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Three substituted 4-pyrazolylbenzoates: hydrogen-bonded supramolecular structures in one, two and three dimensions

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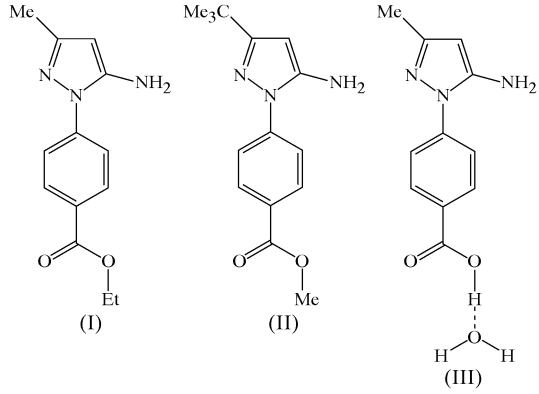
The molecules of ethyl 4-(5-amino-3-methyl-1*H*-pyrazol-1-yl)benzoate, $C_{13}H_{15}N_3O_2$, are linked by two independent N—H···O hydrogen bonds into a chain of edge-fused and alternating $R_4^2(8)$ and $R_2^2(20)$ rings. A combination of N—H···N and N—H···O hydrogen bonds links the molecules of methyl 4-(5-amino-3-*tert*-butyl-1*H*-pyrazol-1-yl)benzoate, $C_{15}H_{19}N_3O_2$, into sheets of alternating $R_2^2(20)$ and $R_6^6(32)$ rings. In 4-(5-amino-3-methyl-1*H*-pyrazol-1-yl)benzoic acid monohydrate, $C_{11}H_{11}N_3O_2{\cdot}H_2O$, the molecular components are linked into a three-dimensional framework structure by a combination of five independent hydrogen bonds, two of O—H···N type and one each of O—H···O, N—H···O and N—H···N types.

Comment

As precursors for the synthesis of pyrazolo[1,5-*a*][1,3,5]-benzotriazepines, which are useful as drugs, agrochemicals and dye intermediates (Tachibana & Kaneko, 1989), we have synthesized several 4-(5-aminopyrazol-1-yl)benzoates by construction of the pyrazole ring from 4-hydrazinobenzoic acid and 3-aminocrotononitrile, and report here the structures of three substituted 4-pyrazolylbenzoic acid derivatives, namely ethyl 4-(5-amino-3-methyl-1*H*-pyrazol-1-yl)benzoate, (I), methyl 4-(5-amino-3-*tert*-butyl-1*H*-pyrazol-1-yl)benzoate, (II), and 4-(5-amino-3-methyl-1*H*-pyrazol-1-yl)benzoic acid monohydrate, (III) (Figs. 1–3).

The intramolecular geometries of compounds (I)–(III) present no unexpected features; the pyrazole rings all exhibit marked bond fixation, and the dihedral angles between the two rings in (I)–(III) are 30.1 (2), 34.2 (2) and 46.5 (2)°, respectively. The principal points of interest in the structures of compounds (I)–(III) are the different modes of supramolecular aggregation, leading to hydrogen-bonded structures in one, two and three dimensions, respectively.



The supramolecular structure of compound (I) is simple. Amino atom N45 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H45*A* and H45*B*, to the O11 atoms in the molecules at (−*x*, 1 − *y*, 1 − *z*) and (*x*, *y*, 1 + *z*), respectively (Table 1). Propagation by translation and inversion of these two hydrogen bonds then generates a chain of edge-fused centrosymmetric rings running parallel to the [001] direction, with $R_2^2(20)$ (Bernstein *et al.*, 1995) rings centred at $(0, \frac{1}{2}, n + \frac{1}{2})$ (where *n* represents zero or an integer), and $R_4^2(8)$ rings centred at $(0, \frac{1}{2}, n)$ (*n* = zero or integer) (Fig. 4). There are no direction-specific interactions between adjacent chains; in particular C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are both absent.

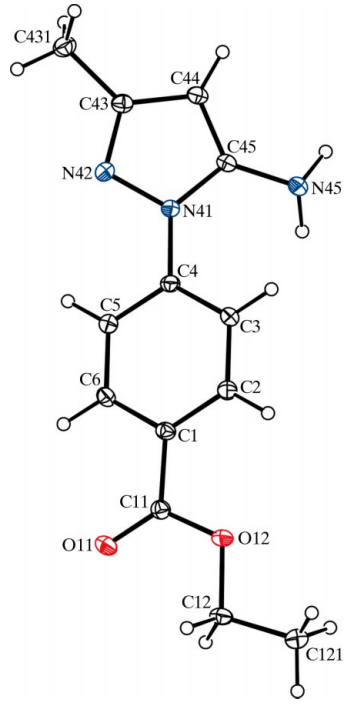


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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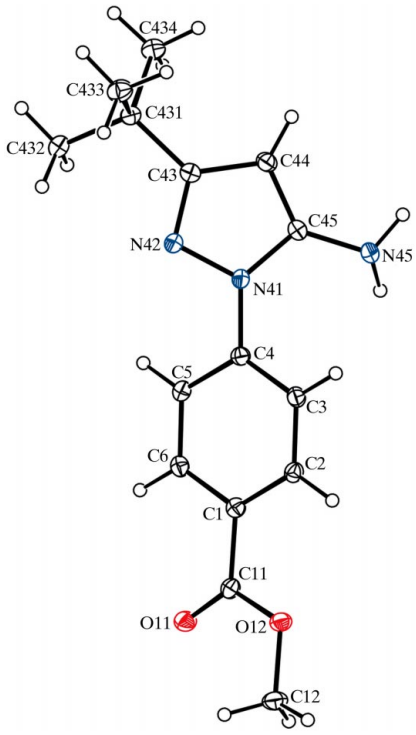

Figure 2
A molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

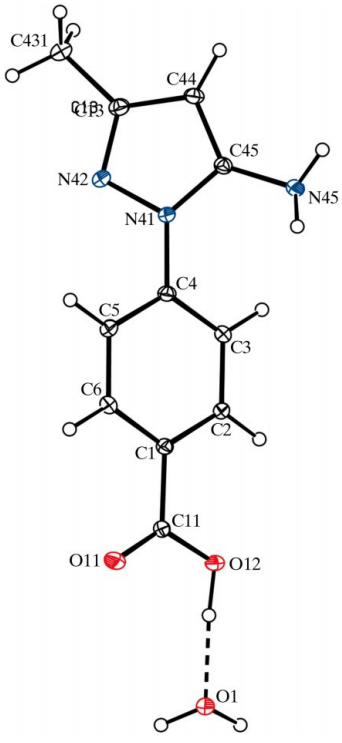

Figure 3
The independent molecular components of (III), showing the atom-labelling scheme and the O—H···O hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

The molecules of compound (II) are linked by a combination of N—H···O and N—H···N hydrogen bonds (Table 2); this may be contrasted with compound (I), where N—H···N hydrogen bonds were absent. The molecules are linked into sheets, and the formation of the sheet is readily analysed in terms of a dimeric building block. Amino atom N45 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H45*A*, to atom O11 in the molecule at ($1-x$, $1-y$, $1-z$), so generating by inversion a dimeric unit characterized by an $R_2^2(20)$ motif. In addition, the N45 atoms in the molecules at (x, y, z) and ($1-x$, $1-y$, $1-z$), which are components of the $R_2^2(20)$ dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), act as hydrogen-bond donors, *via* H45*B*, to the ring atoms N42 of the molecules at ($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$), respectively, which are themselves components of the dimers centred at ($\frac{1}{2}$, 1, 0) and

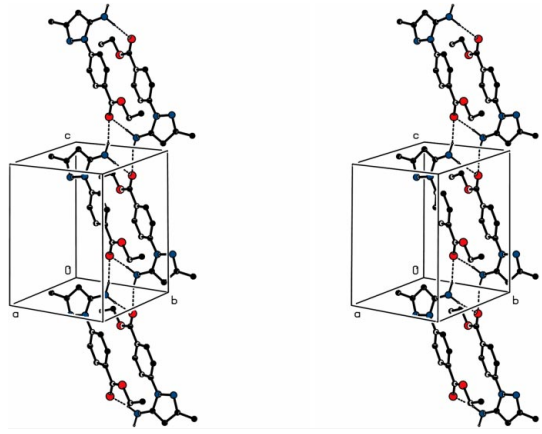

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a chain of alternating $R_2^2(20)$ and $R_4^2(8)$ rings along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

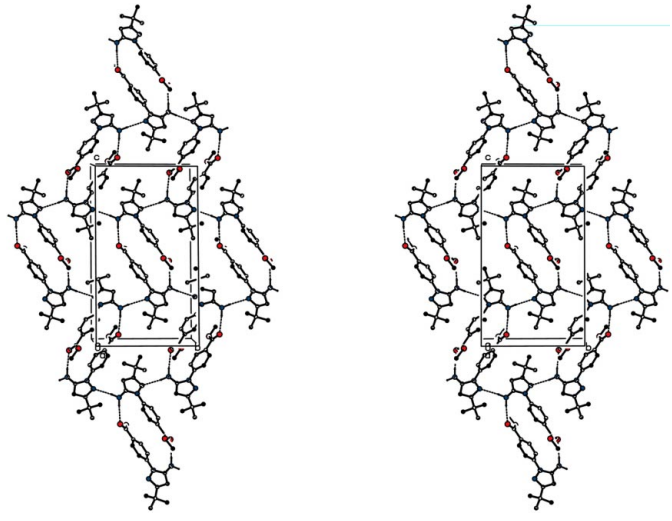

Figure 5
A stereoview of part of the crystal structure of (II), showing the formation of a sheet of $R_2^2(20)$ and $R_6^6(32)$ rings parallel to (100). For the sake of clarity, H atoms bonded to C atoms have been omitted.

($\frac{1}{2}$, 0, 1). In a similar way, atoms N42 at (x, y, z) and ($1-x$, $1-y$, $1-z$) accept hydrogen bonds from atoms N45 in the molecules at ($1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) and (x, $\frac{3}{2}-y$, $\frac{1}{2}+z$), which are components of the dimers centred at ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, 1, 1) respectively. Thus, each dimer is directly linked, *via* N—H···N hydrogen bonds, to four adjacent dimers, and propagation of this interaction by the space group leads to the formation of a sheet parallel to (100) built from alternating $R_2^2(20)$ and $R_6^6(32)$ rings, where both ring types are centrosymmetric (Fig. 5). There are no direction-specific interactions between adjacent sheets, nor is there any interweaving of adjacent sheets, despite the occurrence of the large $R_6^6(32)$ rings; interweaving is prevented by the effective masking of the large rings by pairs of *tert*-butyl groups (Fig. 5).

Compound (III) is a stoichiometric monohydrate, and in the selected asymmetric unit (Fig. 3), the components are linked by a rather short and almost linear O—H···O hydrogen bond (Table 3). Four further hydrogen bonds link the molecular components into a single three-dimensional framework structure, whose formation is readily analysed in terms of three independent one-dimensional substructures, only one of which involves the water molecule. In the first substructure, which runs parallel to the [100] direction, water atom O1 at (x, y, z) acts as a hydrogen-bond donor, *via* H1*A* and H1*B*, respectively, to atom N42 at ($-x$, $1-y$, $1-z$) and N45 at ($1-x$, $1-y$, $1-z$). Propagation by inversion of these two hydrogen bonds then generates a chain of edge-fused centrosymmetric rings with $R_4^4(22)$ rings centred at (n, $\frac{1}{2}$, $\frac{1}{2}$) (n = zero or integer) and $R_4^4(24)$ rings centred at ($n+\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (n = zero or integer) (Fig. 6).

The second substructure runs parallel to the [010] direction and consists of simple chains built from the organic component only; amino atom N45 at (x, y, z) acts as a hydrogen-bond donor, *via* H45*A*, to ring atom N42 at ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), so forming a $C(5)$ chain generated by the 2_1 screw axis along ($\frac{1}{4}$, y, $\frac{1}{4}$) (Fig. 7). The third substructure is also built from only the organic components, and runs along the [10$\bar{1}$] direction; amino atom N45 at (x, y, z) acts as a hydrogen-bond donor, this time *via* H45*B*, to atom O11 at ($\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$), so forming a $C(10)$ chain generated by the *n*-glide plane at $y=\frac{3}{4}$ (Fig. 8). The combination of the chains along [100], [010] and [10$\bar{1}$] suffices to link all the molecules into a single three-dimensional framework structure.

Thus, rather modest changes in the peripheral substituents in compounds (I)–(III) are associated with substantial changes both in the patterns of the hydrogen bonds deployed and in the dimensionality of the resulting supramolecular structures.

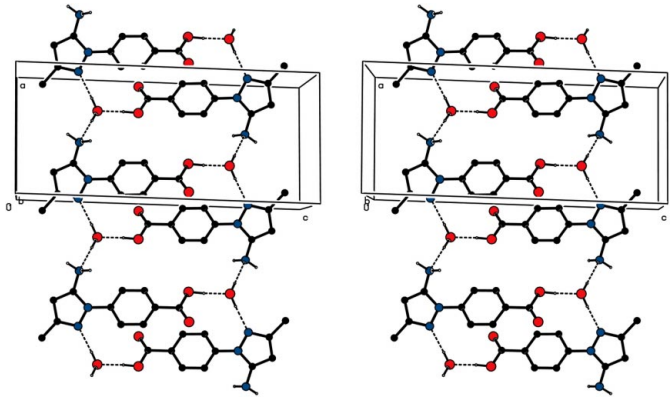

Figure 6
A stereoview of part of the crystal structure of (III), showing the formation of a chain of alternating $R_4^4(22)$ and $R_4^4(24)$ rings along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

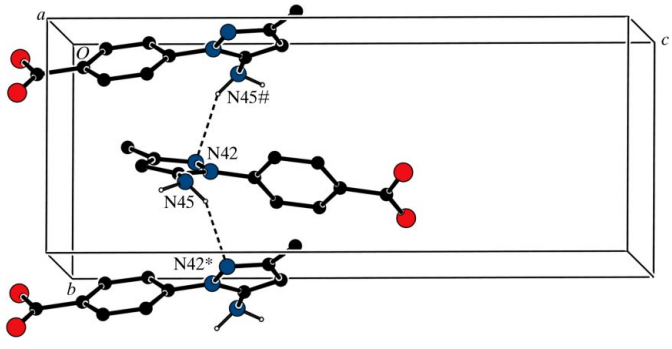

Figure 7
Part of the crystal structure of (III), showing the formation of a $C(5)$ chain along [010]. For the sake of clarity, water molecules and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$), respectively.

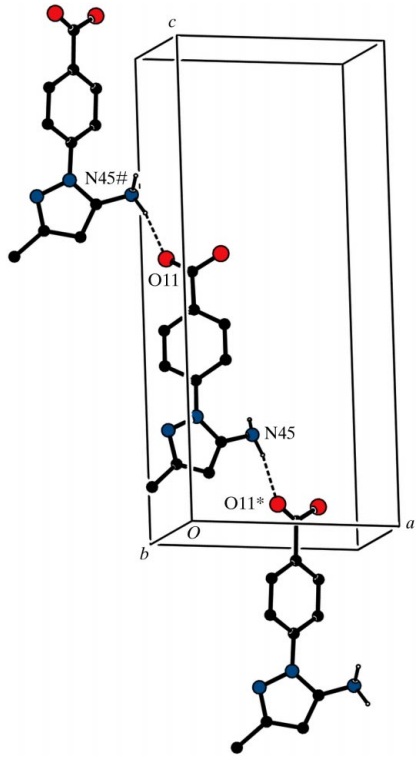

Figure 8
Part of the crystal structure of (III), showing the formation of a $C(10)$ chain along [10$\bar{1}$]. For the sake of clarity, the water molecule and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$) and ($-\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$), respectively.

Experimental

For the synthesis of compounds (I) and (III), 3-aminocrotononitrile (3.3 mmol) was added at ambient temperature to a stirred solution of 4-hydrazinobenzoic acid (3.3 mmol) in ethanol (6 ml). The resulting suspension was stirred for 20 min and then 5 *M* HCl solution (15 ml) was added. The mixture was stirred for 40 min at 368 K and, after cooling (< 263 K), the solution was made either basic or neutral, in separate experiments, using aqueous ammonia solution. From the basic solution, compound (I) was precipitated upon removal of the solvent; compound (I) was collected by filtration and recrystallized from dimethyl sulfoxide to give yellow crystals suitable for single-crystal X-ray diffraction (yield 13%, m.p. 430–431 K). MS (70 eV) *m*/*z* (%): 245 (100, M^+), 217 (21), 200 (39), 134 (11), 122 (26). From the neutral solution, compound (III) was precipitated upon removal of the solvent; the compound was collected by filtration and recrystallized from ethanol to give yellow crystals suitable for single-crystal X-ray diffraction (yield 72%, m.p. 503–504 K). MS (70 eV) *m*/*z* (%): 217 (100, M^+), 200 (28). For the synthesis of compound (II), 4,4-dimethyl-3-oxopentanenitrile (3.3 mmol) was added at ambient temperature to a stirred solution of 4-hydrazinobenzoic acid (3.3 mmol) in methanol (6 ml). The resulting suspension was stirred for 20 min and then 5 *M* HCl solution (15 ml) was added. The mixture was stirred for 40 min at 368 K and, after cooling (< 263 K), the mixture was neutralized using aqueous ammonia solution. The intermediate 4-(5-amino-3-*tert*-butyl-1*H*-pyrazol-1-yl)benzoic acid was precipitated as a yellow solid (yield 80%, m.p. 468–469 K). A suspension of the entire batch of this intermediate in methanol (6 ml) was treated with diazomethane (3.3 mmol) at 273–283 K. Compound (II) was formed as a yellow solid, which was collected by filtration and then recrystallized from methanol to afford yellow crystals suitable for single-crystal X-ray diffraction (overall yield 76%, m.p. 468–469 K). MS (70 eV) *m*/*z* (%): 273 (53, M^+), 258 (100), 231 (83).

Compound (I)

Crystal data

$C_{13}H_{15}N_3O_2$
M_r = 245.28
Triclinic, $P\overline{1}$
a = 7.2228 (4) Å
b = 8.4433 (3) Å
c = 10.5938 (5) Å
α = 98.234 (3)°
β = 107.609 (2)°
γ = 97.907 (3)°
V = 598.12 (5) Å^3
Z = 2
D_x = 1.362 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 (2) K
Plate, yellow
0.28 × 0.14 × 0.06 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.979, T_{max} = 0.994
12140 measured reflections
2748 independent reflections
1904 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.136
S = 1.08
2748 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.0939P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N45—H45A···O11^{i}	0.94	2.30	3.1190 (19)	146
N45—H45B···O11^{ii}	0.94	2.11	3.0252 (18)	165

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

Compound (II)

Crystal data

$C_{15}H_{19}N_3O_2$
M_r = 273.33
Monoclinic, $P2_1/c$
a = 6.1272 (2) Å
b = 11.6374 (3) Å
c = 20.3182 (7) Å
β = 98.629 (2)°
V = 1432.38 (8) Å^3
Z = 4
D_x = 1.267 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 120 (2) K
Lath, yellow
0.48 × 0.22 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.971, T_{max} = 0.990
24177 measured reflections
3269 independent reflections
2353 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.112
S = 1.03
3269 reflections
185 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.2591P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N45—H45A···O11^{i}	0.93	2.22	3.1388 (16)	172
N45—H45B···N42^{ii}	0.92	2.34	3.2386 (17)	166

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

Compound (III)

Crystal data

$C_{11}H_{11}N_3O_2{\cdot}H_2O$
M_r = 235.24
Monoclinic, $P2_1/n$
a = 8.0166 (2) Å
b = 7.5082 (2) Å
c = 18.5507 (5) Å
β = 91.8140 (16)°
V = 1116.01 (5) Å^3
Z = 4
D_x = 1.400 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 (2) K
Block, yellow
0.54 × 0.36 × 0.18 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.961, T_{max} = 0.982
11603 measured reflections
2551 independent reflections
2037 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.5°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 0.2827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.121$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.10$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
2551 reflections	
155 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O1	0.95	1.66	2.6005 (13)	172
O1—H1A···N42^{i}	0.90	1.90	2.8002 (16)	176
O1—H1B···N45^{ii}	0.90	2.06	2.9556 (15)	180
N45—H45A···N42^{iii}	0.91	2.31	3.1446 (17)	152
N45—H45B···O11^{iv}	0.91	2.01	2.9020 (15)	168

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

For compounds (II) and (III), the space groups $P2_1/c$ and $P2_1/n$, respectively, were uniquely assigned from the systematic absences. Crystals of compound (I) are triclinic; space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were assigned standard C—H distances [0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for methyl groups and 1.2 for other H atoms bonded to C atoms]. The H atoms bonded to N or O atoms were permitted to ride at the distances found from difference maps [N—H = 0.91–0.94 Å and O—H = 0.90 Å, with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$.]

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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3055). Services for accessing these data are described at the back of the journal.

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