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Malonamide: an orthorhombic polymorph

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An orthorhombic polymorph of malonamide, $C_3H_6N_2O_2$, 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] and of the tetragonal form described in the previous paper [Nichol & Clegg (2005). *Acta Cryst*. E**61**, o3424–o3426]. A simple $R_4^2(8)$ motif links the molecules together and the symmetry of the molecule means that this extends into a three-dimensional network.

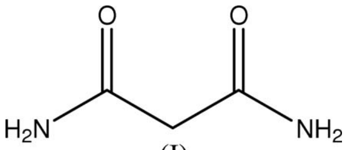
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.001 Å
R factor = 0.031
wR factor = 0.083
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In the previous paper (Nichol & Clegg, 2005), we reported a tetragonal polymorph of malonamide, (I). By crystallizing a second sample from the original reaction solution we have obtained a further polymorph, this time in the orthorhombic crystal system. The only previously known polymorph of malonamide (Chieh *et al.*, 1970) was reported in the space group $P2_1/c$ at room temperature, with two independent molecules in the asymmetric unit and a final R = 0.05. After realizing that we had identified a second crystalline form of this compound, we wished to redetermine the unit cell at room temperature in order to establish whether this was a temperature-induced phase transition or a completely new polymorph stable under the same conditions. To do this we had to recrystallize the sample again and what we actually obtained was (I) as yet another, orthorhombic, polymorph.



(I)

The molecular structure of (I) is shown in Fig. 1. The asymmetric unit consists of one half of the molecule, the complete molecule being generated by a twofold rotation axis which passes through C2. Bond lengths and angles are in good agreement with the mean values for the other polymorphs and the dihedral angle between the O/N/C1/C2 mean plane and its symmetry equivalent (Fig. 2), at 71.90 (4)°, is much closer to the values calculated from the report of Chieh *et al.* (1970) for their two independent molecules (84.8 and 85.3°) than is the case with the tetragonal polymorph [58.68 (4)°].

Fig. 3 shows a packing diagram viewed along the *a* axis. Both independent N—H bonds are involved in hydrogen bonding and each O atom is therefore a bifurcated acceptor. The hydrogen bonding consists of a simple $R_4^2(8)$ graph-set motif (Etter, 1990; Bernstein *et al.*, 1995), illustrated in Fig. 4.

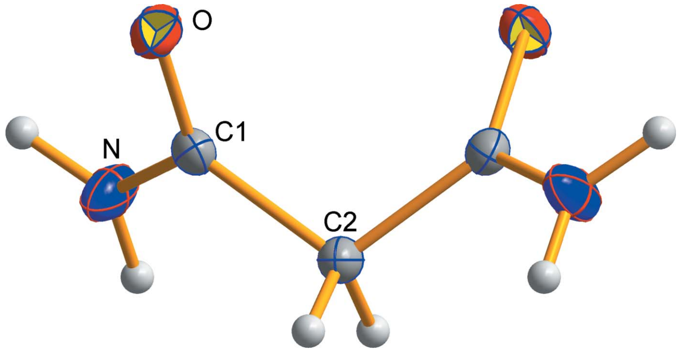


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres. The labelled atoms indicate the asymmetric unit; the complete molecule is generated by a twofold rotation axis ($-x, y, \frac{1}{2} - z$) which passes through C2.

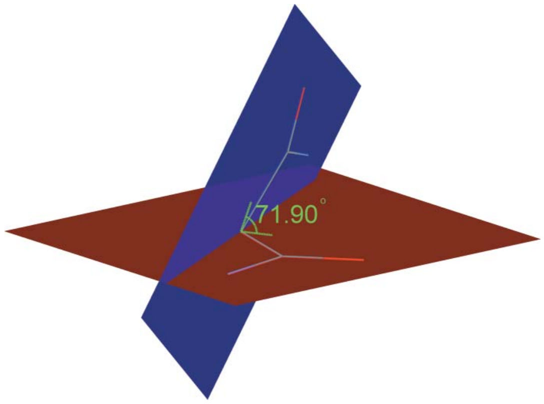


Figure 2
Two mean planes, one drawn through N, O, C1 and C2 and the other through their symmetry-equivalents, and the dihedral angle between the two planes.

The crystallographic rotation symmetry of the molecule means that this simple motif extends into a complex three-dimensional network.

Intrigued by the newly discovered polymorphism of this compound, we have made numerous attempts to obtain again the tetragonal form. Despite carrying out the preparation and crystallization in different locations, we have always obtained the orthorhombic form (the third polymorph, described in this paper) and never one of the others, either monoclinic or tetragonal. We wonder whether this is an example of the phenomenon of 'disappearing polymorphs' (Dunitz & Bernstein, 1995).

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, from which crystals of the tetragonal polymorph were initially obtained after several days (Nichol & Clegg, 2005). The solution was stored in a sealed container for several months. Large plate crystals of (I) were subsequently grown by evaporation of the cold solution on a watch glass over a period of a few hours.

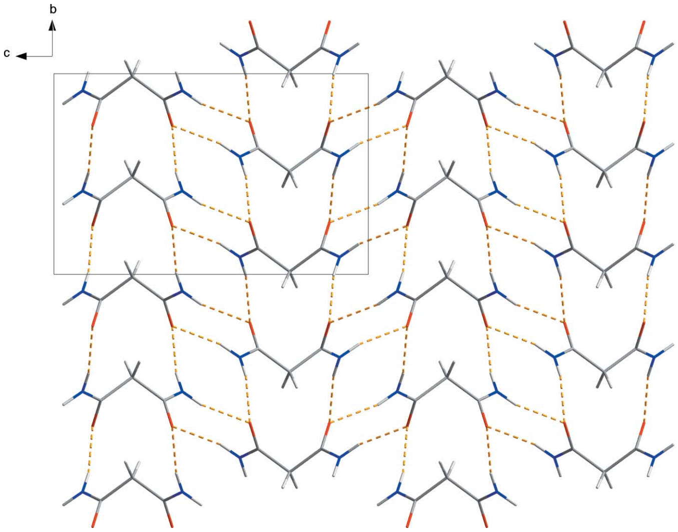


Figure 3
A packing diagram, viewed along the *a* axis. Hydrogen bonds are indicated by dashed orange lines.

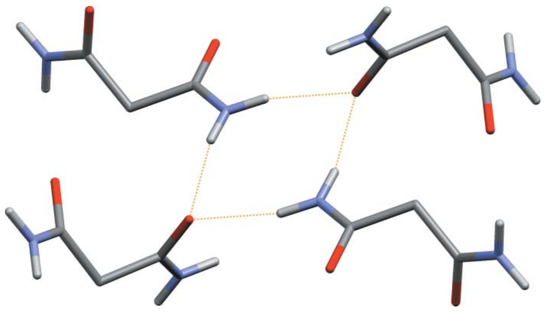


Figure 4
The $R_4^2(8)$ motif; dashed orange lines indicate hydrogen bonding and C—H H atoms have been omitted.

Crystal data

$C_3H_6N_2O_2$
$M_r = 102.10$
Orthorhombic, *Pbcn*
$a = 5.3602$ (9) Å
$b = 7.5178$ (8) Å
$c = 11.791$ (2) Å
$V = 475.14$ (12) Å^3
$Z = 4$
$D_x = 1.427$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6050 reflections
$\theta = 2.5$–$27.5°$
$\mu = 0.12$ mm^{-1}
$T = 150$ (2) K
Block cut from large plate, colourless
0.42 × 0.36 × 0.26 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.911$, $T_{max} = 0.970$
8872 measured reflections
539 independent reflections
490 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.083$
$S = 1.11$
539 reflections
43 parameters
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.1866P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.077 (17)

Table 1
Selected geometric parameters (Å, °).

O—C1	1.2420 (13)	C1—C2	1.5178 (13)
N—C1	1.3257 (14)		
O—C1—C2—C1^{i}	−45.99 (8)	N—C1—C2—C1^{i}	134.54 (10)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O^{ii}	0.89 (2)	2.06 (2)	2.9282 (13)	166 (1)
N—H2N···O^{iii}	0.85 (2)	2.12 (2)	2.9502 (14)	169 (2)

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

All H atoms were located in a difference map and their coordinates were refined freely, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N,C). The C—H bond length refined to 0.964 (13) Å and the two N—H bond lengths refined to 0.887 (16) and 0.846 (19) Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND3* (Brandenburg & Putz, 2004) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: Bruker *SHELXTL* and local programs.

We thank the EPSRC for funding.

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supporting information

Acta Cryst. (2005). E**61**, o3427–o3429 [doi:10.1107/S1600536805030540]

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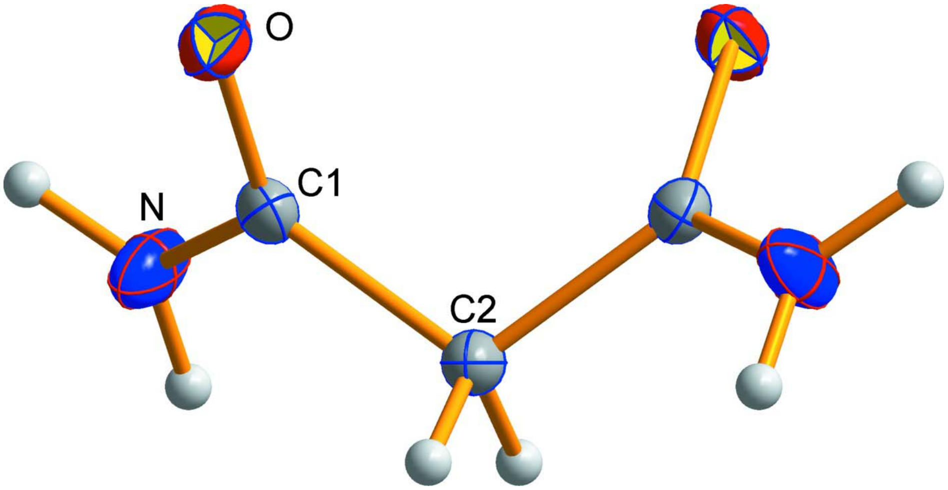

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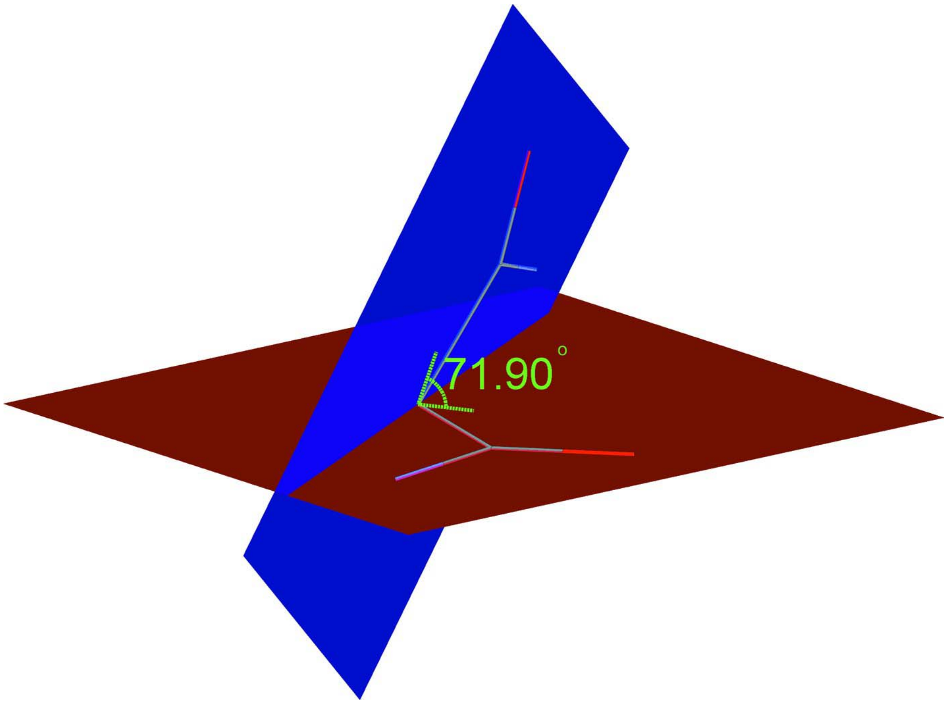

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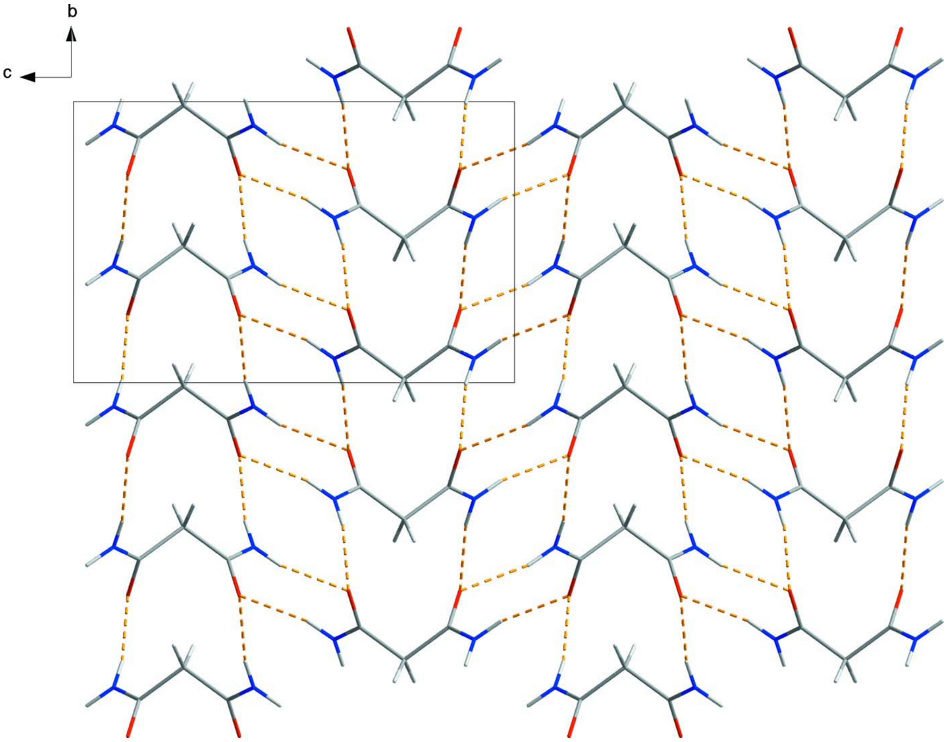

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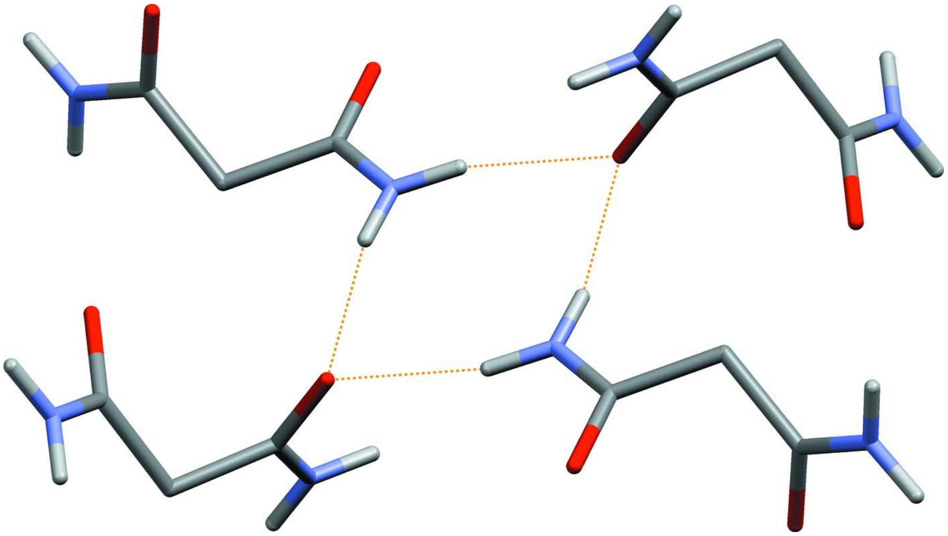

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Malonamide

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$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.11
539 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
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.1866P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL97*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.077 (17)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O	0.06613 (15)	0.25831 (10)	0.37641 (7)	0.0222 (3)
N	−0.2702 (2)	0.08531 (14)	0.40865 (9)	0.0250 (3)
H1N	−0.313 (3)	0.1499 (19)	0.4686 (14)	0.030*
H2N	−0.355 (3)	−0.005 (3)	0.3895 (13)	0.030*
C1	−0.06739 (19)	0.12942 (13)	0.35078 (8)	0.0161 (3)
C2	0.0000	0.01335 (19)	0.2500	0.0161 (4)
H2	0.136 (3)	−0.0629 (16)	0.2721 (11)	0.019*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O	0.0269 (5)	0.0211 (5)	0.0187 (5)	−0.0057 (3)	0.0001 (3)	−0.0038 (3)

N	0.0295 (6)	0.0226 (5)	0.0228 (5)	−0.0060 (4)	0.0109 (4)	−0.0065 (4)
C1	0.0200 (5)	0.0152 (5)	0.0131 (5)	0.0013 (4)	−0.0008 (4)	0.0014 (3)
C2	0.0195 (7)	0.0142 (7)	0.0144 (6)	0.000	0.0012 (5)	0.000

Geometric parameters (Å, º)

O—C1	1.2420 (13)	N—C1	1.3257 (14)
N—H1N	0.887 (16)	C1—C2	1.5178 (13)
N—H2N	0.846 (19)	C2—H2	0.963 (13)
H1N—N—H2N	120.8 (15)	N—C1—C2	117.02 (9)
H1N—N—C1	119.0 (10)	C1—C2—C1^{i}	109.82 (12)
H2N—N—C1	120.1 (11)	C1—C2—H2	108.1 (8)
O—C1—N	122.85 (10)	C1^{i}—C2—H2	112.0 (8)
O—C1—C2	120.12 (9)		
O—C1—C2—C1^{i}	−45.99 (8)	N—C1—C2—C1^{i}	134.54 (10)

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1*N*···O^{ii}	0.887 (16)	2.058 (17)	2.9282 (13)	166.4 (13)
N—H2*N*···O^{iii}	0.846 (19)	2.116 (19)	2.9502 (14)	168.7 (15)

Symmetry codes: (ii) *x*−1/2, −*y*+1/2, −*z*+1; (iii) −*x*−1/2, *y*−1/2, *z*.