenzoate (2 mmol) in dimethyl sulfoxide (2 ml) was stirred at 298 K for 2 h. The resulting solid product was collected by filtration and washed with methanol (10 ml) to give methyl 4-[(5-methyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate, (I). Crystallization of the compound from dimethyl sulfoxide gave orange crystals suitable for single-crystal X-ray diffraction (m.p. 498–499 K; yield 93%). MS (*m*/*z*, %): 276 (100, M^+), 245 (12). For the synthesis of compound (II), a mixture of compound (I) (1 mmol), hydrazine hydrate (3 mmol) and Raney Nickel (50 mg) in methanol (10 ml) was heated under reflux with magnetic stirring for 15 min. The Raney Nickel was removed by filtration of the hot solution and the filtrate was then cooled. The resulting solid was collected by filtration and recrystallized from methanol to yield the intermediate methyl 3-amino-4-[(5-methyl-1*H*-pyrazol-3-yl)amino]-benzoate as a white solid (m.p. 483–484 K; yield 92%). MS (*m*/*z*, %): 246 (33, M^+), 215 (100). A mixture of this intermediate (1 mmol) and trimethyl orthoformate (3 ml) was heated under reflux with magnetic stirring for 1 h. The mixture was then cooled and the resulting solid product was collected by filtration and recrystallized from dimethyl sulfoxide to yield compound (II) as colourless crystals suitable for single-crystal X-ray diffraction (m.p. 518–519 K; yield 90%). MS (*m*/*z*, %): 256 (93, M^+), 225 (100), 197 (24).

Compound (I)

Crystal data

$C_{12}H_{12}N_4O_4$
$M_r = 276.26$
Triclinic, $P\overline{1}$
$a = 5.9233$ (3) Å
$b = 8.8858$ (6) Å
$c = 11.7819$ (6) Å
$\alpha = 85.690$ (4)°
$\beta = 83.500$ (4)°
$\gamma = 84.015$ (3)°
$V = 611.51$ (6) Å^3
$Z = 2$
$D_x = 1.500$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Lath, orange
0.42 × 0.26 × 0.15 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.959$, $T_{max} = 0.983$
12027 measured reflections
2829 independent reflections
2117 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.128$
$S = 1.06$
2829 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.097P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.378 (2)	C6—C1	1.408 (2)
C2—C3	1.391 (2)	C3—N3	1.4512 (18)
C3—C4	1.420 (2)	N3—O31	1.2337 (16)
C4—C5	1.426 (2)	N3—O32	1.2423 (16)
C5—C6	1.367 (2)	C4—N45	1.3556 (18)
C2—C1—C11—O12	−2.0 (2)	C2—C3—N3—O31	−3.7 (2)
C1—C11—O12—C12	−178.75 (12)	C4—N45—C45—N41	6.5 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N45—H45···O32	0.88	1.92	2.6221 (16)	136
N42—H42···O11^{i}	0.88	1.98	2.8400 (17)	164
C44—H44···O31^{ii}	0.95	2.49	3.4180 (18)	164

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

Compound (II)

Crystal data

$C_{13}H_{12}N_4O_2$
$M_r = 256.27$
Triclinic, $P\overline{1}$
$a = 8.3646$ (3) Å
$b = 11.5735$ (6) Å
$c = 12.7953$ (7) Å
$\alpha = 88.328$ (3)°
$\beta = 88.526$ (3)°
$\gamma = 75.362$ (3)°
$V = 1197.75$ (10) Å^3
$Z = 4$
$D_x = 1.421$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.46 × 0.45 × 0.40 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.945, T_{max} = 0.961
25906 measured reflections
5488 independent reflections
3945 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.7°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.173
S = 1.20
5488 reflections
347 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 1.6885P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N21—C22	1.385 (3)	N41—C42	1.380 (3)
C22—N23	1.301 (3)	C42—N43	1.295 (3)
N23—C23*A*	1.392 (3)	N43—C43*A*	1.395 (3)
C23*A*—C27*A*	1.400 (4)	C43*A*—C47*A*	1.398 (4)
C27*A*—N21	1.393 (3)	C47*A*—N41	1.395 (3)
N11—C15—N21—C22	−173.5 (2)	N31—C35—N41—C42	−173.1 (2)
C24—C25—C251—O252	15.7 (4)	C44—C45—C451—O452	14.2 (4)
C25—C251—O252—C252	−177.1 (2)	C45—C451—O452—C452	−177.1 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12···N23^{i}	0.96	1.88	2.836 (4)	173
N32—H32···N43^{ii}	0.96	1.88	2.840 (4)	174
C14—H14···O251^{iii}	0.95	2.46	3.269 (3)	143
C34—H34···O451^{iv}	0.95	2.45	3.248 (3)	141

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

Crystals of both (I) and (II) are triclinic. For each compound, the space group $P\overline{1}$ was selected and confirmed by the successful structure refinement. All H atoms were located in difference maps and then treated as riding atoms. For H atoms bonded to C atoms, C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic and heteroaromatic H atoms or C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. H atoms bonded to N atoms were permitted to ride at the N—H distances deduced from the difference maps [0.88 Å in (I) and 0.96 Å in (II)], with U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *COLLECT* (Nonius, 1999) for (I); *KappaCCD Server Software* (Nonius, 1997) for (II). Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* for (I); *DENZO–SMN* for (II). Data reduction: *DENZO* and *COLLECT* for (I); *DENZO–SMN* for (II). Program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997) for (I); *SHELXS97* for (II). Program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997) for (I); *SHELXL97* for (II). For both compounds, 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: SQ3044). Services for accessing these data are described at the back of the journal.

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