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

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In methyl 4-(5-amino-3-phenyl-1H-pyrazol-1-yl)-3-nitrobenzoate, C_{17}H_{14}N_{4}O_{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-1H-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, the reaction gives a mixture of (I) and (II). In the second substructure, pyrazole 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).
atom N5 at \((x, y, z)\) acts as a hydrogen-bond donor to ketonic atom O141 in the molecule at \((-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)\), so forming a simple \(C(10)\) chain running parallel to the [101] direction and generated by the \(n\)-glide plane at \(y = \frac{1}{2}\) (Fig. 4). The combination of the chains parallel to [010] and [101] generates a sheet parallel to [101], but there are no significant direction-specific interactions between adjacent sheets.

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 \(R_1^2(7)\) 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, 1/2 − z), so forming a further cyclic motif, this time an $R_2^2(10)$ ring generated by the twofold rotation axis along (1/2, y, 1/2). 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.

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-1H-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$_4$O$_4$ 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$_4$O$_4$ requires: C 60.3, H 4.2, N 16.6%.

**Compounds (I)**

**Crystal data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>C$<em>{17}$H$</em>{14}$N$_4$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$</td>
<td>338.32</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/n$</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>12.3518 (8) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>7.5202 (4) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>17.1564 (13) Å</td>
</tr>
<tr>
<td>$β$</td>
<td>100.699 (5)°</td>
</tr>
</tbody>
</table>

$V = 1565.90$ (18) Å$^3$  
$Z = 4$  
Mo $Kα$ radiation  
$μ = 0.11$ mm$^{-1}$  
$T = 120$ (2) K  
0.55 × 0.35 × 0.19 mm

**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 $(1 − x, 2 − y, 1 − z)$.
organic compounds

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

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H···A</th>
<th>D—A</th>
<th>D—H—A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5—H5A⋯N2</td>
<td>0.87</td>
<td>2.33</td>
<td>3.31 (3)</td>
<td>154</td>
</tr>
<tr>
<td>N5—H5B⋯O52</td>
<td>0.87</td>
<td>2.18</td>
<td>3.024 (3)</td>
<td>163</td>
</tr>
<tr>
<td>C16—H16B⋯O123</td>
<td>0.95</td>
<td>2.39</td>
<td>3.304 (3)</td>
<td>161</td>
</tr>
</tbody>
</table>

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

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

| C1—C5 | 1.391 (3) | C5—N5 | 1.364 (2) |
| C1—C6 | 1.396 (3) | C6—O51 | 1.2522 (19) |
| C3—C4 | 1.376 (3) | N5—H52 | 0.87 (2) |
| C3—C5 | 1.389 (3) | N5—H52 | 0.87 (2) |

For (I), the space group P21/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 Uiso(H) = kUeq(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 Uiso(H) = 1.2Ueq(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: OASILC (McArdle, 2003) and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPP A (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.

References


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