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Two isomeric reaction products: hydrogen-bonded sheets in methyl 4-(5-amino-3-phenyl-1*H*-pyrazol-1-yl)-3-nitrobenzoate and hydrogen-bonded chains of edge-fused rings in methyl 3-nitro-4-[(5-phenyl-1*H*-pyrazol-3-yl)amino]benzoate

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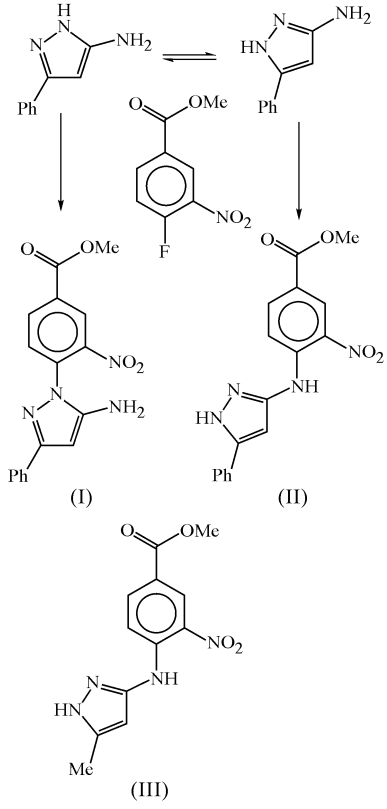
In methyl 4-(5-amino-3-phenyl-1*H*-pyrazol-1-yl)-3-nitrobenzoate, $C_{17}H_{14}N_4O_4$, the molecules are linked into complex sheets by a combination of N—H···N, N—H···O and C—H···O hydrogen bonds. In the isomeric methyl 3-nitro-4-[(5-phenyl-1*H*-pyrazol-3-yl)amino]benzoate, molecules exhibit a polarized molecular–electronic structure and are linked into chains of edge-fused rings by a combination of N—H···O and C—H···O hydrogen bonds.

Comment

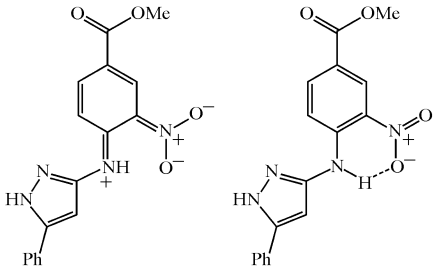
We report here the molecular and supramolecular structures of the title compounds, (I) and (II) (Figs. 1 and 2), which are the products from the two alternative pathways for the reaction of methyl 4-fluoro-3-nitrobenzoate with 5-amino-3-phenylpyrazole. The reaction in which atom N1 of the pyrazole ring acts as the nucleophile generates compound (I), while compound (II) is formed in the reaction in which the amino N atom of the pyrazole ring acts as the nucleophile (see reaction scheme below). The product mixture appears to be very sensitive to the polarity of the solvent employed; in a 1:7 *v*/*v* mixture of dimethyl sulfoxide and methanol as the solvent, compounds (I) and (II) are formed in equimolar quantities, but compound (II) was the sole product isolated from the corresponding reaction in neat dimethyl sulfoxide. An analogous reaction in neat dimethyl sulfoxide using 5-amino-3-methylpyrazole in place of 5-amino-3-phenylpyrazole generated only compound (III), the direct analogue of compound (II) (Portilla *et al.*, 2007). Compound (I) and its analogues should prove to be useful for the synthesis of pyrazolobenzotriazepines, which have applications as drug, agrochemical and dye intermediates (Tachibana & Kaneko, 1989).



In (I), the C—C bond distances within the aryl ring fall in the range 1.381 (3)–1.400 (3) Å, consistent with essentially unperturbed aromatic delocalization, while the remaining bond distances are all typical of their types (Allen *et al.*, 1987). By contrast, in (II), the C53—C54 and C55—C56 bond distances are both significantly shorter than the remaining bonds in this ring (Table 2), while the C52—N52 bond is short for its type. In addition, the N52—O521 bond, which participates in an intramolecular hydrogen bond (Table 3), is long for its type. These observations, taken together, provide evidence for the polarized forms (II*a*) and (II*b*) as important contributors of the overall molecular–electronic structure of compound (II). A similar conclusion was drawn from the intramolecular geometry of compound (III) (Portilla *et al.*, 2007).

The molecules of (I) are linked into sheets by a combination of N—H···N, N—H···O and C—H···O hydrogen bonds (Table 1), and the formation of the sheet is readily analyzed in terms of two simple one-dimensional substructures. Atoms N5 and C16 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors to pyrazole atom N2 and nitro atom O121, respectively, both in the molecule at $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, so forming a $C(5)C(6)[R_2^2(13)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 3). In the second substructure,

atom N5 at (x, y, z) acts as a hydrogen-bond donor to ketonic atom O141 in the molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, so forming a simple $C(10)$ chain running parallel to the [101] direction and generated by the *n*-glide plane at $y = \frac{3}{4}$ (Fig. 4). The combination of the chains parallel to [010] and [101] generates a sheet parallel to $(10\bar{1})$, but there are no significant direction-specific interactions between adjacent sheets.



(II*a*) (II*b*)

In addition to the intramolecular N—H···O hydrogen bond, the structure of (II) contains three significant intermolecular hydrogen bonds (Table 3), which combine to generate a one-dimensional hydrogen-bonded structure of considerable elegance. Atoms N2 and C36 in the molecule at (x, y, z) both act as hydrogen-bond donors to carbonyl atom O541 in the molecule at $(1 - x, 2 - y, 1 - z)$, thereby generating by inversion a cyclic dimer containing concentric $R_2^2(22)$ and $R_2^2(26)$ rings, embedding two symmetry-related $R_2^1(7)$ rings (Fig. 5). In addition, atom C53 in the molecule at

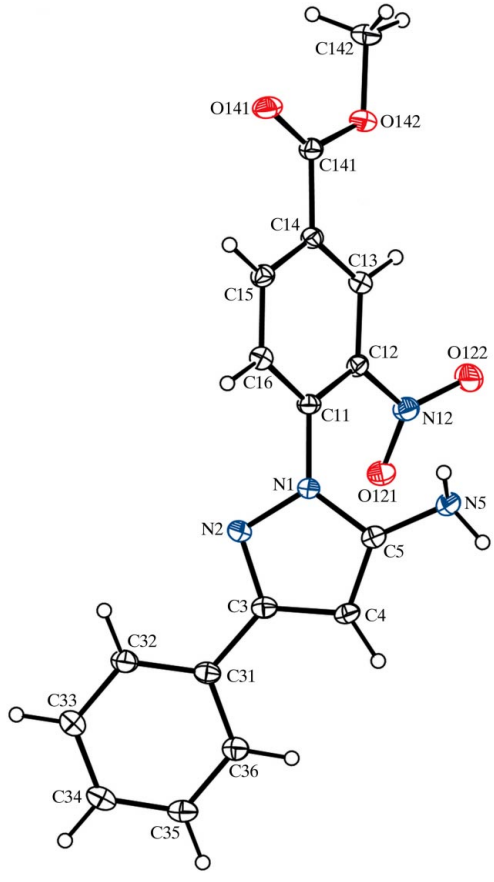


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

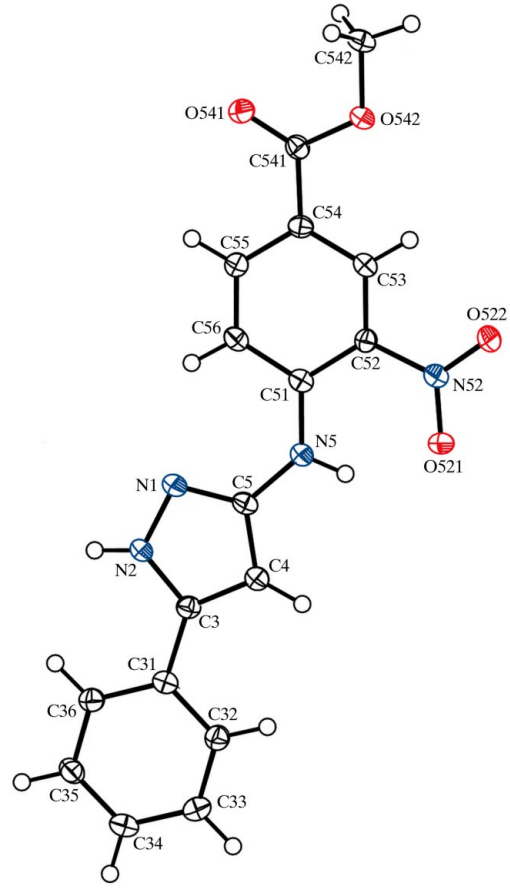


Figure 2
A molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

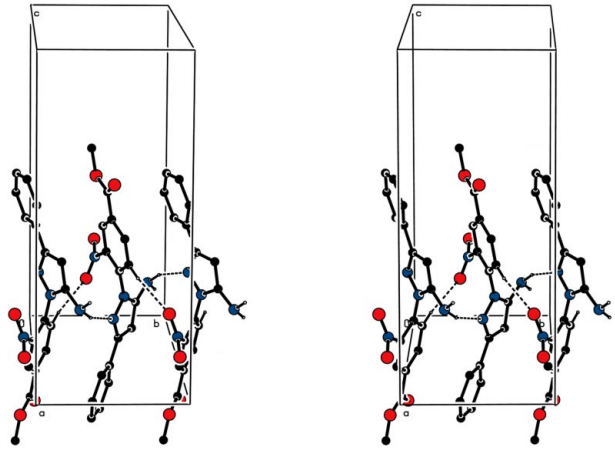


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings along [010]. For the sake of clarity, H atoms bonded to C atoms not involved in the motif shown have been omitted.

(x, y, z) acts as a hydrogen-bond donor to nitro atom O522 in the molecule at ($1 - x$, y, $\frac{1}{2} - z$), so forming a further cyclic motif, this time an $R_2^2(10)$ ring generated by the twofold rotation axis along ($\frac{1}{2}$, y, $\frac{1}{4}$). Propagation of these two motifs by successive inversion and rotation then generates a complex chain of edge-fused rings running parallel to the [001] direction (Fig. 6). Two chains of this type, related to one another by the C-centring operation, pass through each unit cell, but there are no significant direction-specific interactions between adjacent chains.

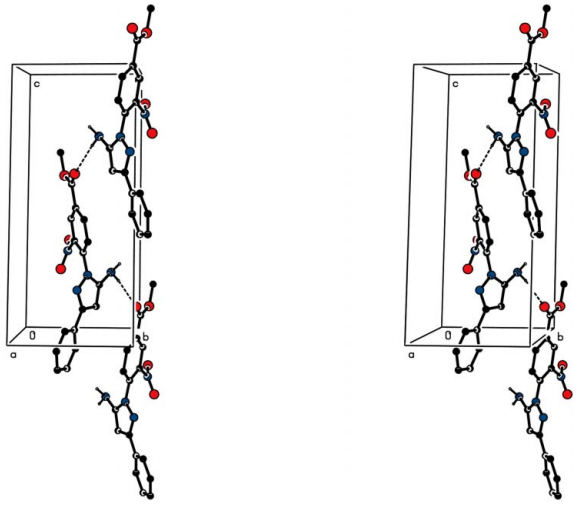


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(10)$ chain along [101]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

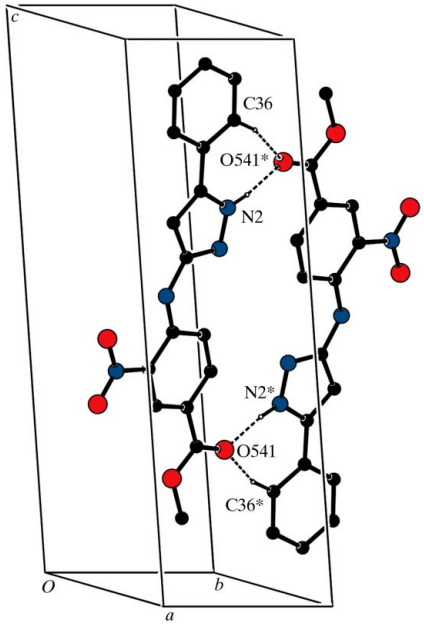


Figure 5
Part of the crystal structure of (II), showing the formation of a centrosymmetric hydrogen-bonded dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1 - x$, $2 - y$, $1 - z$).

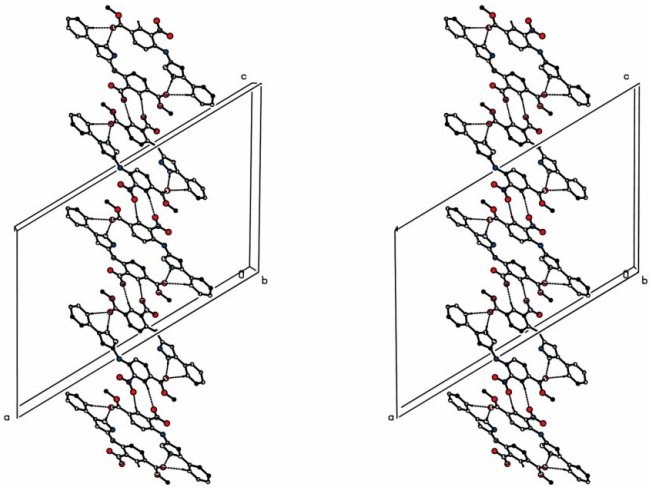


Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain of edge-fused rings along [001]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

In contrast with the complexity of the chain of rings formed by (II), the methyl analogue (III) forms a simpler chain of edge-fused rings containing alternating $R_2^2(16)$ and $R_2^2(22)$ rings, both generated by inversion using C—H···O and N—H···O hydrogen bonds, respectively (Portilla *et al.*, 2007).

Experimental

A solution of 5-amino-3-phenyl-1*H*-pyrazole (2 mmol) and methyl 4-fluoro-3-nitrobenzoate (2 mmol) in dimethyl sulfoxide–methanol (8 ml of a 1:7 *v*/*v* mixture) was heated under reflux with magnetic stirring for 10 min. The mixture was cooled to ambient temperature and the resulting solid was collected by filtration and washed with methanol (3 × 6 ml). Recrystallization of the crude reaction product from dimethyl sulfoxide gave compound (II). The resulting filtrate was evaporated under reduced pressure, and the resulting solid was crystallized successively from methanol and dimethyl sulfoxide to give compound (I). Compound (I) was obtained in 46% yield according to the above procedure as yellow crystals suitable for single-crystal X-ray diffraction (m.p. 476–477 K). Analysis found: C 59.2, H 4.3, N 16.2%; $C_{17}H_{14}N_4O_4$ requires: C 60.3, H 4.2, N 16.6%. Compound (II) was obtained in 48% yield according to the above procedure as orange crystals suitable for single-crystal X-ray diffraction (m.p. 530–531 K), and as the sole product when a similar reaction was carried out in neat dimethyl sulfoxide (2 ml) at 298 K for 2 h (yield 90%). Analysis found: C 60.2, H 4.7, N 16.4%; $C_{17}H_{14}N_4O_4$ requires: C 60.3, H 4.2, N 16.6%.

Compound (I)

Crystal data

$C_{17}H_{14}N_4O_4$
M_r = 338.32
Monoclinic, $P2_1/n$
a = 12.3516 (8) Å
b = 7.5202 (4) Å
c = 17.1564 (13) Å
β = 100.699 (5)°
V = 1565.90 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 (2) K
0.55 × 0.35 × 0.19 mm

Data collection

Bruker–Nonius KappaCCD diffractometer	37526 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3597 independent reflections
T_{min} = 0.951, T_{max} = 0.980	2266 reflections with $I > 2\sigma(I)$
	R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056	227 parameters
$wR(F^2)$ = 0.178	H-atom parameters constrained
S = 1.08	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
3597 reflections	$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···N2^{i}	0.87	2.33	3.131 (3)	154
N5—H5B···O141^{ii}	0.87	2.18	3.024 (3)	163
C16—H16···O121^{i}	0.95	2.39	3.304 (3)	161

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

Compound (II)

Crystal data

$C_{17}H_{14}N_4O_4$	V = 2988.1 (7) Å^3
M_r = 338.32	Z = 8
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 31.0506 (4) Å	μ = 0.11 mm^{-1}
b = 5.4210 (11) Å	T = 120 (2) K
c = 20.7251 (12) Å	0.50 × 0.29 × 0.28 mm
β = 121.071 (6)°	

Data collection

Bruker–Nonius KappaCCD diffractometer	33526 measured reflections
	3420 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	2488 reflections with $I > 2\sigma(I)$
T_{min} = 0.947, T_{max} = 0.967	R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048	227 parameters
$wR(F^2)$ = 0.134	H-atom parameters constrained
S = 1.11	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
3420 reflections	$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

C51—N5	1.364 (2)	C55—C56	1.370 (3)
C51—C52	1.425 (2)	C56—C51	1.419 (3)
C52—C53	1.391 (2)	C52—N52	1.448 (2)
C53—C54	1.378 (3)	N52—O521	1.2522 (19)
C54—C55	1.404 (2)	N52—O522	1.2262 (19)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···O521	0.87	1.89	2.600 (2)	137
N2—H2···O541^{i}	0.87	1.96	2.828 (2)	171
C36—H36···O541^{i}	0.95	2.36	3.266 (3)	159
C53—H53···O522^{ii}	0.95	2.54	3.487 (2)	173

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

For (I), the space group $P2_1/n$ was uniquely assigned from the systematic absences. For (II), the systematic absences permitted Cc and $C2/c$ as possible space groups; $C2/c$ was selected and confirmed by the subsequent structure analysis. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were allowed to ride in geometrically idealized positions, with C—H distances of 0.95 (aromatic and pyrazole) or 0.98 Å (methyl), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups and 1.2 for all other H atoms bonded to C atoms. H atoms bonded to N atoms were permitted to ride at the positions deduced from difference maps, all giving N—H distances of 0.87 Å, with U_{iso}(H) = 1.2U_{eq}(N).

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) and *WinGX* (Farrugia, 1999); 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: SK3149). Services for accessing these data are described at the back of the journal.

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