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Key indicators

Powder X-ray study
 $T = 250$ K
Mean $\sigma(C-C) = 0.002$ Å
 R factor = 0.054
 wR factor = 0.070

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

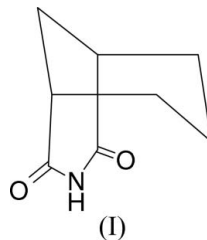
Powder study of 3-azabicyclo[3.3.1]nonane-2,4-dione form 2

A polycrystalline sample of a new polymorph of the title compound, $C_8H_{11}NO_2$, was produced during a variable-temperature X-ray powder diffraction study. The crystal structure was solved at 1.67 Å resolution by simulated annealing from laboratory powder data collected at 250 K. Subsequent Rietveld refinement yielded an R_{wp} of 0.070 to 1.54 Å resolution. The structure contains two molecules in the asymmetric unit, which form a $C_2^2(8)$ chain motif *via* N—H···O hydrogen bonds.

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Comment

The crystal structure of the title compound, (I), was solved by simulated annealing using laboratory capillary X-ray powder diffraction data. The compound crystallizes in space group $P2_1/c$ with two independent molecules of 3-azabicyclononane-2,4-dione in the asymmetric unit (Fig. 1).



The crystal structure of this polymorph (form 2) is approximately a cell-doubled modification of the stable room-temperature form of 3-azabicyclononane-2,4-dione (form 1) (Howie & Skakle, 2001), with the cell doubling in the c direction [18.8867 (4) *versus* 9.3384 (6) Å]. Form 2 is metastable with respect to form 1 at room temperature, with full conversion taking less than 1 h. However, with rapid cooling to 250 K (the data collection temperature), form 2 is kinetically trapped and stable for over 10 h.

The basic hydrogen-bond motif in (I) is a chain [graph set $C_2^2(8)$; Etter, 1990] running parallel to the a axis. Each chain contains alternating independent molecules linked by N—H···O hydrogen bonds (Table 1). Form 2 packs the chains in a manner similar to form 1, with the chains lying side by side to form layers (Fig. 2) parallel to the ab plane. The layers are related by the 2_1 screw axis and the stacking of the layers differs between the two forms, with form 1 showing an AB repeat packing and form 2 an $ABCD$ repeat packing (Fig. 3). This stacking difference can be attributed to form 2 having two symmetry-independent molecules. The stacking in form 2 can be envisaged as related to that of form 1 by a translation of approximately half a unit cell parallel to the b axis of the C and

D layers. With no strong interactions between the layers, the conversion from form 2 to form 1 would be facile and may account for the rapid conversion at room temperature.

Experimental

A polycrystalline sample of (I) was prepared by heating a sample of the raw material (form 1) to 420 K and subsequently quenching *in situ* to 250 K. The sample was held in a rotating 0.7 mm borosilicate glass capillary and the temperature controlled using an Oxford Cryosystems Cryostream Plus 700 series device. Data were collected over a period of 7.5 h using a variable-counting-time scheme (Shankland *et al.*, 1997; Hill & Madsen, 2002) in the range $7\text{--}60^\circ 2\theta$. The final data set showed no evidence of diffraction associated with the form 1 structure.

Crystal data

$\text{C}_8\text{H}_{11}\text{NO}_2$
 $M_r = 153.18$
 Monoclinic, $P2_1/c$
 $a = 7.67102 (18) \text{ \AA}$
 $b = 10.5483 (2) \text{ \AA}$
 $c = 18.8867 (4) \text{ \AA}$
 $\beta = 95.5800 (12)^\circ$
 $V = 1521.00 (6) \text{ \AA}^3$
 $Z = 8$

$D_x = 1.338 \text{ Mg m}^{-3}$
 Cu $K\alpha_1$ radiation
 $\mu = 0.79 \text{ mm}^{-1}$
 $T = 250 \text{ K}$
 Specimen shape: cylinder
 $12 \times 0.7 \times 0.7 \text{ mm}$
 Specimen prepared at 420 K
 Particle morphology: polycrystalline
 mass, white

Data collection

Bruker AXS D8 Advance
 diffractometer
 Specimen mounting: 0.7 mm
 borosilicate capillary
 Specimen mounted in transmission
 mode

Scan method: step
 Absorption correction: none
 $2\theta_{\min} = 7.0$, $2\theta_{\max} = 60.0^\circ$
 Increment in $2\theta = 0.017^\circ$

Refinement

$R_p = 0.054$
 $R_{wp} = 0.070$
 $R_{\text{exp}} = 0.016$
 $R_B = 3.058$
 $S = 4.31$
 Profile function: Fundamental
 parameters with axial divergence
 correction.
 142 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $w = 1/\sigma(Y_{\text{obs}})^2$
 $(\Delta/\sigma)_{\max} = 0.111$
 Preferred orientation correction: a
 spherical harmonics-based
 preferred orientation correction
 (Järvinen, 1993) was applied with
 TOPAS (Coelho, 2003) during
 the Rietveld refinement.

Table 1

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N1--H1}\cdots\text{O1w}^i$	0.90 (1)	2.11 (1)	3.006 (4)	172 (1)
$\text{N1w--H1w}\cdots\text{O1}^{ii}$	0.91 (1)	2.03 (1)	2.931 (4)	172 (1)

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

The diffraction pattern indexed to a monoclinic cell [$M(18) = 28.0$, $F(18) = 65.9$; *DICVOL91*; Boultif & Louër, 1991] and space group $P2_1/c$ was assigned from volume considerations and a statistical consideration of the systematic absences (Markvardsen *et al.*, 2001). $P2_1/a$ and $P2_1/n$ were discounted as they did not account for the peak attributable to form 2 at $15.63^\circ 2\theta$.

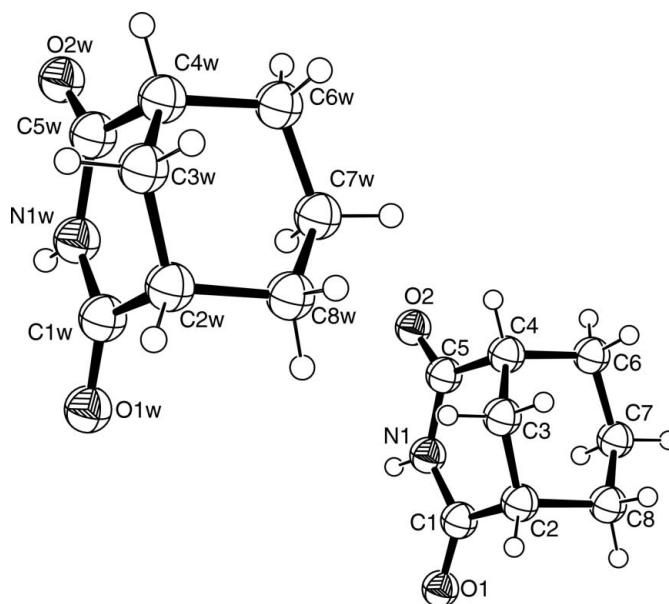


Figure 1

The asymmetric unit of (I) with the atom-numbering scheme. Displacement spheres are shown at the 50% probability level.

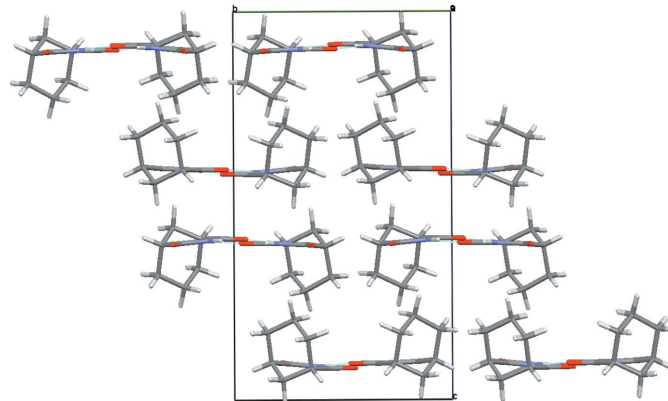


Figure 2

Four layers, each containing two ribbons, stacking in an *ABCD* repeat pattern. The view is parallel to the axis of propagation of the ribbons and the *a* axis.

The data were background subtracted and truncated to $54.8^\circ 2\theta$ for Pawley fitting (Pawley, 1981; $\chi^2_{\text{Pawley}} = 18.50$) and the structure solved using the simulated annealing (SA) global optimization procedure, described previously (David *et al.*, 1998), that is now implemented in the *DASH* computer program (David *et al.*, 2001). The internal coordinate description (including H atoms) of the molecules was constructed from standard bond lengths, bond angles and bond torsions where appropriate. The structure was solved using data to $54.8^\circ 2\theta$, comprising 402 reflections. The structure was refined against data in the range $7.0\text{--}60.0^\circ 2\theta$ (448 reflections). The restraints were set such that bonds and angles did not deviate more than 0.01 \AA and 1° , respectively, from their initial values during the refinement. Atoms C1, C5, C4, C2, O1, N1, O2 and H1 (first molecule) and atoms C1w, C5w, C4w, C1w, O1w, N1w, O2w and H1w (second molecule) of 3-azabicyclo[3.3.1]nonane-2,4-dione were restrained to be coplanar.

The SA structure solution involved the optimization of two independent molecules totaling 12 degrees of freedom (positional and

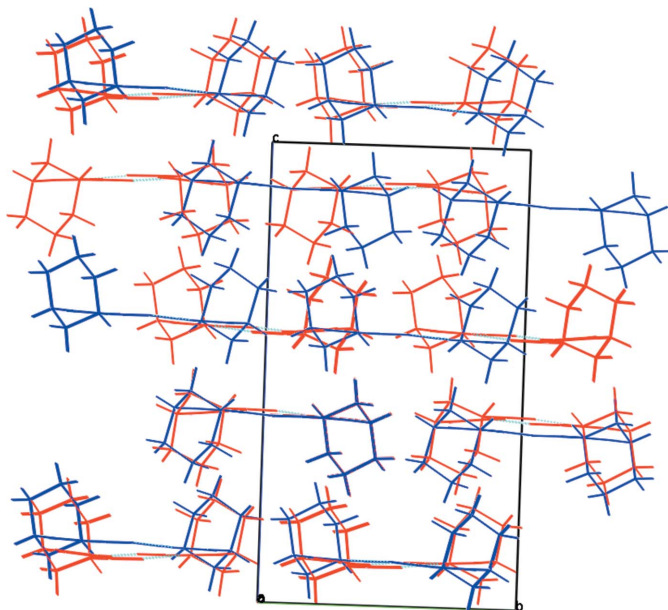


Figure 3

Overlay of the layer stacking of form 1 (blue) and form 2 (red). The members of the uppermost layer and two bottom layers coincide, while the remaining two layers do not. Hydrogen bonds are shown as dashed lines.

orientational). All degrees of freedom were assigned random values at the start of the simulated annealing run. The best SA solution had a favourable $\chi^2_{SA}/\chi^2_{Pawley}$ ratio of 4.5, had a chemically reasonable packing arrangement and exhibited no significant misfit to the data.

The solved structure was subsequently refined against data in the range $7.0\text{--}60.0^\circ$ 2θ using a restrained Rietveld (1969) method as implemented in *TOPAS* (Coelho, 2003), with R_{wp} falling to 0.0698 during the refinement. All atomic positions (including H atoms) for the structure of (I) were refined, subject to a series of restraints on bond lengths, bond angles and planarity. A spherical harmonics (8th order) correction of intensities for preferred orientation was applied in the final refinement (Järvinen, 1993). An 8th order correction yielded a significant improvement in R_{wp} compared with lower orders. The need for such a high level of correction is most likely due to the effect of the *in situ* method of sample preparation on particle morphology. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 4.

Data collection: *DIFFRAC plus XRD Commander* (Kienle & Jacob, 2003); cell refinement: *TOPAS* (Coelho, 2003); data reduction: *DASH* (David *et al.*, 2001); program(s) used to solve structure: *DASH*; program(s) used to refine structure: *TOPAS*; molecular graphics: *MERCURY* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004).

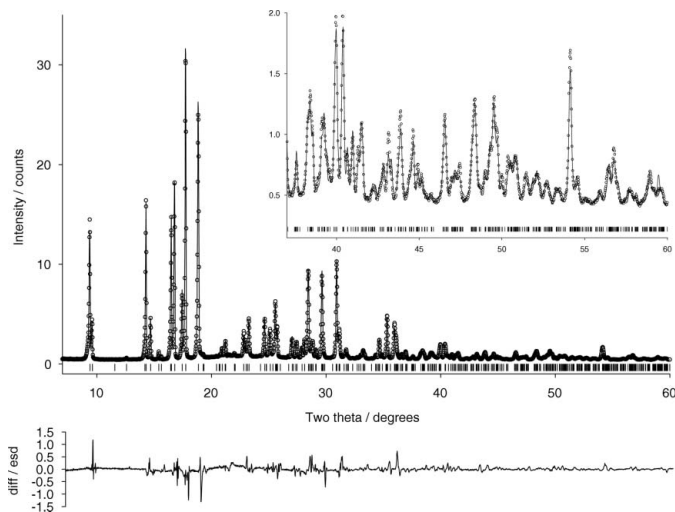


Figure 4

Final observed (points), calculated (line) and difference $[(y_{\text{obs}} - y_{\text{calc}}) / \sigma(y_{\text{obs}})]$ profiles for the Rietveld refinement of the title compound.

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