

## Malonamide: an orthorhombic polymorph

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## Key indicators

Single-crystal X-ray study  
 $T = 150$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.083  
Data-to-parameter ratio = 12.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

An orthorhombic 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] 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.

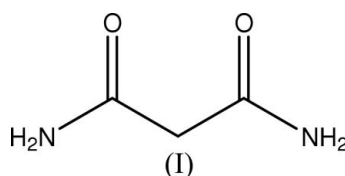
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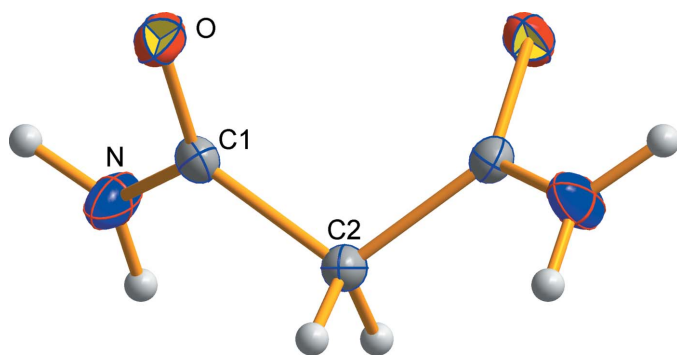
## Comment

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.

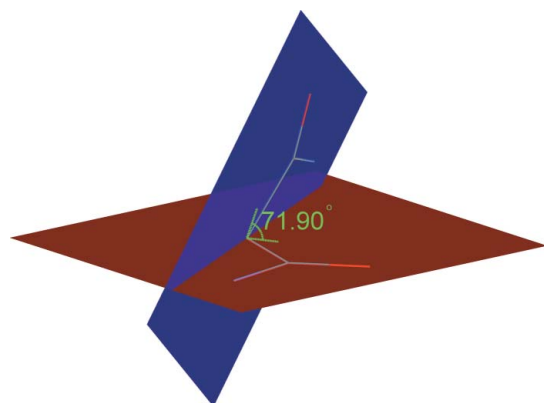


The molecular structure of (I) is shown in Fig. 1. The asymmetric unit consists of one half of the molecule, the complete molecule being generated by a twofold rotation axis which passes through C2. Bond lengths and angles are in good agreement with the mean values for the other polymorphs and the dihedral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

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**

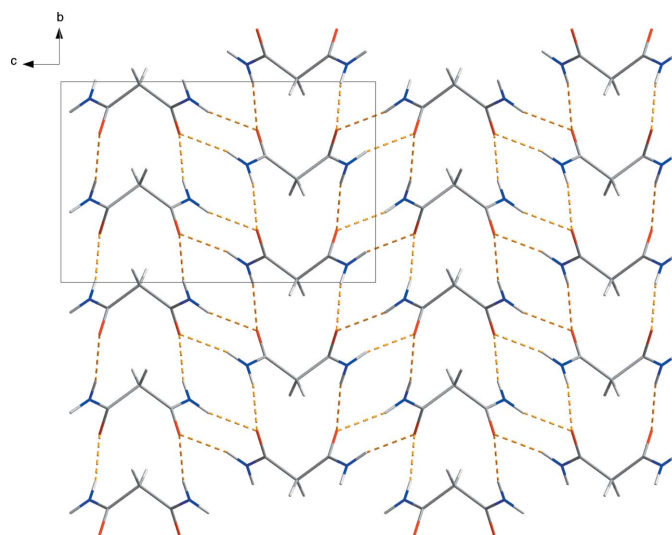
Two mean planes, one drawn through N, O, C1 and C2 and the other through their symmetry-equivalents, and the dihedral angle between the two planes.

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

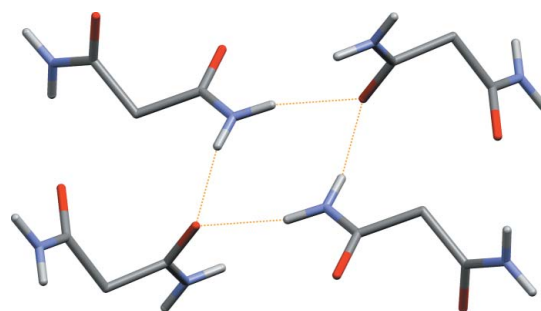
Intrigued by the newly discovered polymorphism of this compound, we have made numerous attempts to obtain again the tetragonal form. Despite carrying out the preparation and crystallization in different locations, we have always obtained the orthorhombic form (the third polymorph, described in this paper) 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  $\text{Na}_2\text{CO}_3$  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

$\text{C}_3\text{H}_6\text{N}_2\text{O}_2$   
 $M_r = 102.10$   
 Orthorhombic,  $Pbcn$   
 $a = 5.3602$  (9) Å  
 $b = 7.5178$  (8) Å  
 $c = 11.791$  (2) Å  
 $V = 475.14$  (12) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.427$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 6050 reflections  
 $\theta = 2.5$ – $27.5^\circ$   
 $\mu = 0.12$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block cut from large plate, colourless  
 $0.42 \times 0.36 \times 0.26$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -6 \rightarrow 6$   
 $k = -9 \rightarrow 9$   
 $l = -15 \rightarrow 15$

### 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.20$  e Å<sup>-3</sup>  
 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 <sup>i</sup>	−45.99 (8)	N—C1—C2—C1 <sup>i</sup>	134.54 (10)

Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .**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 <sup>ii</sup>	0.89 (2)	2.06 (2)	2.9282 (13)	166 (1)
N—H2N $\cdots$ O <sup>iii</sup>	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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$ . 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.

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