

Gary S. Nichol and
William Clegg*School of Natural Sciences (Chemistry), Bedson
Building, University of Newcastle upon Tyne,
Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 150\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.028
 wR factor = 0.085
Data-to-parameter ratio = 5.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Violuric acid monohydrate: a definitive
redetermination at 150 K

A redetermination at 150 K of the structure of violuric acid monohydrate, $\text{C}_4\text{H}_3\text{N}_3\text{O}_4\cdot\text{H}_2\text{O}$, confirms that the space group is non-centrosymmetric $Cmc2_1$, despite indications from the intensity statistics and possible molecular symmetry that it could be centrosymmetric $Cmcm$. Issues raised in the original reports [Craven & Mascarenhas (1964). *Acta Cryst.* **17**, 407–414; Craven & Takei (1964). *Acta Cryst.* **17**, 415–420] suggested either a disordered model or an ordered one with high thermal motion. The redetermination shows that an ordered model is correct, and the low-temperature data collection leads to normal displacement parameters. The precision of the structure is significantly improved in this new study. The violuric acid molecule is entirely planar, and every atom in the structure lies on a crystallographic mirror plane. Violuric acid and water molecules form hydrogen-bonded sheets.

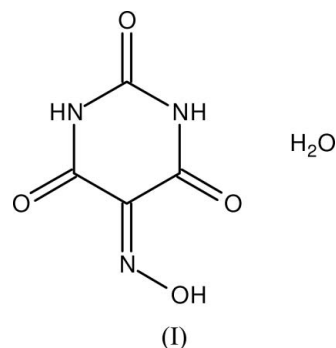
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Comment

Part of our research has concentrated on the structural chemistry of *s*-block metal complexes of cyanuric acid, barbituric acid and other related compounds, well known for their pharmaceutical properties. Violuric acid is a 5-substituted derivative of barbituric acid, and the isonitroso substituent gives extra scope for metal coordination and hydrogen bonding, compared with unsubstituted barbituric acid.



The crystal structure of violuric acid dihydrate (I) has already been reported from room-temperature X-ray (Craven & Mascarenhas, 1964) and neutron (Craven & Takei, 1964) diffraction studies, refined to final R values of 0.059 and 0.070, respectively. The two studies were combined to produce a single result; the positions of the non-H atoms were located from X-ray data and the positions of the H (actually D as a deuterated sample was used) atoms were located from the neutron data. In their reports the authors highlighted unusual issues with the data and the final result, some of which they were unable to resolve to a satisfactory conclusion. These

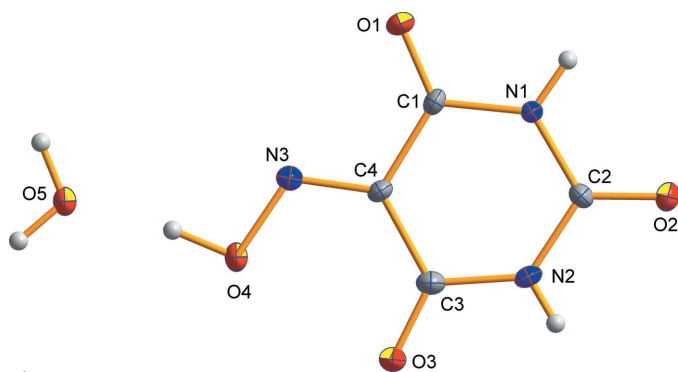


Figure 1
The asymmetric unit of (I), with 50% displacement ellipsoids and H atoms as small spheres of arbitrary size.

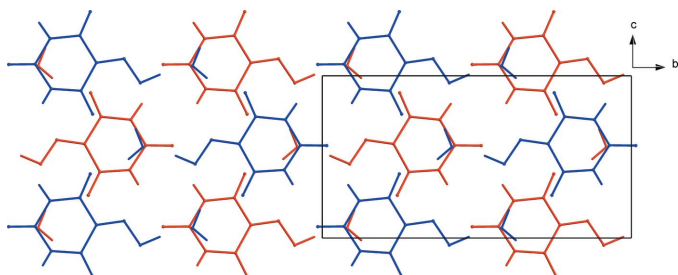


Figure 2
A view along the *a* axis of the packing of (I). One sheet is coloured blue and the other sheet is red, to show the relative displacement along the *c* axis of molecules in the two sheets, preventing ring stacking.

included the choice of space group; extremely high atomic displacement parameters of the isonitroso group and the water molecule, suggesting possible disorder; and poor bond-length precision.

With these uncertainties in mind, and encouraged by our previous research which had revealed that two other barbiturates undergo a phase transition on cooling (Nichol & Clegg, 2005*a,b*), we redetermined the structure of violuric acid monohydrate at 150 K for the purpose of having a reference structure for the metal complexes, also studied at 150 K. No phase transition was observed in this case, but we were able to address the issues raised in the initial 1964 studies.

The asymmetric unit of (I) is shown in Fig. 1. Systematic absence data for this structure indicated that the space group could be one of *Cmcm*, *Cmc2₁* or *Ama2* (with exchanged axes). The data set intensity statistics strongly indicated a centrosymmetric space group (mean $|E^2 - 1| = 0.95$). However, the structure could not be solved in space group *Cmcm*, so space group *Cmc2₁* (the previously reported space group) was selected, giving an entirely satisfactory solution and refinement. The *ADDSYM* function of *PLATON* (Spek, 2003) detected potentially missed further mirror and inversion symmetry, suggesting that *Cmcm* was indeed the true space group. In this space group, however, the refinement is very poor, giving a final $R = 0.20$. The extra mirror symmetry detected by *ADDSYM* would bisect the violurate ring along the axis running through the C=N bond and the carbonyl group opposite, making the two N-H groups and the

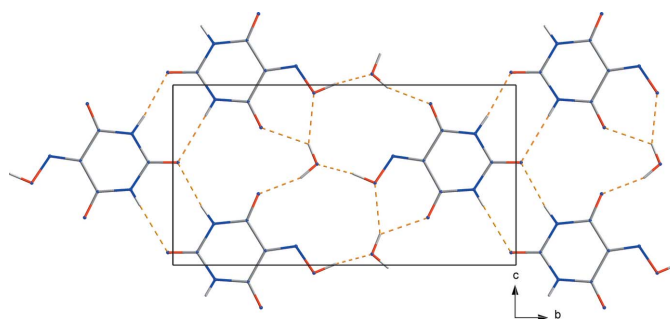


Figure 3
The hydrogen bonding (dashed lines) observed in a single sheet of (I), viewed along the *a* axis.

remaining carbonyl groups symmetry-equivalent. While the geometry of the ring itself is compatible with this extra mirror plane, the isonitroso group is not; this would involve disorder of the N—O bond over the mirror plane. This disorder is not compatible with the crystal packing and hydrogen bonding, so we can safely disregard the pseudo-symmetry and state with confidence that this structure is non-centrosymmetric, in space group *Cmc2₁*.

The originally reported X-ray crystal structure contains atoms with extremely high displacement parameters, causing the authors to consider also a model with all atoms disordered across the mirror plane of *Cmc2₁*; this also gave a satisfactory refinement result and they were unable to reject it conclusively. By redetermining the structure at 150 K we find the atomic displacements to be reduced appreciably and we can be confident that the structure is not disordered. The molecular geometry (Table 1) is determined here with much improved precision, and some apparent anomalies in the original results are removed.

With every atom constrained to lie on a crystallographic mirror plane, the crystal packing consists of stacked sheets with a very close spacing of 3.0377 (6) Å, half the *a*-axis length. Fig. 2 shows a projection along the *a* axis, with all the molecules of one sheet coloured blue and all the molecules of another coloured red; it can be seen that there is no ring-stacking between the violuric acid molecules in adjacent sheets, as their relative displacement along the *c* axis means that the water molecule overlaps the violurate ring in the next sheet.

The hydrogen-bonding arrangement within each sheet, shown in Fig. 3, is slightly unusual in that all the carbonyl groups are acceptors; it is far more commonly observed in the packing of barbiturate derivatives that one group is not involved in hydrogen bonding (Lewis *et al.*, 2005). A familiar $R_2^2(8)$ hydrogen-bonding graph-set motif (Bernstein *et al.*, 1995) links the violurate rings together, while the water molecule is neatly hydrogen-bonded to the third carbonyl group and to the oxygen atom of the isonitroso group. As noted by Craven & Takei (1964), one of the water H atoms acts as a bifurcated donor. While this is now a fairly common observation, in 1964 it was very unusual, and the authors devoted some discussion, including examination of an alternative centrosymmetric model with pseudo-tetrahedral water

hydrogen bonding, to this now commonly accepted interaction.

Experimental

Commercially available violuric acid (1 mmol) was dissolved in a small amount of distilled water with gentle heating. Storage overnight at 278 K resulted in large octahedral colourless crystals of (I).

Crystal data

$C_4H_5N_3O_4 \cdot H_2O$
 $M_r = 175.11$
 Orthorhombic, $Cmc2_1$
 $a = 6.0754$ (11) Å
 $b = 14.343$ (3) Å
 $c = 7.5288$ (13) Å
 $V = 656.1$ (2) Å³
 $Z = 4$
 $D_x = 1.773$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 2281 reflections
 $\theta = 2.2$ – 28.3°
 $\mu = 0.17$ mm⁻¹
 $T = 150$ (2) K
 Octahedron, colourless
 $0.50 \times 0.50 \times 0.50$ mm

Data collection

Bruker SMART 1K CCD diffractometer
 Thin-slice ω scans
 Absorption correction: none
 2856 measured reflections
 468 independent reflections

448 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.018$
 $\theta_{max} = 28.3^\circ$
 $h = -8 \rightarrow 8$
 $k = -18 \rightarrow 19$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.085$
 $S = 1.10$
 468 reflections
 87 parameters
 Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.0025P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.39$ e Å⁻³
 $\Delta\rho_{min} = -0.26$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.008 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-----------|----------|-------------|
| O1–C1 | 1.209 (3) | N2–C2 | 1.367 (4) |
| O2–C2 | 1.224 (3) | N2–C3 | 1.382 (4) |
| O3–C3 | 1.210 (4) | N3–C4 | 1.293 (3) |
| O4–N3 | 1.349 (3) | C1–C4 | 1.478 (4) |
| N1–C1 | 1.385 (3) | C3–C4 | 1.485 (4) |
| N1–C2 | 1.378 (4) | | |
| C1–N1–C2 | 126.1 (2) | N1–C2–N2 | 116.4 (2) |
| C2–N2–C3 | 126.9 (3) | N2–C3–C4 | 115.2 (3) |
| O4–N3–C4 | 115.9 (2) | C1–C4–C3 | 119.70 (18) |
| N1–C1–C4 | 115.6 (2) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|----------|--------------|--------------|----------------|
| O4–H4 \cdots O5 | 0.98 (4) | 1.58 (4) | 2.552 (2) | 172 (4) |
| O5–H5A \cdots O1 ⁱ | 0.86 (5) | 1.91 (5) | 2.744 (3) | 161 (5) |
| O5–H5B \cdots O3 ⁱⁱⁱ | 0.90 (5) | 2.11 (5) | 2.789 (3) | 131 (4) |
| O5–H5B \cdots O4 ⁱⁱ | 0.90 (5) | 2.15 (5) | 2.978 (3) | 152 (4) |
| N1–H1N \cdots O2 ⁱⁱⁱ | 0.90 (5) | 2.08 (5) | 2.972 (3) | 173 (4) |
| N2–H2N \cdots O2 ^{iv} | 0.76 (5) | 2.30 (5) | 3.060 (3) | 180 (5) |

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

All H atoms were located in a difference Fourier map and were freely refined, except that water H atoms were assigned $U_{iso}(H) = 1.2U_{eq}(O)$; refined bond lengths are 0.86 (5) and 0.90 (5) Å for water O–H, 0.76 (5) and 0.90 (5) Å for amide N–H atoms, and 0.94 (4) Å for hydroxy O–H. In the absence of significant anomalous scattering, Friedel pairs were merged.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC for funding.

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supporting information

Acta Cryst. (2005). E61, o3788–o3790 [https://doi.org/10.1107/S160053680503343X]

Violuric acid monohydrate: a definitive redetermination at 150 K

Gary S. Nichol and William Clegg

Violuric acid monohydrate

Crystal data

$C_4H_3N_3O_4 \cdot H_2O$

$M_r = 175.11$

Orthorhombic, $Cmc2_1$

Hall symbol: C 2c -2

$a = 6.0754$ (11) Å

$b = 14.343$ (3) Å

$c = 7.5288$ (13) Å

$V = 656.1$ (2) Å³

$Z = 4$

$F(000) = 360$

$D_x = 1.773$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2281 reflections

$\theta = 2.2$ – 28.3°

$\mu = 0.17$ mm⁻¹

$T = 150$ K

Octahedron, colourless

$0.50 \times 0.50 \times 0.50$ mm

Data collection

Bruker SMART 1K CCD
diffractometer

Radiation source: sealed tube

Graphite monochromator

thin-slice ω scans

2856 measured reflections

468 independent reflections

448 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$

$\theta_{max} = 28.3^\circ$, $\theta_{min} = 2.8^\circ$

$h = -8 \rightarrow 8$

$k = -18 \rightarrow 19$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.085$

$S = 1.10$

468 reflections

87 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.0025P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.39$ e Å⁻³

$\Delta\rho_{min} = -0.26$ e Å⁻³

Extinction correction: SHELXL97,

$Fc^* = kFc[1 + 0.001 \times Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.008 (2)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------|--------------|------------|----------------------------------|
| O1 | 0.5000 | 0.75071 (16) | 0.8953 (3) | 0.0286 (5) |
| O2 | 0.5000 | 1.01444 (10) | 0.5700 (3) | 0.0196 (4) |
| O3 | 0.5000 | 0.74307 (13) | 0.2641 (3) | 0.0280 (5) |
| O4 | 0.5000 | 0.58881 (13) | 0.4565 (3) | 0.0231 (5) |
| H4 | 0.5000 | 0.526 (3) | 0.507 (5) | 0.023 (8)* |
| O5 | 0.5000 | 0.41962 (13) | 0.5613 (3) | 0.0229 (4) |
| H5A | 0.5000 | 0.374 (3) | 0.487 (7) | 0.027* |
| H5B | 0.5000 | 0.396 (3) | 0.672 (7) | 0.027* |
| N1 | 0.5000 | 0.88054 (15) | 0.7296 (3) | 0.0160 (5) |
| H1N | 0.5000 | 0.916 (3) | 0.827 (7) | 0.023 (10)* |
| N2 | 0.5000 | 0.87691 (16) | 0.4198 (4) | 0.0177 (6) |
| H2N | 0.5000 | 0.904 (3) | 0.332 (6) | 0.023 (9)* |
| N3 | 0.5000 | 0.64146 (18) | 0.6049 (3) | 0.0183 (6) |
| C1 | 0.5000 | 0.78444 (16) | 0.7481 (4) | 0.0166 (6) |
| C2 | 0.5000 | 0.92913 (16) | 0.5717 (5) | 0.0151 (4) |
| C3 | 0.5000 | 0.7807 (2) | 0.4079 (4) | 0.0166 (6) |
| C4 | 0.5000 | 0.73073 (17) | 0.5806 (4) | 0.0146 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|----------|----------|--------------|
| O1 | 0.0586 (12) | 0.0164 (10) | 0.0109 (9) | 0.000 | 0.000 | 0.0028 (8) |
| O2 | 0.0297 (7) | 0.0118 (7) | 0.0173 (9) | 0.000 | 0.000 | 0.0016 (9) |
| O3 | 0.0565 (11) | 0.0150 (8) | 0.0124 (12) | 0.000 | 0.000 | -0.0003 (9) |
| O4 | 0.0413 (8) | 0.0105 (9) | 0.0175 (11) | 0.000 | 0.000 | -0.0002 (8) |
| O5 | 0.0408 (8) | 0.0109 (8) | 0.0169 (9) | 0.000 | 0.000 | -0.0003 (9) |
| N1 | 0.0285 (10) | 0.0099 (10) | 0.0097 (12) | 0.000 | 0.000 | 0.0002 (8) |
| N2 | 0.0273 (10) | 0.0158 (14) | 0.0101 (12) | 0.000 | 0.000 | 0.0034 (9) |
| N3 | 0.0278 (8) | 0.0146 (9) | 0.0125 (16) | 0.000 | 0.000 | -0.0004 (8) |
| C1 | 0.0258 (11) | 0.0102 (12) | 0.0138 (14) | 0.000 | 0.000 | 0.0032 (10) |
| C2 | 0.0213 (8) | 0.0120 (9) | 0.0120 (10) | 0.000 | 0.000 | -0.0023 (10) |
| C3 | 0.0217 (10) | 0.0173 (15) | 0.0110 (15) | 0.000 | 0.000 | -0.0001 (9) |
| C4 | 0.0218 (8) | 0.0124 (9) | 0.0097 (10) | 0.000 | 0.000 | 0.0026 (12) |

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

| | | | |
|-------|-----------|--------|-----------|
| O1—C1 | 1.209 (3) | N1—C1 | 1.385 (3) |
| O2—C2 | 1.224 (3) | N1—C2 | 1.378 (4) |
| O3—C3 | 1.210 (4) | N2—H2N | 0.76 (5) |
| O4—H4 | 0.98 (4) | N2—C2 | 1.367 (4) |

| | | | |
|------------|-----------|----------|-------------|
| O4—N3 | 1.349 (3) | N2—C3 | 1.382 (4) |
| O5—H5A | 0.86 (5) | N3—C4 | 1.293 (3) |
| O5—H5B | 0.90 (5) | C1—C4 | 1.478 (4) |
| N1—H1N | 0.90 (5) | C3—C4 | 1.485 (4) |
| H4—O4—N3 | 101 (2) | N1—C1—C4 | 115.6 (2) |
| H5A—O5—H5B | 108 (4) | O2—C2—N1 | 121.0 (3) |
| H1N—N1—C1 | 119 (3) | O2—C2—N2 | 122.6 (3) |
| H1N—N1—C2 | 115 (3) | N1—C2—N2 | 116.4 (2) |
| C1—N1—C2 | 126.1 (2) | O3—C3—N2 | 120.2 (3) |
| H2N—N2—C2 | 116 (3) | O3—C3—C4 | 124.6 (3) |
| H2N—N2—C3 | 117 (3) | N2—C3—C4 | 115.2 (3) |
| C2—N2—C3 | 126.9 (3) | N3—C4—C1 | 113.3 (2) |
| O4—N3—C4 | 115.9 (2) | N3—C4—C3 | 127.0 (3) |
| O1—C1—N1 | 119.4 (3) | C1—C4—C3 | 119.70 (18) |
| O1—C1—C4 | 125.0 (2) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H4...O5 | 0.98 (4) | 1.58 (4) | 2.552 (2) | 172 (4) |
| O5—H5A...O1 ⁱ | 0.86 (5) | 1.91 (5) | 2.744 (3) | 161 (5) |
| O5—H5B...O3 ⁱⁱ | 0.90 (5) | 2.11 (5) | 2.789 (3) | 131 (4) |
| O5—H5B...O4 ⁱⁱ | 0.90 (5) | 2.15 (5) | 2.978 (3) | 152 (4) |
| N1—H1N...O2 ⁱⁱⁱ | 0.90 (5) | 2.08 (5) | 2.972 (3) | 173 (4) |
| N2—H2N...O2 ^{iv} | 0.76 (5) | 2.30 (5) | 3.060 (3) | 180 (5) |

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