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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.032
 wR factor = 0.082
Data-to-parameter ratio = 7.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Malonamide: a tetragonal polymorph

A tetragonal polymorph of malonamide, $\text{C}_3\text{H}_6\text{N}_2\text{O}_2$, is reported. The unit-cell dimensions, crystallographic symmetry and some aspects of the molecular geometry are significantly different from those of the known monoclinic form [Chieh *et al.* (1970). *J. Chem. Soc. A*, pp. 179–184]. An $R_3^2(12)$ hydrogen-bonding motif links molecules together into a three-dimensional network.

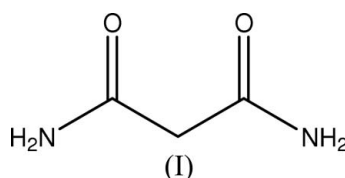
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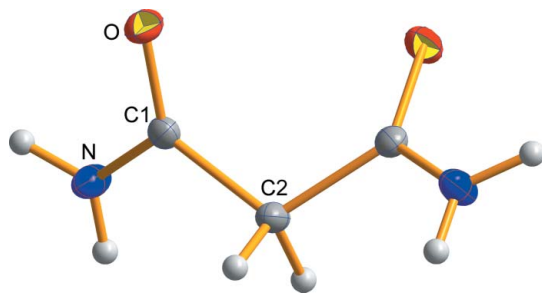
Online 28 September 2005

Comment

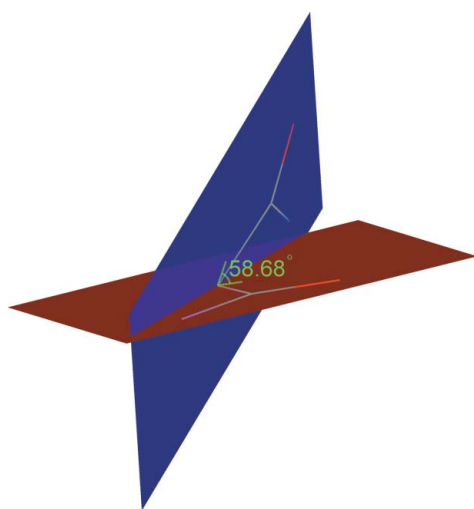
Crystals of malonamide, (I), were obtained from a reaction between 4,6-dihydropyrimidine and Na_2CO_3 in water. Data collected at 150 K showed that it had crystallized in space group $P4_32_12$ with $Z' = 0.5$ and $Z = 4$. It was only some time after structure solution that, by carrying out a search of the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002), we realised a crystal structure of malonamide had previously been reported (Chieh *et al.*, 1970) in space group $P2_1/c$ with two independent molecules in the asymmetric unit and a final $R = 0.05$. This indicates either that the structure undergoes a phase transition above 150 K or that we had identified a second polymorph. However, by the time this was realized the original crystalline sample had been lost, although the original aqueous solution remained. In an attempt to answer this question we crystallized more of the product, with the intention of carrying out unit-cell determinations at 150 K and room temperature in order to show any phase transition. What we actually determined was a further, orthorhombic, polymorph of (I), described in the following paper (Nichol & Clegg, 2005). This third polymorph did not undergo a phase transition between room temperature and 150 K and, based on this observation, we are satisfied that the structure presented here is probably a genuine polymorph and not the consequence of a phase transition from the previously reported form as a result of cooling.



The molecular structure of (I) is shown in Fig. 1. The asymmetric unit consists of one half of the molecule, and the complete molecule is generated from the asymmetric unit by a twofold axis which passes through C2. Bond lengths and angles are in good agreement with the mean values reported by Chieh *et al.* (1970); however, the torsion angle about the C1–C2 bond is significantly different. Fig. 2 shows a wire-

**Figure 1**

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres. The labelled atoms indicate the asymmetric unit; the molecule is generated by a twofold rotation axis ($y, x, -z$) which passes through C2.

**Figure 2**

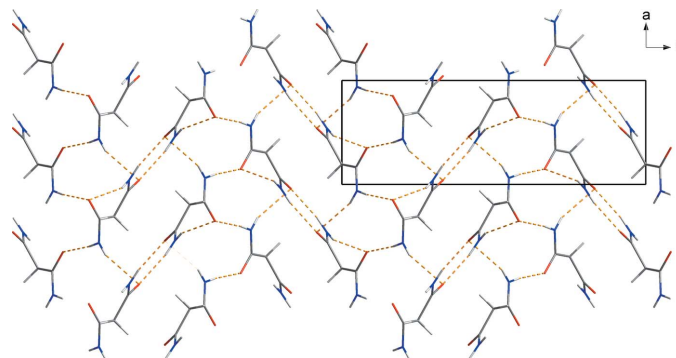
Two mean planes, one drawn through N, O, C1 and C2 and the other through their symmetry equivalents, and the dihedral angle between the two planes.

frame diagram of (I) with two mean planes fitted through O, N, C1 and C2 and through the respective symmetry equivalents. Both planes intersect at C2 and the angle between the two planes is $58.68(4)^\circ$. This value is over 27° less than the angles reported by Chieh *et al.* (1970) for both independent molecules (84.8 and 85.3°).

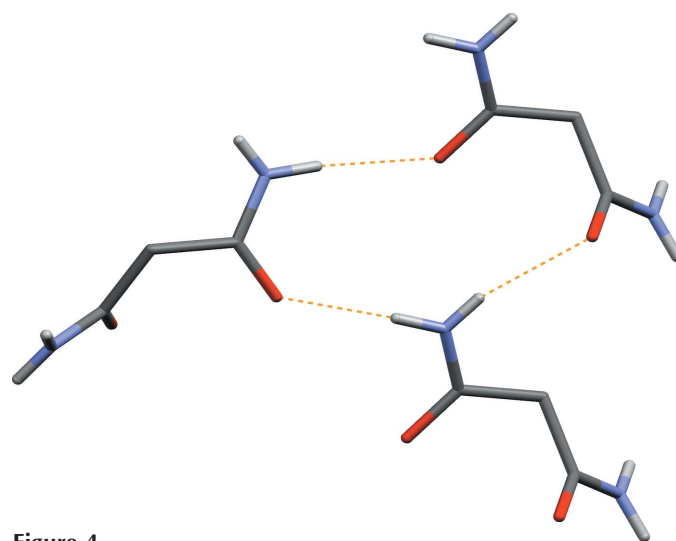
Fig. 3 shows a packing diagram viewed along the b axis. What initially looks like a complicated network is actually the result of just two independent N—H...O hydrogen bonds (one for each of the amino H atoms), with the O atom acting as a bifurcated acceptor. The result of this is a three-dimensional network of $R_3^3(12)$ hydrogen-bonding motifs, illustrated in Fig. 4 (Etter, 1990; Bernstein *et al.*, 1995).

Experimental

Equimolar amounts of 4,6-dihoxypyrimidine and Na_2CO_3 were dissolved in 20 ml of hot distilled water, forming a pale-yellow solution. Large plate-shaped crystals of (I) were grown by slow evaporation of the cold solution on a watch glass over a period of approximately 5 d.

**Figure 3**

A packing diagram, viewed along the b axis. Hydrogen bonds are indicated by orange dashed lines.

**Figure 4**

The $R_3^3(12)$ hydrogen-bonding motif. Hydrogen bonds are indicated by orange dashed lines and C-bound H atoms are omitted.

Crystal data

$\text{C}_3\text{H}_6\text{N}_2\text{O}_2$
 $M_r = 102.10$
 Tetragonal, $P4_32_12$
 $a = 5.3140(3) \text{ \AA}$
 $c = 15.5360(12) \text{ \AA}$
 $V = 438.71(5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.546 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 54 reflections
 $\theta = 2.5\text{--}27.5^\circ$
 $\mu = 0.13 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
 Plate, light yellow
 $0.50 \times 0.50 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.902$, $T_{\max} = 0.997$
 6874 measured reflections
 340 independent reflections

324 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -5 \rightarrow 6$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.082$
 $S = 1.23$
 340 reflections
 43 parameters
 Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.0691P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.12 (3)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------------------|-------------|-------------------------|-------------|
| O—C1 | 1.2382 (17) | C1—C2 | 1.5176 (17) |
| N—C1 | 1.3251 (19) | | |
| O—C1—C2—C1 ⁱ | −36.66 (9) | N—C1—C2—C1 ⁱ | 145.23 (12) |

Symmetry code: (i) $y, x, -z$.**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|----------|-------------|-------------|---------------|
| N—H1N \cdots O ⁱⁱ | 0.87 (2) | 2.05 (2) | 2.9195 (16) | 171 (2) |
| N—H2N \cdots O ⁱⁱⁱ | 0.79 (2) | 2.36 (2) | 3.1112 (17) | 158 (2) |

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{4}$; (iii) $y - 1, x, -z$.

All H atoms were located in a difference map and their coordinates were refined freely, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$. The C—H bond length refined to 0.986 (19) Å and the two N—H bond lengths refined to 0.87 (2) and 0.79 (2) Å. Friedel pairs were merged during the final refinement cycles due to the lack of significant anomalous dispersion; the choice of chiral space group $P4_32_12$ rather than $P4_12_12$ is arbitrary.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg

et al., 2003); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *DIAMOND3* (Brandenburg & Putz, 2004) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank the EPSRC for funding.

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supporting information

Acta Cryst. (2005). E61, o3424–o3426 [doi:10.1107/S1600536805030539]

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S1. Comment

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Fig. 3 shows a packing diagram viewed along the b axis. What initially looks like a complicated network is actually the result of just two independent N—H \cdots O hydrogen bonds (one for each of the amino H atoms), with the O atom acting as a bifurcated acceptor. The result of this is a three-dimensional network of $R_3^3(12)$ hydrogen-bonding motifs, illustrated in Fig. 4 (Etter, 1990; Bernstein *et al.*, 1995).

S2. Experimental

Equimolar amounts of 4,6-dihydroxypyrimidine and Na_2CO_3 were dissolved in 20 ml of hot distilled water, forming a pale-yellow solution. Large plate-shaped crystals of (I) were grown by slow evaporation of the cold solution on a watch glass over a period of approximately 5 d.

S3. Refinement

All H atoms were located in a difference map and their coordinates were refined freely, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C})$. The C—H bond length refined to 0.986 (19) Å and the two N—H bond lengths refined to 0.87 (2) and 0.79 (2) Å. Friedel pairs were merged during the final refinement cycles due to the lack of significant anomalous dispersion.

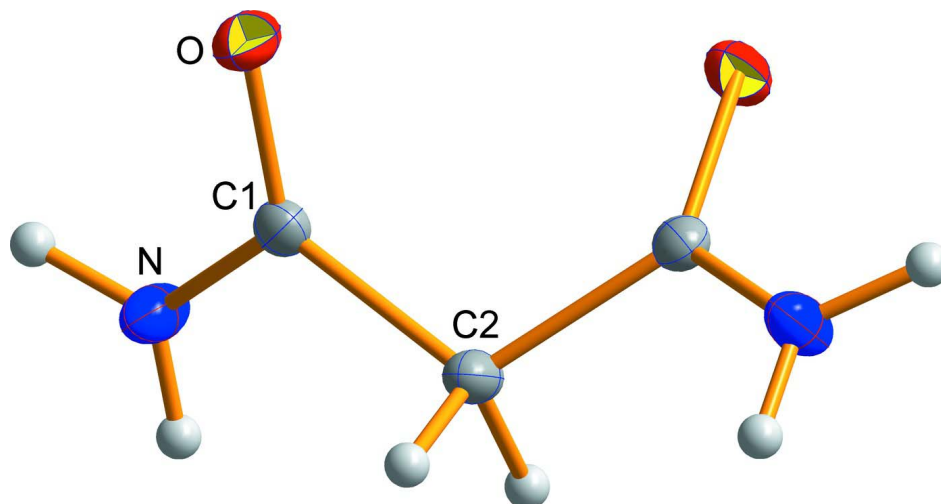


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres. The labelled atoms indicate the asymmetric unit; the molecule is generated by a twofold rotation axis ($y, x, -z$) which passes through C2.

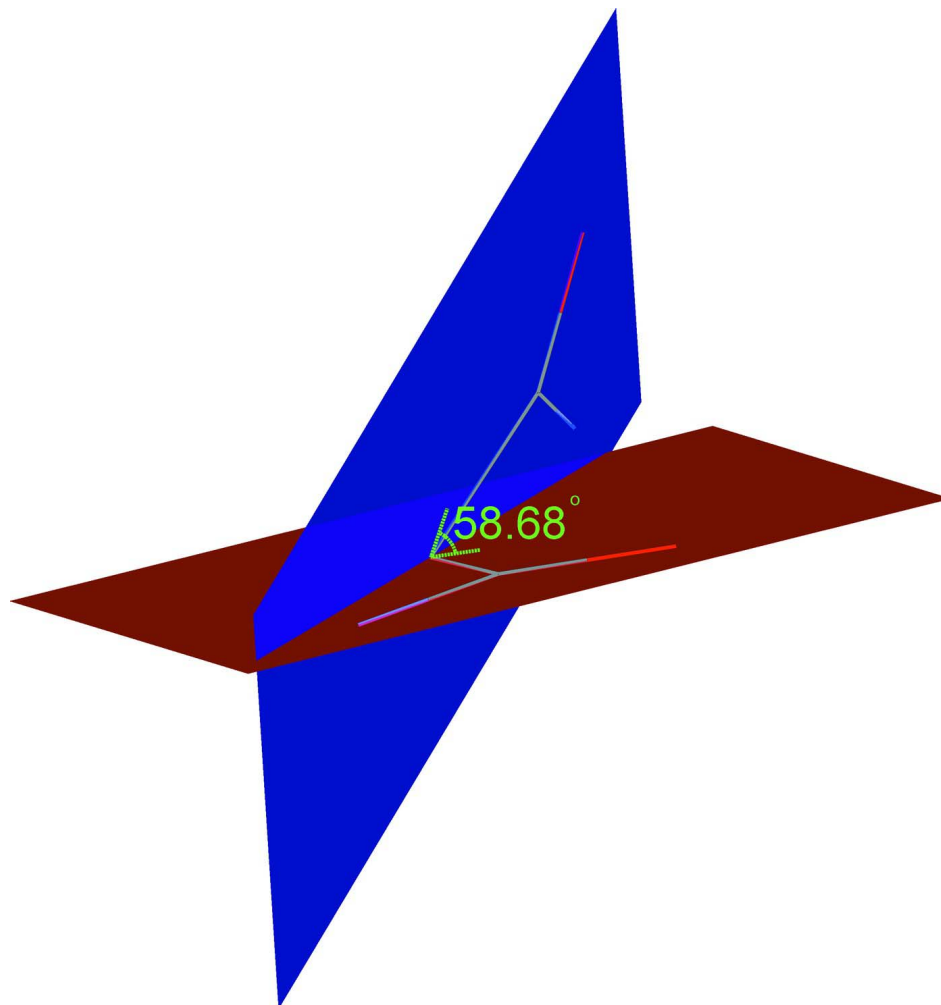
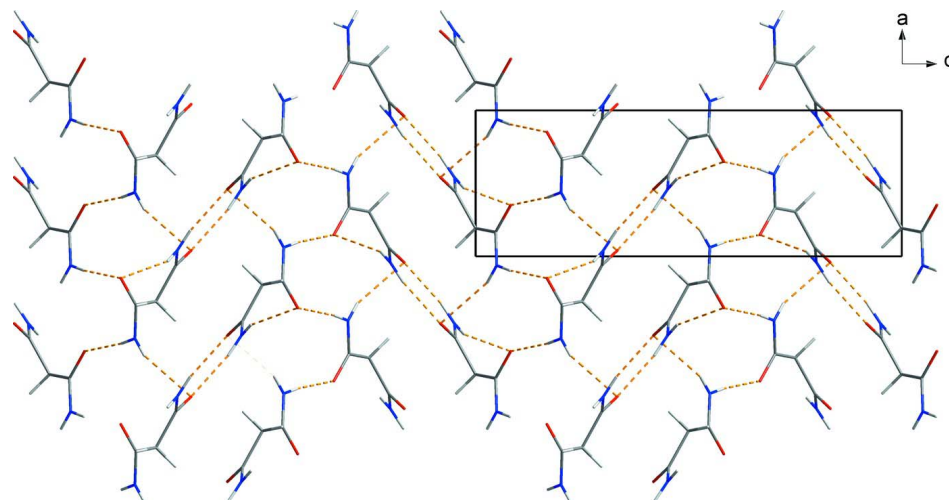
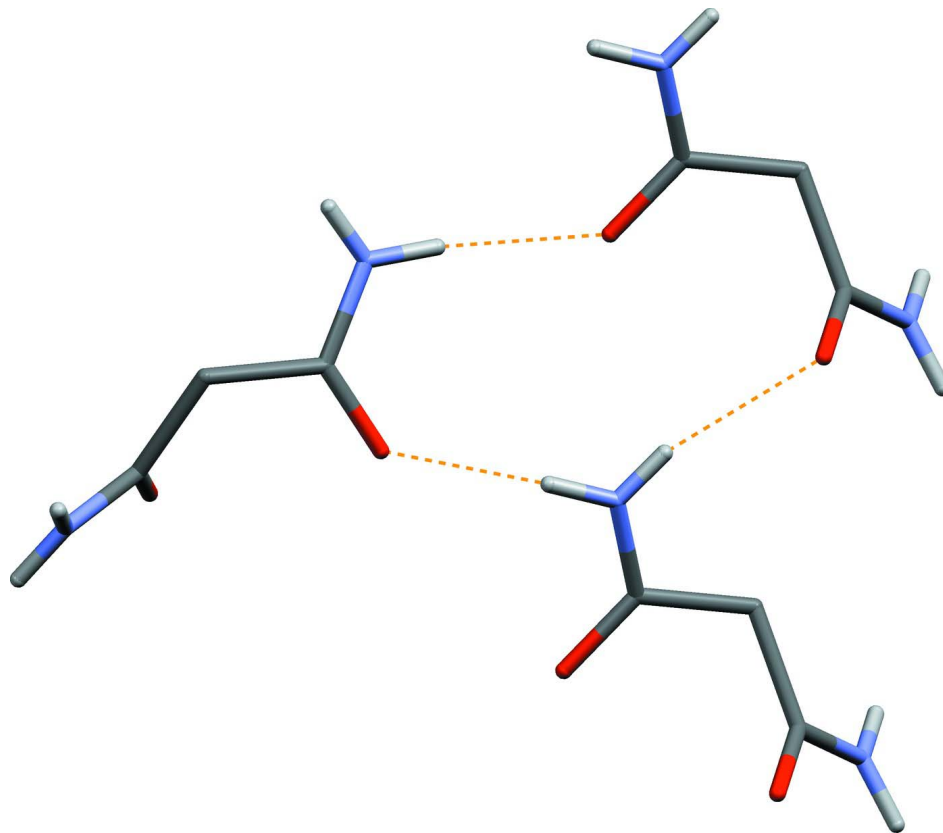


Figure 2

Two mean planes, one drawn through N, O, C1 and C2 and the other through their symmetry equivalents, and the dihedral angle between the two planes.

**Figure 3**

A packing diagram, viewed along the b axis. Hydrogen bonds are indicated by orange dashed lines.

**Figure 4**

The $R_3^3(12)$ hydrogen-bonding motif. Hydrogen bonds are indicated by orange dashed lines and C-bound H atoms are omitted.

Malonamide

Crystal data

C₃H₆N₂O₂
M_r = 102.10
 Tetragonal, *P*4₃2₁2
 Hall symbol: P 4nw 2abw
a = 5.3140 (3) Å
c = 15.5360 (12) Å
V = 438.71 (5) Å³
Z = 4
F(000) = 216

D_x = 1.546 Mg m⁻³
 Mo *Kα* radiation, λ = 0.71073 Å
 Cell parameters from 54 reflections
 θ = 2.5–27.5°
 μ = 0.13 mm⁻¹
T = 150 K
 Block, light yellow
 0.50 × 0.50 × 0.02 mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2003)
T_{min} = 0.902, *T_{max}* = 0.997

6874 measured reflections
 340 independent reflections
 324 reflections with *I* > 2σ(*I*)
R_{int} = 0.018
 θ_{max} = 27.5°, θ_{min} = 5.3°
h = -6→6
k = -5→6
l = -20→20

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.032
wR(*F*²) = 0.082
S = 1.23
 340 reflections
 43 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 Only H-atom coordinates refined
w = 1/[σ²(*F_o*²) + (0.0509*P*)² + 0.0691*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.19 e Å⁻³
 Δρ_{min} = -0.20 e Å⁻³
 Extinction correction: *SHELXL97*,
*F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}
 Extinction coefficient: 0.12 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{iso}</i> */ <i>U_{eq}</i> |
|-----|--------------|------------|-------------|---|
| O | 0.35135 (18) | 0.5410 (2) | 0.08252 (5) | 0.0193 (4) |
| N | -0.0616 (2) | 0.5402 (3) | 0.04955 (8) | 0.0182 (4) |
| H1N | -0.095 (4) | 0.675 (4) | 0.0800 (11) | 0.022* |
| H2N | -0.177 (4) | 0.469 (4) | 0.0277 (12) | 0.022* |
| C1 | 0.1676 (3) | 0.4422 (3) | 0.04704 (8) | 0.0134 (4) |
| C2 | 0.1932 (2) | 0.1932 (2) | 0.0000 | 0.0147 (4) |
| H2 | 0.166 (3) | 0.064 (4) | 0.0448 (10) | 0.018* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|-------------|
| O | 0.0154 (6) | 0.0201 (6) | 0.0222 (5) | -0.0024 (4) | -0.0014 (4) | -0.0069 (4) |
| N | 0.0137 (7) | 0.0158 (7) | 0.0252 (7) | 0.0002 (5) | -0.0013 (5) | -0.0063 (5) |
| C1 | 0.0148 (7) | 0.0133 (7) | 0.0121 (5) | -0.0017 (5) | 0.0015 (5) | 0.0008 (5) |
| C2 | 0.0130 (6) | 0.0130 (6) | 0.0180 (8) | -0.0020 (7) | 0.0020 (5) | -0.0020 (5) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------------------------|-------------|-------------------------|-------------|
| O—C1 | 1.2382 (17) | N—C1 | 1.3251 (19) |
| N—H1N | 0.87 (2) | C1—C2 | 1.5176 (17) |
| N—H2N | 0.79 (2) | C2—H2 | 0.986 (19) |
| H1N—N—H2N | 117 (2) | N—C1—C2 | 116.07 (11) |
| H1N—N—C1 | 121.7 (13) | C1—C2—C1 ⁱ | 112.84 (16) |
| H2N—N—C1 | 120.5 (15) | C1—C2—H2 | 104.6 (10) |
| O—C1—N | 123.02 (13) | C1 ⁱ —C2—H2 | 113.9 (11) |
| O—C1—C2 | 120.88 (12) | | |
| O—C1—C2—C1 ⁱ | -36.66 (9) | N—C1—C2—C1 ⁱ | 145.23 (12) |

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

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|----------|-------------|-------------|---------------|
| N—H1N \cdots O ⁱⁱ | 0.87 (2) | 2.05 (2) | 2.9195 (16) | 170.8 (16) |
| N—H2N \cdots O ⁱⁱⁱ | 0.79 (2) | 2.36 (2) | 3.1112 (17) | 157.6 (19) |

Symmetry codes: (ii) $x-1/2, -y+3/2, -z+1/4$; (iii) $y-1, x, -z$.