organic papers

Powder study of 3-azabicyclo[3.3.1]nonane-2,4-dione 1-methylnaphthalene hemisolvate

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Key indicators

Powder X-ray study
$T = 295$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.046
wR factor = 0.057

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

The crystal structure of the title compound, $C_8H_{11}N_1O_2$·$0.5C_{11}H_{10}$, was solved by simulated annealing from laboratory X-ray powder diffraction data, collected at room temperature. Subsequent Rietveld refinement, using data collected to 1.51 Å resolution, yielded an R_{wp} value of 0.057. The compound crystallizes with two molecules of 3-azabicyclononane-2,4-dione and one molecule of 1-methylnaphthalene in the asymmetric unit.

Comment

The title compound, (I), was crystallized from 1-methylnaphthalene during a preliminary solvent screen in preparation for an automated parallel crystallization study of 3-azabicyclo[3.3.1]nonane-2,4-dione. The sample was identified as a new form using multi-sample foil transmission X-ray powder diffraction analysis (Florence et al., 2003).


(I)
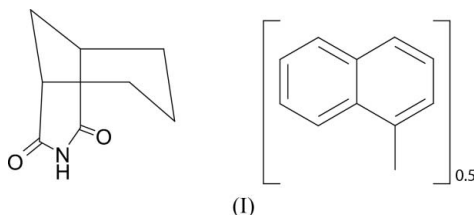
The crystal structure of (I) was solved by simulated annealing using laboratory X-ray powder diffraction data. The compound crystallizes in space group $P2_1/c$ with two molecules of 3-azabicyclononane-2,4-dione and one molecule of 1-methylnaphthalene in the asymmetric unit (Fig. 1). In the crystal structure, intermolecular N—H···O hydrogen bonds (Table 1) link two independent 3-azabicyclononane-2,4-dione molecules into a chain (Fig. 1) running along the b axis. The structure of this chain is very similar to that found in the unsolvated form 1 of 3-azabicyclononane-2,4-dione (Howie & Skakle, 2001). However, in form 1 the chain is propagated by a glide symmetry operation, whereas in (I) it propagates via a 2_1 screw axis. The paired hydrogen-bonded chains in (I) constitute a pseudo-layer parallel to the bc plane. Between two pseudo-layers related by translation along the a axis, channels parallel to the b axis are observed. These channels are filled by stacks of 1-methylnaphthalene solvent molecules, which are oriented nearly perpendicular to the b axis (Fig. 2).

Experimental

A polycrystalline sample of (I) was recrystallized by cooling a saturated 1-methylnaphthalene solution from 313 to 283 K. The sample
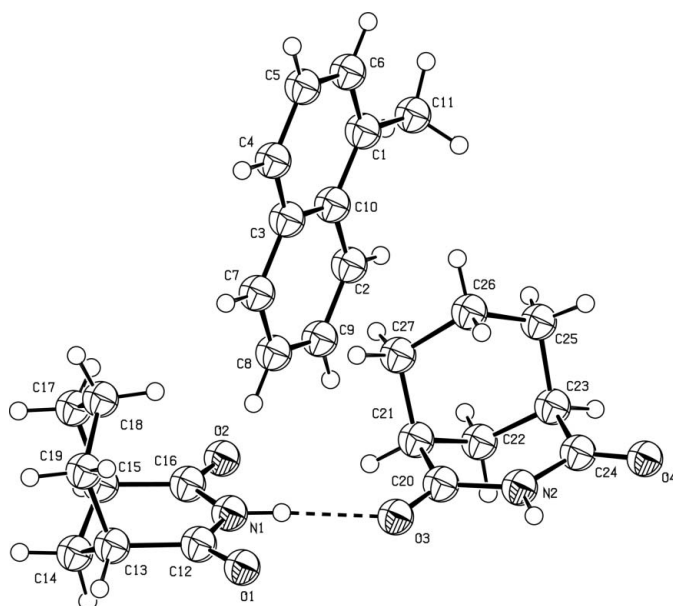
Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. The dashed line indicates the N—H···O hydrogen bond between 3-azabicyclononane-2,4-dione molecules. Displacement spheres are shown at the 50% probability level.
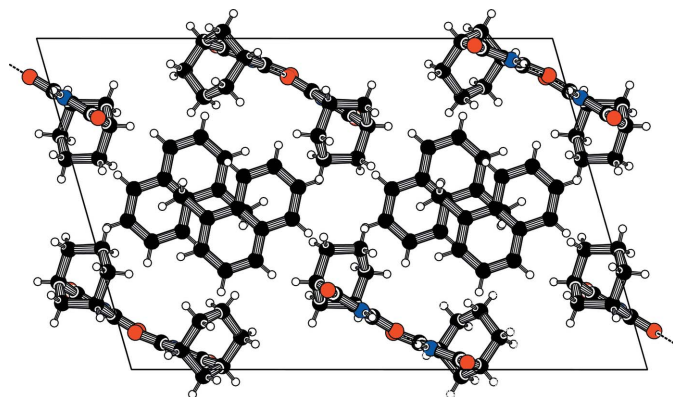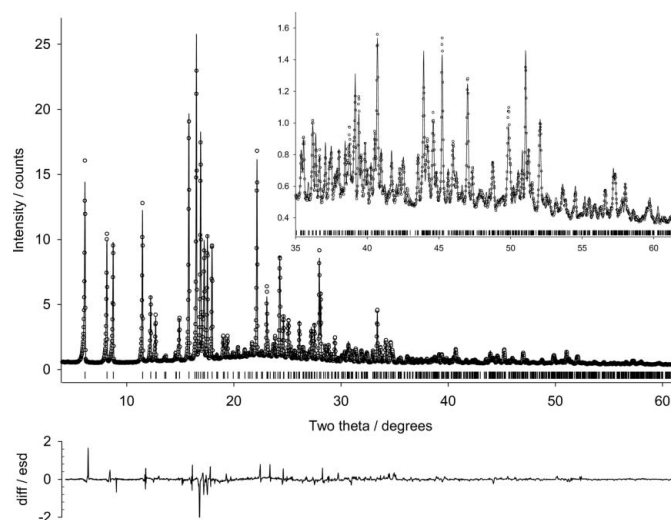

Figure 2
The crystal packing of (I) viewed down the b axis and showing the stacks of solvent molecules situated between the pseudo-layers formed by 3-azabicyclononane-2,4-dione molecules. Illustrated using *PLATON* (Spek, 2003).

was loaded into a 0.7 mm borosilicate glass capillary and rotated throughout the data collection to minimize preferred orientation effects. Data were collected using a variable count time (VCT) scheme in which the step time is increased with 2θ (Shankland *et al.*, 1997; Hill & Madsen, 2002).

Crystal data

$C_8H_{11}NO_2 \cdot 0.5C_{11}H_{10}$	$D_x = 1.251$ Mg m^{-3}
$M_r = 224.28$	Cu $K\alpha_1$ radiation
Monoclinic, $P2_1/c$	$\mu = 0.67$ mm^{-1}
$a = 15.02360$ (18) Å	$T = 295$ K
$b = 7.32295$ (12) Å	Specimen shape: cylinder
$c = 22.5164$ (3) Å	$12 \times 0.7 \times 0.7$ mm
$\beta = 106.0201$ (6)°	Specimen prepared at 298 K
$V = 2380.99$ (6) Å^3	Particle morphology: needle, white
$Z = 8$	

Figure 3
Final observed (points), calculated (line) and difference $[(y_{obs}-y_{calc})/\sigma(y_{obs})]$ profiles for the Rietveld refinement of the title compound.

Data collection

Bruker AXS D8 Advance diffractometer	Scan method: step
	Absorption correction: none
Specimen mounting: 0.7 mm borosilicate capillary	$2\theta_{min} = 4.0$, $2\theta_{max} = 62.5°$
	Increment in $2\theta = 0.017°$
Specimen mounted in transmission mode	

Refinement

$R_p = 0.046$	Only H-atom coordinates refined
$R_{wp} = 0.057$	$w = 1/\sigma(Y_{obs})^2$
$R_{exp} = 0.013$	$(\Delta/\sigma)_{max} = 0.01$
$R_B = 3.499$	Preferred orientation correction:
$S = 2.00$	A spherical harmonics-based
Profile function: Fundamental parameters with axial divergence correction.	preferred orientation correction (Järvinen, 1993) was applied with *TOPAS* (Coelho, 2003) during the Rietveld refinement
211 parameters	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O3	0.900 (5)	1.966 (6)	2.865 (2)	175.8 (4)
N2—H22···O2^i	0.901 (5)	1.921 (10)	2.812 (8)	170.1 (5)

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

The diffraction pattern indexed to a monoclinic cell [$M(20) = 44.5$, $F(20) = 146.5$; *DICVOL91*; Boultif & Louer, 1991] and the space group $P2_1/c$ was assigned from volume considerations and a statistical consideration of the systematic absences (Markvardsen *et al.*, 2001). The data set was background subtracted and truncated to 51.8° 2θ for Pawley fitting (Pawley, 1981; $\chi^2_{Pawley} = 15.77$) 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 SA structure solution used 453 reflections and involved the optimization of three fragments totaling 18 degrees of freedom (six positional and orientational for each fragment present in the asymmetric unit). All

degrees of freedom were assigned random values at the start of the simulated annealing. The best SA solution had a favourable $\chi^2_{SA}/\chi^2_{Pawley}$ ratio of 3.47 and a chemically reasonable lattice packing arrangement, with no significant misfit to the diffraction data.

The solved structure was then refined against the data in the range 4–61.4° 2θ using a restrained Rietveld (1969) method as implemented in *TOPAS* (Coelho, 2003), with R_{wp} falling to 0.0566 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.

The restraints were set such that bonds and angles did not deviate more than 0.01 Å and 0.8°, respectively, from their initial values during the refinement. Atoms C12, C13, C15, C16, O1, N1, O2 and H1 (first molecule) and atoms C20, C21, C23, C24, O3, N2, O4 and H22 (second molecule) of 3-azabicyclo[3.3.1]nonane-2,4-dione were restrained to be coplanar. Restraints were also applied to the methylnaphthalene molecule, for planarity purposes. A spherical harmonics (4th order) correction of intensities for preferred orientation was applied in the final refinement (Järvinen, 1993). The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 3. U_{iso}(H) values were fixed at 0.076 Å^2.

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: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*, *enCIFer* (Allen *et al.*, 2004) and *SHELXL97* (Sheldrick, 1997).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Boultif, A. & Louër, D. (1991). *J. Appl. Cryst.* **24**, 987–993.

Coelho, A. A. (2003). *TOPAS User Manual.* Version 3.1. Bruker AXS GmbH, Karlsruhe, Germany.

David, W. I. F., Shankland, K., Cole, J., Maginn, S., Motherwell, W. D. S. & Taylor, R. (2001). *DASH.* Version 3.0 User Manual. Cambridge Crystallographic Data Centre, Cambridge, England.

David, W. I. F., Shankland, K. & Shankland, N. (1998). *Chem. Commun.* pp. 931–932.

Florence, A. J., Baumgartner, B., Weston, C., Shankland, N., Kennedy, A. R., Shankland, K. & David, W. I. F. (2003). *J. Pharm. Sci.* **92**, 1930–1938.

Hill, R. J. & Madsen, I. C. (2002). *Structure Determination from Powder Diffraction Data*, edited by W. I. F. David, K. Shankland, L. B. McCusker and Ch. Baerlocher, pp.114–116. Oxford University Press.

Howie, R. A. & Skakle, J. M. S. (2001). *Acta Cryst.* E**57**, o822–o824.

Järvinen, M. (1993). *J. Appl. Cryst.* **26**, 525–531.

Kienle, M. & Jacob, M. (2003). *DIFFRAC plus XRD Commander.* Version 2.3. Bruker AXS GmbH, Karlsruhe, Germany.

Markvardsen, A. J., David, W. I. F., Johnson, J. C. & Shankland, K. (2001). *Acta Cryst.* A**57**, 47–54.

Pawley, G. S. (1981). *J. Appl. Cryst.* **14**, 357–361.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Shankland, K., David, W. I. F. & Sivia, D. S. (1997). *J. Mater. Chem.* **7**, 569–572.

Sheldrick, G. M. (1997). *SHELXL97.* University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.