

Contrasting three-dimensional framework structures in the isomeric pair 2-iodo-*N*-(2-nitrophenyl)benzamide and *N*-(2-iodophenyl)-2-nitrobenzamide

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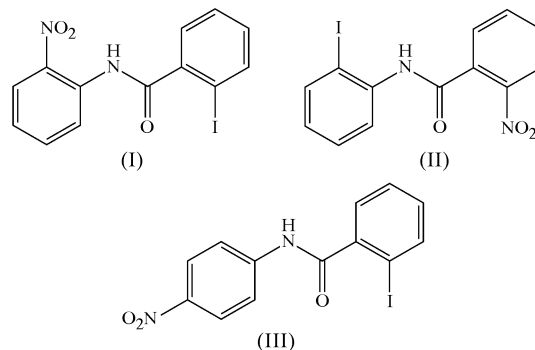
In 2-iodo-*N*-(2-nitrophenyl)benzamide, C₁₃H₉IN₂O₃, the molecules are linked into a three-dimensional framework structure by a combination of a C—H···O hydrogen bond, and iodo–nitro, carbonyl–carbonyl and aromatic π – π stacking interactions. In the isomeric compound *N*-(2-iodophenyl)-2-nitrobenzamide, the framework structure is built from N—H···O, C—H···O and C—H··· π (arene) hydrogen bonds and an iodo–nitro interaction.

Comment

The isomeric benzamides 2-iodo-*N*-(2-nitrophenyl)benzamide, (I), and *N*-(2-iodophenyl)-2-nitrobenzamide, (II), offer the possibility of a wide variety of potential intermolecular interactions. These include N—H···O and C—H···O hydrogen bonds, each with two possible types of acceptor O atoms (amide and nitro), C—H··· π (arene) hydrogen bonds (again with two distinct acceptor rings), aromatic π – π stacking interactions, and two- or three-centre iodo–nitro interactions. We have recently reported that the supramolecular aggregation of 2-iodo-*N*-(4-nitrophenyl)benzamide, (III), depends on a combination of N—H···O(carbonyl) and C—H···O(nitro) hydrogen bonds, together with weak π – π stacking interactions (Garden *et al.*, 2005), and we now report the supramolecular structures for the isomers (I) and (II).

The molecules in (I) and (II) (Figs. 1 and 2, respectively) adopt conformations which have no internal symmetry, as shown by the leading torsion angles (Table 1). Accordingly, the molecules of (I) and (II) have no internal symmetry, and

hence they are chiral. Compound (I) crystallizes in the centrosymmetric space group $P\bar{1}$, so that equal numbers of both enantiomers are present in each crystal, but compound (II) crystallizes in the non-centrosymmetric space group $P2_12_12_1$; hence, in the absence of any inversion twinning, only one enantiomer is present in a given crystal of compound (II). The bond lengths and angles show no unusual values.



The supramolecular structures formed by isomers (I) and (II) are both three-dimensional, but they are different not only in their detailed construction but also in the types of direction-specific intermolecular interactions which are active.

In compound (I) (Fig. 1), there is an intramolecular N—H···O hydrogen bond (Table 2), but the N—H bond plays no role in the intermolecular aggregation. This is instead determined by a combination of a C—H···O hydrogen bond, a two-centre iodo–nitro interaction and two aromatic π – π stacking interactions, which combine to generate a three-dimensional framework, the formation of which is readily analysed in terms of three one-dimensional substructures.

For two of the substructures, the basic building block is a hydrogen-bonded dimer. Aryl atom C25 in the molecule at (x, y, z) acts as donor to amide atom O17 in the molecule at $(1-x, 1-y, 1-z)$, so generating a centrosymmetric $R_2^2(14)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 3). These dimers are linked into two distinct chains by aromatic π – π stacking interactions.

Because of the near planarity of the molecules in compound (I), the C11–C16 ring at (x, y, z) is nearly parallel to the C21–C26 rings in the molecules at $(-x, -y, 1-z)$ and $(-x, 1-y,$

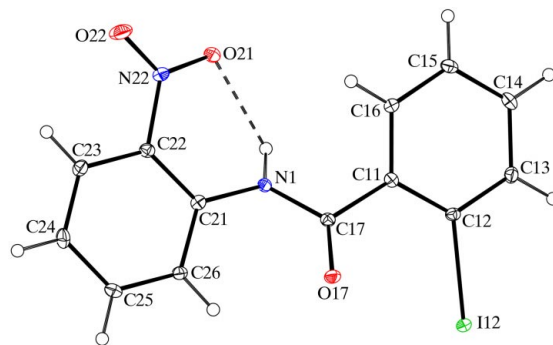


Figure 1

The molecule 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.

$1 - z$), with dihedral angles between adjacent planes of only $5.2(2)^\circ$. For the molecules at (x, y, z) and $(-x, -y, 1 - z)$, the corresponding ring-centroid separation is $3.827(2) \text{ \AA}$, with an interplanar spacing of *ca* 3.49 \AA and a ring offset of *ca* 1.57 \AA . The molecules at (x, y, z) and $(-x, -y, 1 - z)$ are components of the hydrogen-bonded dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, respectively, so that propagation by inversion of these two interactions generates a π -stacked chain of rings running parallel to the $[110]$ direction (Fig. 4). For the mol-

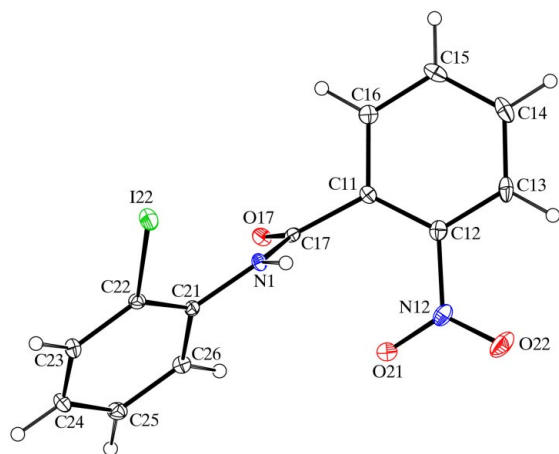


Figure 2
The molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

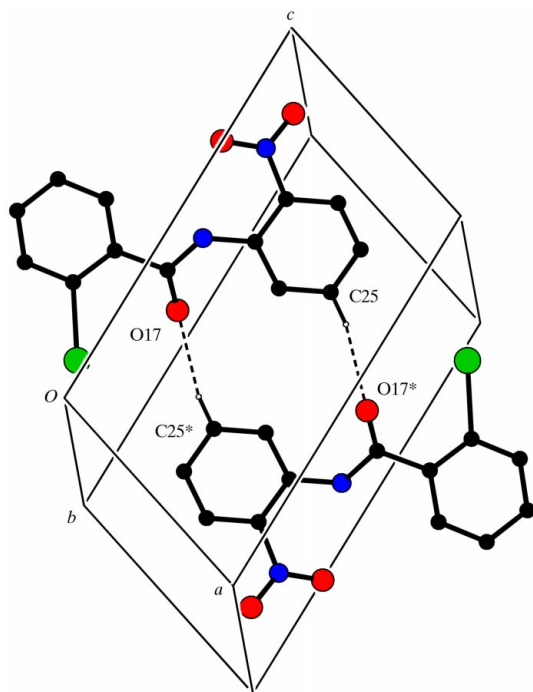


Figure 3
Part of the crystal structure of compound (I), showing the formation of a cyclic $R_2^2(14)$ dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

ecules at (x, y, z) and $(-x, 1 - y, 1 - z)$, which are components of the hydrogen-bonded dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively, the ring-centroid separation is $3.808(2) \text{ \AA}$, with an interplanar separation of *ca* 3.52 \AA and a ring offset of *ca* 1.45 \AA . This interaction thus generates a π -stacked chain of rings running parallel to the $[100]$ direction (Fig. 5).

The final substructure depends solely on a two-centre iodo-nitro interaction, with $\text{I12} \cdots \text{O22}^i = 3.4101(16) \text{ \AA}$ and $\text{C12} - \text{I12} \cdots \text{O22}^i = 159.71(6)^\circ$ [symmetry code: (i) $x, y, -1 + z$], so forming a $C(9)$ chain (Starbuck *et al.*, 1999) running parallel to the $[001]$ direction (Fig. 6). The combination of $[100]$, $[110]$ and $[001]$ chains then generates a three-dimensional structure,

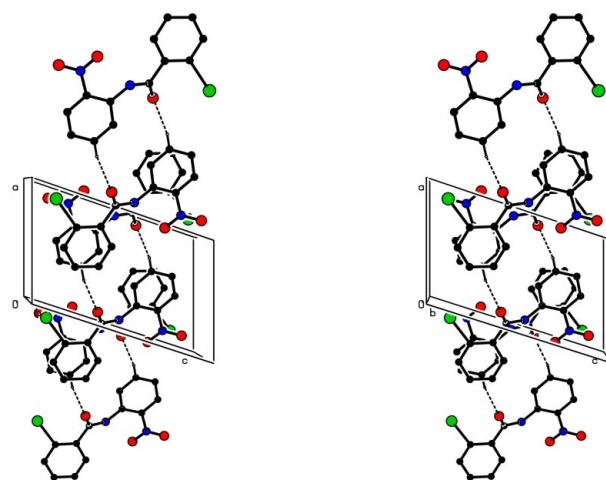


Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a π -stacked chain of hydrogen-bonded dimers along $[110]$. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

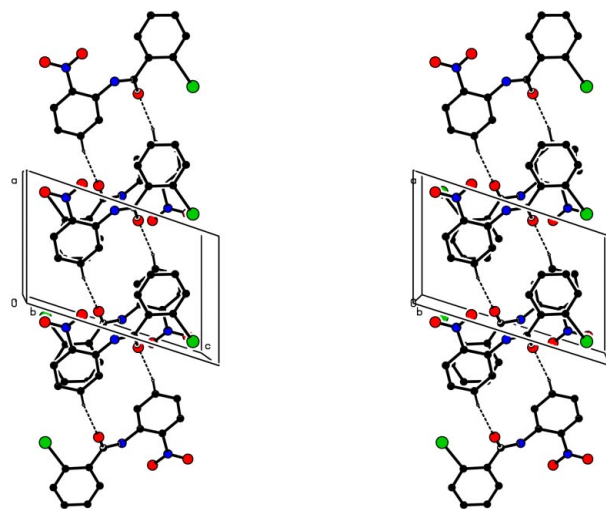


Figure 5
A stereoview of part of the crystal structure of compound (I), showing the formation of a π -stacked chain of hydrogen-bonded dimers along $[100]$. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

which is augmented by a carbonyl–carbonyl interaction of type II (Allen *et al.*, 1998). The carbonyl groups in the molecules at (x, y, z) and $(-x, 1 - y, 1 - z)$ are strictly parallel, with $O17 \cdots C17^{ii} = 2.976(2) \text{ \AA}$ and $C17 - O17 \cdots C17^{ii} = 92.8(2)^\circ$ [symmetry code: (ii) $-x, 1 - y, 1 - z$].

The molecules of compound (II) (Fig. 2) are linked into a three-dimensional framework structure by a combination of $N-H \cdots O$, $C-H \cdots O$ and $C-H \cdots \pi(\text{arene})$ hydrogen bonds (Table 3) and a two-centre iodo–nitro interaction. The

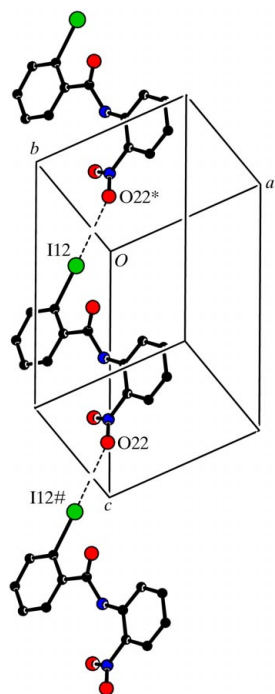


Figure 6
Part of the crystal structure of compound (I), showing the formation of an [001] chain built from iodo–nitro interactions. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y, -1 + z)$ and $(x, y, 1 + z)$, respectively.

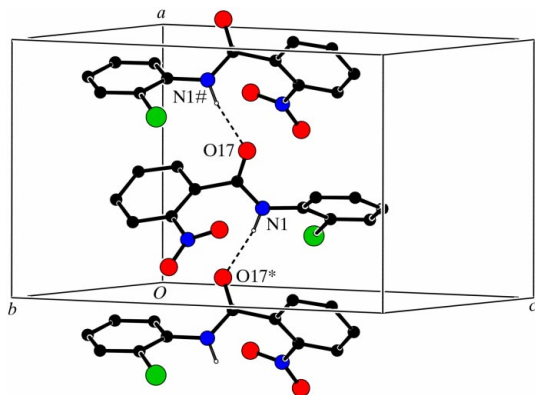


Figure 7
Part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded $C(4)$ chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + y, \frac{3}{2} - y, 1 - z)$ and $(\frac{1}{2} + y, \frac{3}{2} - y, 1 - z)$, respectively.

formation of this framework is readily analysed in terms of three one-dimensional substructures. In the first substructure, amide atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O17 in the molecule at $(-\frac{1}{2} + y, \frac{3}{2} - y, 1 - z)$, so forming the $C(4)$ (Bernstein *et al.*, 1995) motif characteristic of simple amides running parallel to the [100] direction and generated by the 2_1 screw axis along $(x, \frac{3}{4}, \frac{1}{2})$ (Fig. 7).

The second substructure arises from the co-operative action of two fairly weak interactions. Aryl atom C24 in the molecule at (x, y, z) acts as hydrogen-bond donor to amide atom O17 in the molecule at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, while atom C24 at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ in turn acts as donor to atom O17 at $(x,$

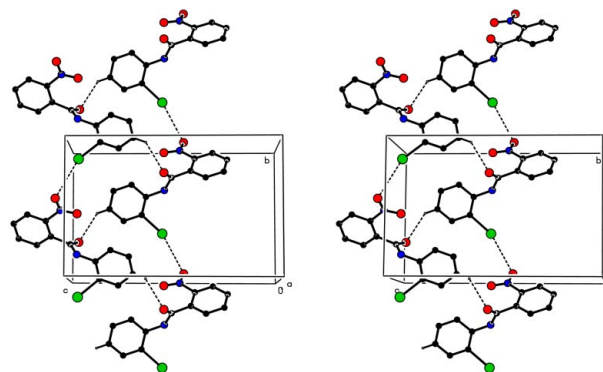


Figure 8
A stereoview of part of the crystal structure of compound (II), showing the formation of a chain of edge-fused rings along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

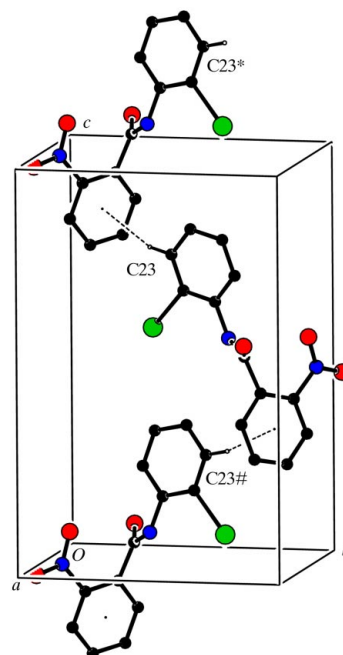


Figure 9
Part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded chain along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$, respectively.

1 + y, z), so forming a C(8) chain running parallel to the [010] direction (Fig. 8). At the same time, atoms I22 at (x, y, z) and O22 at (x, 1 + y, z) form a two-centre iodo–nitro interaction, with $I \cdots O^{iii} = 3.3677$ (17) Å and $C-I \cdots O^{iii} = 159.71$ (6)° [symmetry code: (iii) x, 1 + y, z], so forming a C(9) chain (Starbuck *et al.*, 1999). The combination of these two interactions then generates a chain of edge-fused $R_3^3(19)$ rings generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 8).

The third one-dimensional substructure in (II) is built from a single C–H $\cdots\pi$ (arene) hydrogen bond. Aryl atom C23 in the molecule at (x, y, z) acts as donor to the C11–C16 ring in the molecule at $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$, so forming a chain running parallel to the [001] direction and generated by the 2_1 screw axis along $(\frac{1}{4}, \frac{1}{2}, z)$ (Fig. 9). The combination of the chains along [100], [010] and [001] suffices to generate a continuous three-dimensional framework.

In conclusion, for the two isomeric title compounds, (I) and (II), the difference between their molecular structures can be regarded as a simple reversal of the amidic function –NH–CO– between (I) and (II), yet they manifest very different ranges of direction-specific intermolecular interactions with consequently very different supramolecular structures.

Experimental

The title amides were obtained by reaction of equimolar mixtures (2 mmol of each) of 2-*XC*₆H₄COCl and 2-*YC*₆H₄NH₂ [for (I), X = I and Y = NO₂; for (II), X = NO₂ and Y = I] in chloroform (50 ml). After heating each mixture under reflux for 1 h, the solvent was removed under reduced pressure and the resulting solid residues were recrystallized from ethanol, yielding crystals suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

C₁₃H₉IN₂O₃ $Z = 2$
 $M_r = 368.12$ $D_x = 2.025$ Mg m⁻³
 Triclinic, $P\bar{1}$ Mo $K\alpha$ radiation
 Cell parameters from 2759 reflections
 $a = 7.2773$ (2) Å $\theta = 3.6$ –27.5°
 $b = 7.62070$ (10) Å $\mu = 2.66$ mm⁻¹
 $c = 11.6821$ (3) Å $T = 120$ (2) K
 $\alpha = 100.248$ (2)° Plate, yellow
 $\beta = 107.7770$ (10)° $0.34 \times 0.20 \times 0.04$ mm
 $\gamma = 92.529$ (2)°
 $V = 603.73$ (2) Å³

Data collection

Nonius KappaCCD area-detector diffractometer 2759 independent reflections
 φ and ω scans 2646 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) $R_{int} = 0.023$
 $T_{min} = 0.465$, $T_{max} = 0.901$ $\theta_{max} = 27.5^\circ$
 12249 measured reflections $h = -9 \rightarrow 9$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 0.5992P]$
 $R[F^2 > 2\sigma(F^2)] = 0.018$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.045$ $(\Delta/\sigma)_{max} = 0.001$
 $S = 1.07$ $\Delta\rho_{max} = 1.18$ e Å⁻³
 2759 reflections $\Delta\rho_{min} = -0.65$ e Å⁻³
 172 parameters
 H-atom parameters constrained

Table 1

Selected torsion angles (°) for compounds (I) and (II).

	(I)	(II)
C11–C17–N1–C21	–168.48 (17)	–173.38 (16)
C12–C11–C17–N1	–149.64 (18)	76.1 (2)
C22–C21–N1–C17	147.54 (19)	–143.98 (19)
C11–C12–N12–O21		12.0 (3)
C21–C22–N22–O21	16.7 (3)	

Table 2

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

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
N1–H1 \cdots O21	0.88	2.11	2.649 (2)	119
C25–H25 \cdots O17 ⁱ	0.95	2.38	3.312 (3)	168
C26–H26 \cdots O17	0.95	2.34	2.883 (3)	116

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Compound (II)

Crystal data

C₁₃H₉IN₂O₃ Mo $K\alpha$ radiation
 $M_r = 368.12$ Cell parameters from 2970 reflections
 Orthorhombic, $P2_12_12_1$ $\theta = 4.1$ –27.5°
 $a = 8.8908$ (2) Å $\mu = 2.47$ mm⁻¹
 $b = 9.7468$ (2) Å $T = 120$ (2) K
 $c = 15.0112$ (2) Å Rod, colourless
 $V = 1300.82$ (4) Å³ $0.40 \times 0.10 \times 0.10$ mm
 $Z = 4$
 $D_x = 1.880$ Mg m⁻³

Data collection

Nonius KappaCCD area-detector diffractometer 2906 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{int} = 0.028$
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) $\theta_{max} = 27.5^\circ$
 $T_{min} = 0.439$, $T_{max} = 0.791$ $h = -10 \rightarrow 11$
 18237 measured reflections $k = -12 \rightarrow 12$
 2970 independent reflections $l = -19 \rightarrow 18$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{max} = 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.017$ $\Delta\rho_{max} = 0.47$ e Å⁻³
 $wR(F^2) = 0.036$ $\Delta\rho_{min} = -0.49$ e Å⁻³
 $S = 1.08$ Extinction correction: SHELXL97 (Sheldrick, 1997)
 2970 reflections Extinction coefficient: 0.0129 (4)
 173 parameters Absolute structure: Flack (1983),
 H-atom parameters constrained with 1249 Friedel pairs
 $w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 0.3804P]$ Flack parameter: –0.001 (13)
 where $P = (F_o^2 + 2F_c^2)/3$

Table 3

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

Cg1 is the centroid of the C11–C16 ring.

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
N1–H1 \cdots O17 ⁱ	0.88	1.94	2.792 (2)	161
C24–H24 \cdots O17 ⁱⁱ	0.95	2.54	3.321 (3)	140
C23–H23 \cdots Cg1 ⁱⁱⁱ	0.95	2.94	3.846 (2)	160

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

Crystals of compound (I) are triclinic. The space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. For compound (II), the space group $P2_12_12_1$ was uniquely determined from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C–H = 0.95 Å and N–H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The absolute configuration of the molecules in the crystal of (II) selected for data collection was established by use of the Flack (1983) parameter, although this configuration has no chemical significance.

For both compounds, data collection: *COLLECT* (Nonius, 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: SK1872). Services for accessing these data are described at the back of the journal.

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