Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701
Editor: **George Ferguson**

Cyclic and acyclic products from the reactions between methyl 3-oxobutanoate and arylhydrazines

James L. Wardell, Janet M. S. Skakle, John N. Low and Christopher Glidewell

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Cyclic and acyclic products from the reactions between methyl 3-oxobutanoate and arylhydrazines

James L. Wardell,[a] Janet M. S. Skakle,[b] John N. Low[b] and Christopher Glidewell[c]*

[a]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

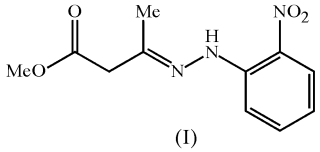
Received 14 June 2007
Accepted 15 June 2007
Online 14 July 2007

The molecules of methyl 3-(2-nitrophenylhydrazono)butanoate, $C_{11}H_{13}N_3O_4$, (I), and methyl 3-(2,4-dinitrophenylhydrazono)butanoate, $C_{11}H_{12}N_4O_6$, (II), both prepared from methyl 3-oxobutanoate and the corresponding nitrophenylhydrazine, exhibit polarized molecular electronic structures; in each of (I) and (II), the molecules are linked into chains by a single C—H···O hydrogen bond. The molecules of 5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole, $C_{10}H_{10}N_2O$, (III), prepared by the reaction of methyl 3-oxobutanoate and phenylhydrazine, are linked into chains by a single O—H···N hydrogen bond. The reaction between methyl 3-oxobutanoate and 3-nitrophenylhydrazine yields 5-hydroxy-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazole, (IV), which when crystallized from acetone yields 4-isopropylidene-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5(4*H*)-one, $C_{13}H_{13}N_3O_3$, (V).

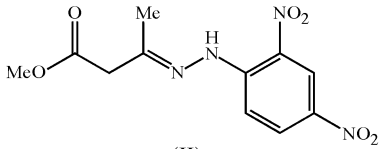
Comment

We have for a number of years been interested in the structures of hydrazones (for examples, see Glidewell *et al.*, 2003, 2004, 2006; Peralta *et al.*, 2007; Wardell *et al.*, 2005). As part of this wider study, we have now investigated the reactions of methyl 3-oxobutanoate (methyl acetoacetate) with a range of simple arylhydrazines. The reaction products include the acyclic 3-arylhydrazinobutanoate esters (I) and (II), the cyclized 1-aryl-5-hydroxypyrazoles (III) and (IV), and the condensation products such as (V), initially obtained during attempts to crystallize the pyrazole derivatives from ketonic solvents. We report here the structures of compounds (I)–(III) and (V), and we integrate the various structural types into a single mechanistic scheme. The structure of (III) reported here represents a second polymorph of this compound; a monoclinic polymorph crystallizes with $Z' = 2$ in the space group $P2_1/c$ (Bechtel *et al.*, 1973*a*; Chmutova *et al.*, 2001).

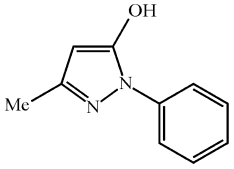
Compounds (I)–(III) (Figs. 1–3) were readily obtained from the reactions between methyl 3-oxobutanoate and the appropriate arylhydrazines, *viz*. 2-nitrophenylhydrazine for (I), 2,4-dinitrophenylhydrazine for (II) and phenylhydrazine for (III). The analogous reaction using 3-nitrophenylhydrazine gave the product (IV), but the crystals initially obtained from methanol solution were of very poor quality and were twinned. The diffraction data obtained from these crystals were correspondingly poor, and we have been unable to reduce R significantly below 0.11; thus, we do not report the structure of (IV) in detail here. Nonetheless, the atom connectivity revealed by these very poor data unambiguously corresponds to that of compound (IV), directly analogous to compound (III). Attempted recrystallization of compound (IV) from acetone solution yielded instead the condensation product (V) (Fig. 4), evidently a product of the reaction between (IV) itself and the acetone solvent.



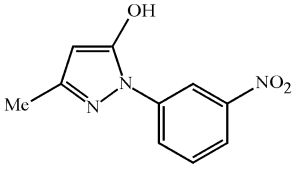
(I)



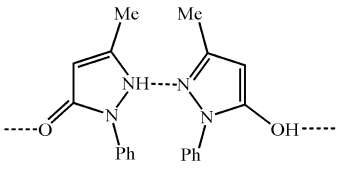
(II)



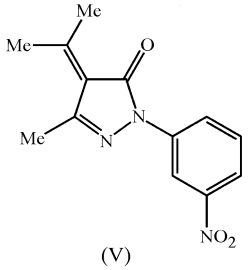
(III)



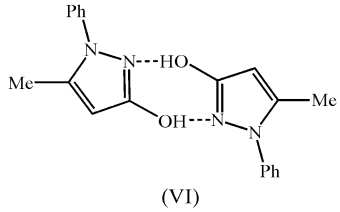
(IV)



(III*a*)



(V)



(VI)

The bond lengths in the aryl rings of (I) and (II) show significant variation (Table 1). In particular, the C3—C4 and C5—C6 bonds are substantially shorter than the other ring bonds; in addition, the C2—N12 and C4—N14 bonds are long for their type, while the nitro N—O bonds are all long (Allen *et al.*, 1987). The observations indicate that the polarized

  DOI: 10.1107/S0108270107029447

quinonoid forms (I*a*), and (II*a*) and (II*b*), respectively, are significant contributors to the overall electronic structures of (I) and (II). This behaviour is typical of that observed in 2-nitro- and 4-nitroanilines, but not in 3-nitroanilines (Cannon *et al.*, 2001; Garden *et al.*, 2001, 2002; Glidewell *et al.*, 2001; Zakaria *et al.*, 2001), and it indicates a reduction in the basicity and nucleophilicity of atom N1 in such 2- and 4-substituted species as compared with both the 3-nitro derivatives and the un-nitrated analogues. The aryl rings in (I) and (II) are almost coplanar with the chain-extended fragment between atoms C1 and C13 (Figs. 1 and 2), and the nitro groups are nearly coplanar with the rings, as shown by the relevant torsion angles (Table 1). These nearly planar conformations may be influenced by the intramolecular N—H···O interactions (Table 2). The ester fragments between atoms C12 and C15 are also nearly planar, but in each compound there is a substantial bend in the side chain at the C12—C13 bond.

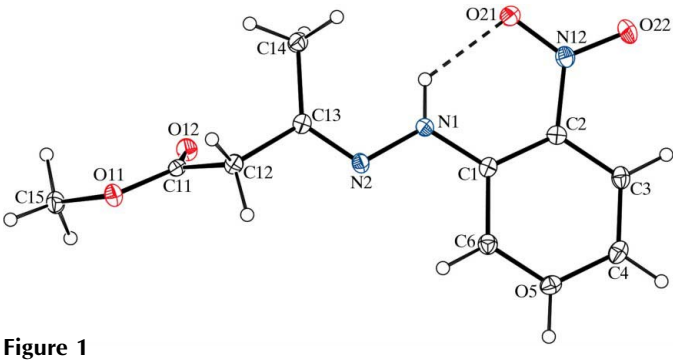


Figure 1
A molecule of (I), showing the atom-labelling scheme and the intramolecular N—H···O hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level.

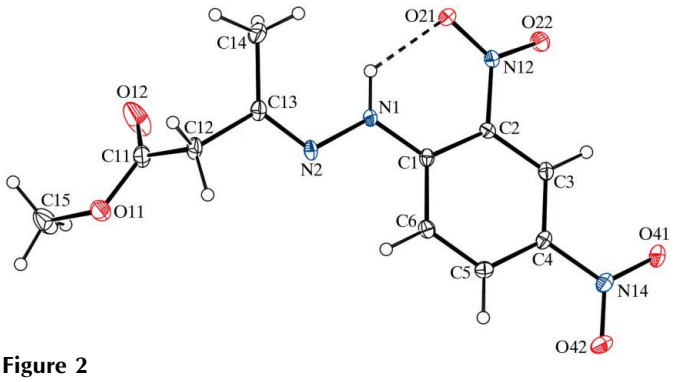


Figure 2
A molecule of (II), showing the atom-labelling scheme and the intramolecular N—H···O hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level.

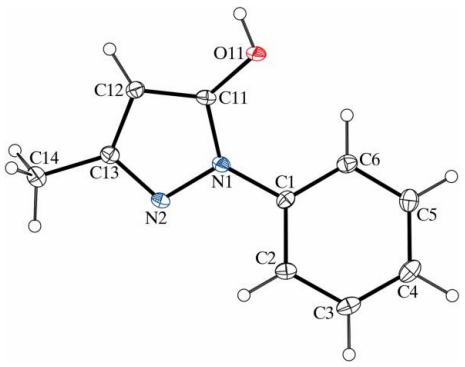
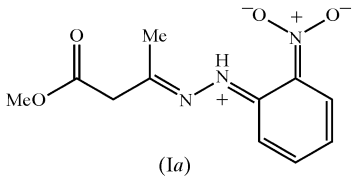
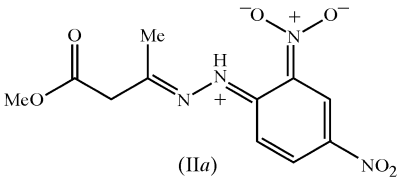
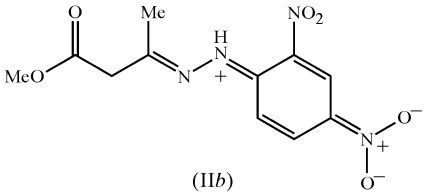


Figure 3
A molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.







The heterocyclic rings in (III) and (V) exhibit very different bond lengths (Table 2), consistent with significant π-delocalization in (III) and complete bond fixation in (V). The exocyclic C—O bond lengths, in particular, are consistent with the location of the hydroxyl H atom in (III) as deduced from difference maps. The inter-ring dihedral angle is 22.0 (2)° in (III) and 6.2 (2)° in (V), where the nitro group makes a dihedral angle of only 4.9 (2)° with the aryl ring.

The formation of the various products arising from the reactions of methyl acetoacetate with aryl hydrazines can readily be envisaged in terms of an initial condensation to form the acyclic (*E*)-hydrazone of type (*A*), exemplified here

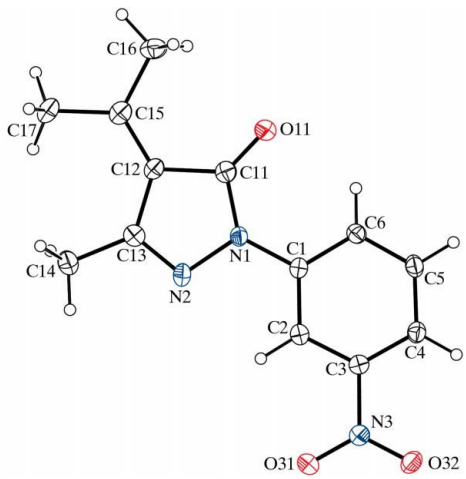
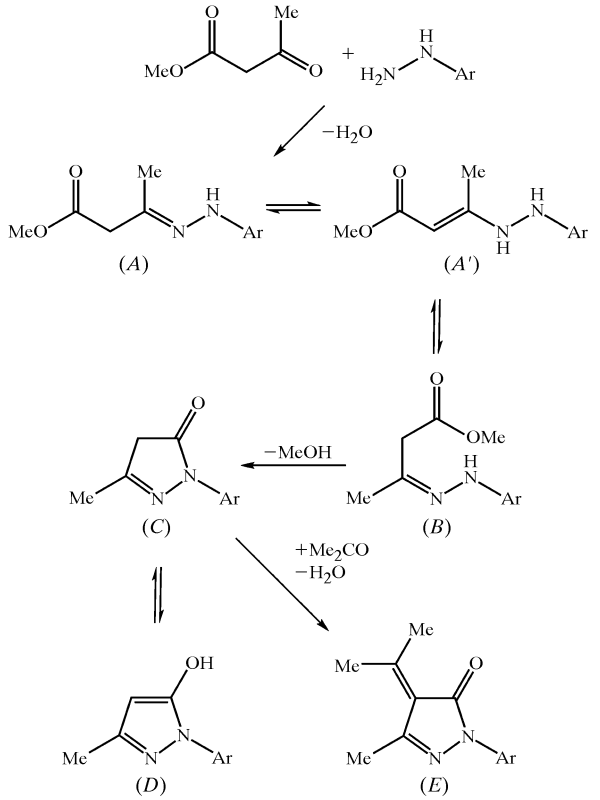


Figure 4
A molecule of (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

by compounds (I) and (II). Provided that hydrazine atom N1 is sufficiently nucleophilic then the intermediate (*B*) can readily cyclize, with loss of methanol, to form (*C*), whose tautomer (*D*) is exemplified by (III). Intermediate (*B*) is simply the *Z* isomer of (*A*) and its formation most plausibly involves the tautomer (*A*′), in which effectively free rotation about the N2—C13 bond is possible. Condensation of (*C*) with carbonyl compounds yields the *exo*-methylene derivatives (*E*), exemplified here by compound (V). We have noted above the evidence for the significance of polarized electronic forms in (I) and (II), and an important consequence of such charge separation is the reduction in nucleophilicity of atom N1 when the aryl group contains 2-nitro and/or 4-nitro substituents. The structural evidence from (I) and (II) is thus consistent with the failure of these two compounds to undergo cyclization under the reaction conditions that produce (III) and (IV). When atom N1 is more nucleophilic, as in the presence of either an unsubstituted phenyl ring or a 3-nitrophenyl ring, cyclization to form (*C*) and (*D*) is thus feasible.



While there are no direction-specific interactions of any kind in the structure of (V), the molecules in (I), (II) and (III) are all linked into chains; in each of (I) and (II), the chain is built from a single C—H···O hydrogen bond, and that in (III) by a single O—H···N hydrogen bond (Table 3). In (I), methylene atom C12 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to carbonyl atom O12 in the molecule at (*x*, −1 + *y*, *z*), so generating by translation a *C*(4) (Bernstein *et al.*, 1995) chain running parallel to the [010] direction (Fig. 5). In (II), the hydrogen-bond donor and acceptor are both different from those utilized in (I). In (II), aryl atom C6 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to nitro atom O42 in the molecule at $(-\frac{1}{2}+x, \frac{3}{2}-y, 1-z)$, so forming a *C*(6) chain running parallel to [100] and generated by the 2_1 screw axis along $(x, \frac{3}{4}, \frac{1}{2})$ (Fig. 6). In (III), hydroxy atom O11 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to pyrazole atom N2 in the molecule at $(\frac{3}{2}-x, y, -\frac{1}{2}+z)$, so forming a *C*(5) chain running parallel to the [001] direction and generated by the *c*-glide plane at $x = \frac{3}{4}$ (Fig. 7). There are no direction-specific interactions between the chains in compounds (I) and (III), but those in (II) are weakly linked by a dipolar carbonyl–nitro interaction. Carbonyl atom O12 in

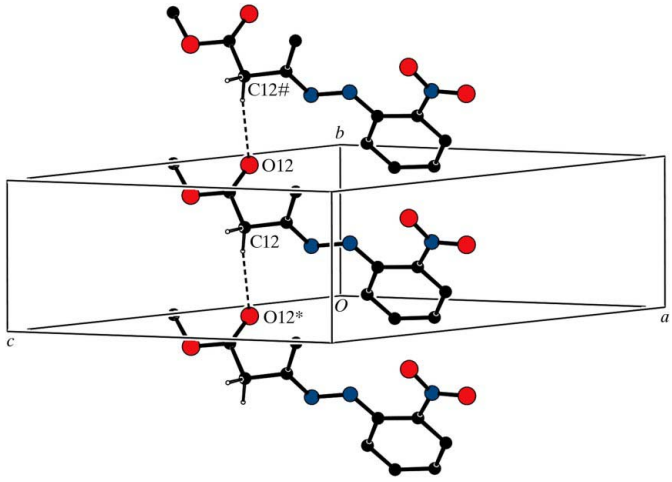


Figure 5
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain along [010]. For the sake of clarity, H atoms bonded to the C or N atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions (*x*, −1 + *y*, *z*) and (*x*, 1 + *y*, *z*), respectively.

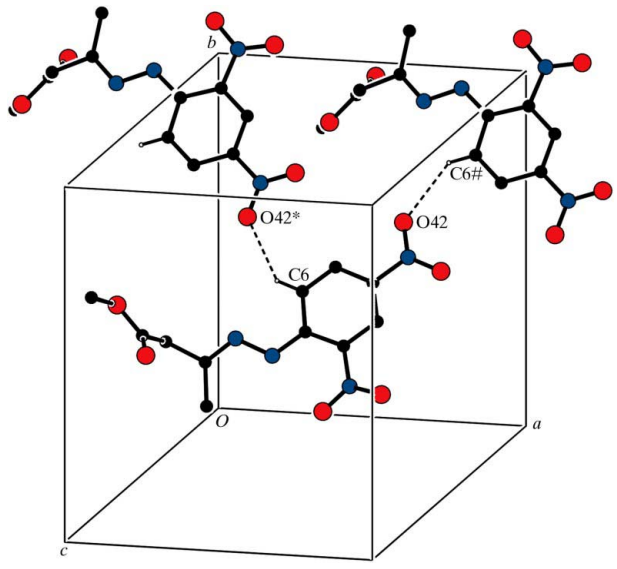


Figure 6
Part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain along [100]. For the sake of clarity, H atoms bonded to the C or N atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2}+x, \frac{3}{2}-y, 1-z)$ and $(\frac{1}{2}+x, \frac{3}{2}-y, 1-z)$, respectively.

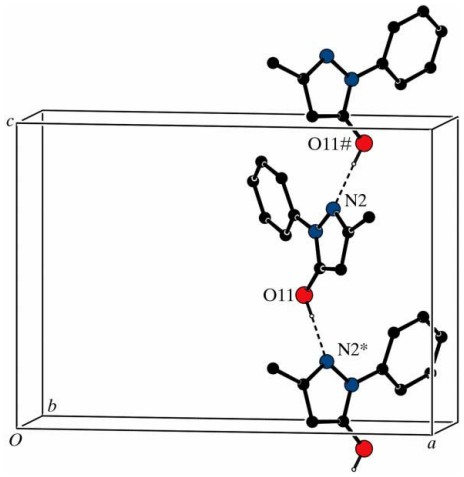


Figure 7
Part of the crystal structure of (III), showing the formation of a hydrogen-bonded chain along [001]. For the sake of clarity, H atoms bonded to the C or N atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{3}{2} - x, y, -\frac{1}{2} + z)$ and $(\frac{3}{2} - x, y, \frac{1}{2} + z)$, respectively.

the molecule at (x, y, z), which forms part of the hydrogen-bonded chain along $(x, \frac{3}{4}, \frac{1}{2})$, makes a nearly linear contact with nitro atom N12 in the molecule at $(-\frac{1}{2} + x, y, \frac{3}{2} - z)$, which lies in the hydrogen-bonded chain along $(x, \frac{3}{4}, 1)$ [$O\cdots N^{i}$ = 2.885 (2) Å and $C-O\cdots N^{i}$ = 173.7 (2)°; symmetry code: (i) $-\frac{1}{2} + x, y, \frac{3}{2} - z$], and the effect of this contact is to link the [100] chains weakly into a sheet parallel to (010).

The monoclinic polymorph of (III) (Bechtel *et al.*, 1973*a*; Chmutova *et al.*, 2001) is, in fact, a 1:1 cocrystal of the two tautomeric forms 5-hydroxy-3-methyl-1-phenylpyrazole and 3-methyl-1-phenyl-2*H*-pyrazolin-5-one, (III*a*), and the molecules are linked by alternating O—H···O and N—H···N hydrogen bonds into $C_2^2(10)$ chains. By contrast, the sulfur analogue of (II) exists in the crystalline state solely as the thione tautomer (Chmutova *et al.*, 2001). Isomeric with (III) is 3-hydroxy-5-methyl-1-phenylpyrazole, (VI), which exists in the crystalline state as a single tautomer; the compound crystallizes with $Z' = 2$ in the space group *Pbca* and the molecules are linked by two independent O—H···N hydrogen bonds into $R_2^2(8)$ dimers, which do not exhibit even approximate symmetry (Bechtel *et al.*, 1973*b*).

Experimental

For the synthesis of (I), a solution of methyl acetoacetate (1 mmol) and 2-nitrophenylhydrazine (1 mmol) in methanol (10 ml) was heated under reflux for 30 min; the solution was cooled to ambient temperature and then evaporated to dryness. The product, (I), was recrystallized from ethanol. IR (KBr, cm^{-1}): 3330, 1731, 1613, 1575. Heating a solution of (I) in ethanol for 1 h at reflux temperature led to no cyclization or other change. Compound (II) was similarly prepared from methyl acetoacetate and 2,4-dinitrophenylhydrazine, but the heating time was 90 min; compound (II) was recrystallized from ethanol. IR (KBr, cm^{-1}): 3327, 1740, 1620, 1594. Compound (III) was prepared from the reaction of methyl acetoacetate and phenylhydrazine, exactly as for (I). The product was recrystallized from ethanol [m.p. 398–400 K; literature m.p. 400 K (Singh, 2005)]. IR (KBr, cm^{-1}): 3130–2700, 1569, 1534. For the synthesis of (IV), a solution of methyl acetoacetate (1 mmol) and 3-nitrophenylhydrazine hydrochloride (1 mmol) in methanol (20 ml) was heated under reflux for 30 min; the solution was cooled to ambient temperature and then evaporated to dryness. The residue was recrystallized from ethanol, but this material was not suitable for single-crystal X-ray diffraction. IR (KBr, cm^{-1}): 3120, 3100–2300, 1591, 1556, 1530. Further recrystallization of (IV) from acetone gave (V). IR (KBr, cm^{-1}): 1688, 1614, 1529.

Compound (I)

Crystal data

$C_{11}H_{13}N_3O_4$
M_r = 251.24
Monoclinic, $P2_1/n$
a = 12.1494 (4) Å
b = 5.1355 (2) Å
c = 18.6969 (6) Å
β = 102.079 (2)°
V = 1140.73 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 (2) K
0.28 × 0.22 × 0.04 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.975, T_{max} = 0.995
13943 measured reflections
2617 independent reflections
1931 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.117
S = 1.05
2617 reflections
166 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Compound (II)

Crystal data

$C_{11}H_{12}N_4O_6$
M_r = 296.25
Orthorhombic, *Pbca*
a = 10.6100 (3) Å
b = 12.1878 (4) Å
c = 20.522 (2) Å
V = 2653.7 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 120 (2) K
0.43 × 0.35 × 0.14 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.961, T_{max} = 0.983
20035 measured reflections
3033 independent reflections
2289 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.116
S = 1.05
3033 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Compound (III)

Crystal data

$C_{10}H_{10}N_2O$
M_r = 174.20
Orthorhombic, $Pca2_1$
a = 15.0138 (9) Å
b = 5.2952 (3) Å
c = 10.9469 (6) Å
V = 870.29 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 120 (2) K
0.22 × 0.09 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer	8739 measured reflections 1051 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003) T_{min} = 0.974, T_{max} = 0.998	913 reflections with $I > 2\sigma(I)$ R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	1 restraint
$wR(F^2)$ = 0.093	H-atom parameters constrained
S = 1.12	$\Delta\rho_{max}$ = 0.17 e Å^{-3}
1051 reflections	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
120 parameters	

Compound (V)

Crystal data

$C_{13}H_{13}N_3O_3$	V = 1198.17 (10) Å^3
M_r = 259.26	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 8.8910 (3) Å	μ = 0.11 mm^{-1}
b = 10.1699 (6) Å	T = 120 (2) K
c = 13.4731 (7) Å	0.36 × 0.24 × 0.14 mm
β = 100.415 (3)°	

Data collection

Bruker–Nonius KappaCCD diffractometer	15923 measured reflections 2752 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003) T_{min} = 0.958, T_{max} = 0.985	1840 reflections with $I > 2\sigma(I)$ R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	175 parameters
$wR(F^2)$ = 0.165	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.53 e Å^{-3}
2752 reflections	$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected bond distances and torsion angles (Å, °) for (I) and (II).

	(I)	(II)
C1—C2	1.411 (2)	1.420 (2)
C2—C3	1.403 (2)	1.388 (2)
C3—C4	1.368 (3)	1.374 (2)
C4—C5	1.401 (2)	1.402 (2)
C5—C6	1.368 (2)	1.373 (2)
C6—C1	1.414 (2)	1.413 (2)
C1—N1	1.366 (2)	1.3612 (19)
C2—N12	1.438 (2)	1.4517 (19)
N12—O21	1.2482 (18)	1.2394 (16)
N12—O22	1.2363 (17)	1.2290 (16)
C4—N14	–	1.4503 (19)
N14—O41	–	1.2352 (17)
N14—O42	–	1.2378 (17)
C2—C1—N1—N2	−178.57 (14)	173.08 (13)
C1—N1—N2—C13	−178.70 (15)	−179.46 (14)
N1—N2—C13—C12	−178.15 (13)	178.09 (13)
N2—C13—C12—C11	−113.65 (17)	−101.57 (17)
C13—C12—C11—O11	−171.48 (13)	155.12 (14)
C12—C11—O11—C15	−178.88 (13)	176.87 (16)
C1—C2—N12—O21	−3.8 (2)	14.1 (2)
C3—C4—N14—O41		0.9 (2)

Table 2
Selected bond lengths (Å) for (III) and (V).

	(III)	(V)
N1—N2	1.387 (3)	1.433 (3)
N2—C13	1.333 (3)	1.288 (3)
C13—C12	1.394 (3)	1.452 (3)
C12—C11	1.378 (3)	1.500 (3)
C11—N1	1.364 (3)	1.371 (3)
C11—O11	1.329 (3)	1.205 (3)
C12—C15	–	1.361 (3)

Table 3
Hydrogen bonds and short intramolecular contacts (Å, °) for (I)–(III) and (V).

D—H···A	D—H	H···A	D···A	D—H···A
(I)				
N1—H1···O21	0.88	1.97	2.6077 (19)	128
C12—H12A···O12^{i}	0.99	2.42	3.3894 (19)	166
(II)				
N1—H1···O21	0.93	1.95	2.6258 (17)	128
C6—H6···O42^{ii}	0.95	2.51	3.293 (2)	139
(III)				
O11—H11···N2^{iii}	0.84	1.79	2.633 (3)	178
C6—H6···O1	0.95	2.31	2.881 (3)	118
(V)				
C6—H6···O1	0.95	2.24	2.871 (3)	123

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

For (I), (II) and (V), respectively, the space groups $P2_1/n$, $Pbca$ and $P2_1/c$ were uniquely assigned from the systematic absences. For (III), the systematic absences permitted $Pca2_1$ and $Pbcm$ (= $Pcam$) as possible space groups; $Pca2_1$ was selected and confirmed by the successful structure analysis. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were placed in geometrically idealized positions and allowed to ride, with C—H distances of 0.95 (aromatic and pyrazole), 0.98 (CH_3) or 0.99 Å (CH_2), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups and k = 1.2 otherwise. H atoms bonded to N or O atoms were allowed to ride at the distances deduced from difference maps [N—H = 0.88 Å in (I) or 0.93 Å in (II), and O—H = 0.84 Å, with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O)]. In the absence of significant resonant scattering it was not possible to establish the correct orientation of the structure of (III) with respect to the polar-axis direction; accordingly, the Friedel-equivalent reflections were merged prior to the final refinements. Compound (IV) has unit-cell dimensions a = 25.648 (4) Å, b = 3.8259 (6) Å, c = 24.790 (5) Å and β = 118.739 (14)° in the space group $P2/c$; the compound was crystallized from ethanol as a hemihydrochloride salt, $2C_{10}H_{9.5}N_3O_3^{0.5+}\cdot Cl^-$ and the crystals were twinned, as well as exhibiting very poor overall quality.

For all compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC National Crystallography Service, University of Southampton, UK. The authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3141). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bechtel, F., Gaultier, J. & Hauw, C. (1973*a*). *Cryst. Struct. Commun.* **3**, 469–472.

Bechtel, F., Gaultier, J. & Hauw, C. (1973*b*). *Cryst. Struct. Commun.* **3**, 473–476.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Cannon, D., Glidewell, C., Low, J. N., Quesada, A. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 216–221.

Chmutova, G. A., Kataeva, O. N., Ahlbrecht, H., Kurbangalieva, A. R., Movchan, A. I., Lenstra, A. T. H., Geise, H. J. & Litvinov, I. A. (2001). *J. Mol. Struct.* **570**, 215–223.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Garden, S. J., Fontes, S. P., Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 701–709.

Garden, S. J., Glidewell, C., Low, J. N., McWilliam, S. A., Pinto, A. C., Skakle, J. M. S., Torres, J. C. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 1212–1214.

Glidewell, C., Cannon, D., Quesada, A., Low, J. N., McWilliam, S. A., Skakle, J. M. S. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 455–458.

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2003). *Acta Cryst.* C**59**, o98–o101.

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004). *Acta Cryst.* C**60**, o686–o689.

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2006). *Acta Cryst.* B**62**, 666–675.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Peralta, M. A., Souza, M. N. V. de, Wardell, S. M. S. V., Wardell, J. L., Low, J. N. & Glidewell, C. (2007). *Acta Cryst.* C**63**, o68–o72.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Singh, S. P. (2005). *Synth. Commun.* **25**, 611–619.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Wardell, S. M. S. V., Souza, M. V. N. de, Wardell, J. L., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* C**61**, o683–o689.

Zakaria, C. M., Low, J. N., Skakle, J. M. S., McWilliam, S. A., Wardell, J. L. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 1207–1208.