

Violuric acid monohydrate: a second polymorph with more extensive hydrogen bonding

Kathy Guille, Ross W. Harrington and William Clegg*

School of Natural Sciences (Chemistry), Newcastle University, Newcastle upon Tyne NE1 7RU, England

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

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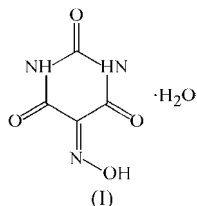
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Crystals of a second polymorph of violuric acid monohydrate [systematic name: pyrimidine-2,4,5,6(1*H*,3*H*)-tetrone monohydrate], $C_4H_3N_3O_4 \cdot H_2O$, have higher density and a more extensive hydrogen-bonding arrangement than the previously reported polymorph. Violuric acid and water molecules form essentially planar hydrogen-bonded sheets, which are stacked in an offset ...*ABCABC*... repeat pattern involving no ring-stacking interactions.

Comment

For some time now, an area of our research has concentrated on the synthesis and crystallographic characterization of *s*-block metal complexes of anions of barbituric acid, violuric acid and other related ligands because of the pharmaceutical importance of their derivatives. Barbituric acid is also known for its ability to form polymorphs and has thus been used as a model compound for developing computational polymorph prediction techniques (Lewis *et al.*, 2004). Violuric acid is a 5-substituted derivative of barbituric acid, with a C=N–OH unit allowing extra coordination and hydrogen-bonding possibilities compared with barbituric acid.



The structure of violuric acid monohydrate, (I), was first determined in 1964, by both X-ray diffraction (Craven & Mascarenhas, 1964) and neutron diffraction (Craven & Takei, 1964) at room temperature, in order to determine the tautomeric form, the detailed molecular structure and the nature of the hydrogen bonding. The neutron diffraction study permitted the precise determination of the D-atom positions. For these two studies, the space group was suggested as

orthorhombic $Cmc2_1$, with all the atoms lying on crystallographic mirror planes and an interlayer separation of 3.11 Å. Both papers reported unsatisfactory features of the structure refinement and suggested either unresolved static or dynamic disorder, together with uncertainty about the true space group.

A definitive redetermination at 150 K (Nichol & Clegg, 2005) confirmed that the correct space group was $Cmc2_1$ and that the structure, at this lower temperature, is fully ordered and gives entirely satisfactory results for the geometry and displacement parameters; there appeared to be no phase transition between room temperature and 150 K. In this first polymorph (referred to here as polymorph *A*), the violuric acid molecule is exactly planar. Violuric acid and water molecules form planar hydrogen-bonded sheets. The crystal packing consists of stacked sheets separated by 3.0377 (6) Å (half the *a*-axis length) and there is no ring stacking between adjacent sheets. All the O atoms of the carbonyl groups act as acceptor atoms for hydrogen bonds; this is uncommon for barbituric derivatives, where one carbonyl group is usually not involved in hydrogen bonding (Lewis *et al.*, 2005). An $R_2^2(8)$ motif (Bernstein *et al.*, 1995) links the violuric acid rings together, and the water molecule is hydrogen bonded to the third carbonyl group and to the O atom of the isonitroso group. One of the H atoms of the water molecule thus acts as a bifurcated donor.

We have now obtained a second polymorph, *B*, of violuric acid monohydrate. The asymmetric unit is shown in Fig. 1 and consists of one molecule of violuric acid and one water molecule, both lying in general positions with no imposed crystallographic symmetry. Nevertheless, the violuric acid molecule is essentially planar, with an r.m.s. deviation of 0.021 Å, and the O atom of the water molecule lies only 0.065 Å from this mean plane. The water H atoms also lie approximately in this plane, enabling the formation of a hydrogen-bonded sheet, which is parallel to $(\bar{1}03)$; adjacent sheets are separated by an average of 3.08 Å (Fig. 2), slightly more than in the orthorhombic polymorph *A*. The stacking sequence of sheets here is an offset ...*ABCABC*..., whereas it is ...*ABAB*... in polymorph *A*. In neither polymorph, *A* nor *B*, are there any ring-stacking interactions.

Fig. 3 shows the hydrogen bonding within a sheet, and the details of the hydrogen bonds are given in Table 1. There are

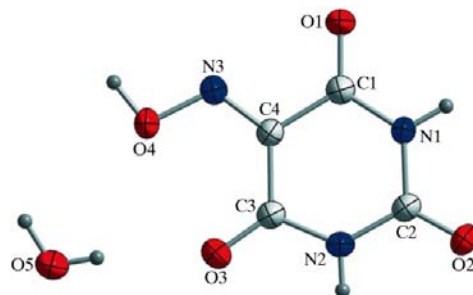


Figure 1
The asymmetric unit of (I), shown with 50% probability displacement ellipsoids.

both similarities and significant differences between this and the arrangement in polymorph *A*. In both structures, the water molecule acts as a donor to a carbonyl group through one H atom, and as a bifurcated donor to both a carbonyl and the isonitroso O atom of a second violuric acid molecule (the last of these being much the weakest hydrogen bond in the structure and probably marginal in significance). The water O atom accepts a hydrogen bond from an NH group in polymorph *B*, but from the NOH group in polymorph *A*; in *B*, the NOH group donates to two carbonyl O atoms in two different molecules. The second NH group in *B* serves as a bifurcated donor, to a carbonyl group and the N atom of the NOH group of a single violuric acid molecule, whereas both NH groups in *A* act as simple donors to carbonyl O atoms. In *A*, two carbonyl groups of each violuric acid molecule accept hydrogen bonds only from water molecules (one each), while the third accepts two hydrogen bonds (from two NH groups); in *B*, one carbonyl group is a single acceptor (from water), one accepts hydrogen bonds from water and from NOH, and the other accepts from NH and NOH. Thus, the water molecule shows the same degree of hydrogen bonding in both polymorphs (three as donor and one as acceptor), but the violuric acid molecule forms more hydrogen bonds in *B* (five as donor and seven as acceptor) than in *A* (three as donor and five as acceptor); only in *B* does the N atom of the NOH group accept a hydrogen bond. Comparison of the two structures shows that some potential hydrogen-bonding interactions in polymorph *A* do not occur because the donor-acceptor distances are too great (Desiraju & Sharma, 1996; Taylor *et al.*, 1984*a,b*). The calculated density of polymorph *B* (1.788 Mg m^{-3}) is a little higher than that of polymorph *A* (1.773 Mg m^{-3}), both of these values being rather high for an organic compound as a result of the extensive hydrogen bonding.

The specific individual ring motifs generated by the hydrogen bonding in polymorph *B*, with their binary graph-set notation (Bernstein *et al.*, 1995), are as follows: (i) the bifurcated hydrogen bonding of the N1—H1 group to atoms O1ⁱ and N3ⁱ generates an $R_1^2(5)$ motif involving two violuric acid

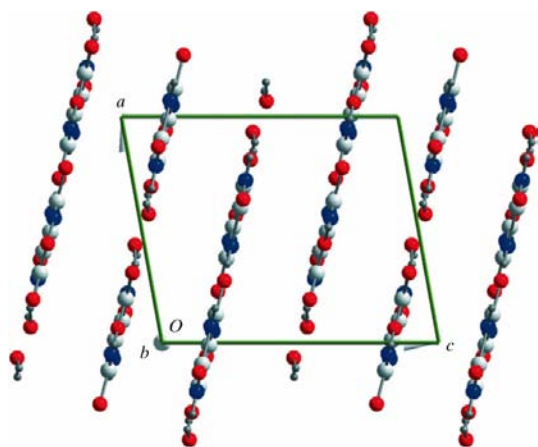


Figure 2
A parallel projection, along the *b* axis, of the packing of (I).

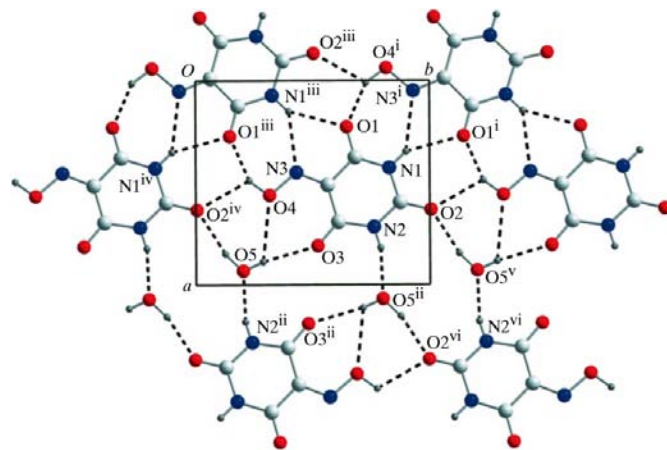


Figure 3
The hydrogen bonding (dashed lines) in a single sheet; see Table 1 and *Comment* for symmetry codes.

molecules (symmetry codes are as given in Table 1); (ii) one branch of this bifurcated hydrogen bond, N1—H1...N3ⁱ, together with O4ⁱ—H4ⁱ...O1 (symmetry-equivalent to O4—H4...O1ⁱⁱⁱ in Table 1) generates an $R_2^2(7)$ motif between the same pair of molecules; the other branch, N1—H1...O1ⁱ, is symmetry-equivalent to N1^{iv}—H1^{iv}...O1ⁱⁱⁱ, which generates an $R_2^3(6)$ motif with O4—H4...O1ⁱⁱⁱ and O4—H4...O2^{iv}, linking three violuric acid molecules; (iii) the bifurcated hydrogen bonding of the O5—H5A group to atoms O3 and O4 generates an $R_2^2(6)$ motif involving one violuric acid and one water molecule; (iv) O5—H5A...O4, O5—H5B...O2^{iv} and O4—H4...O2^{iv} generate an $R_3^2(6)$ motif linking the water molecule to two violuric acid molecules; (v) O5—H5A...O3, N2—H2...O5ⁱⁱ and their inversion-related equivalents O5ⁱⁱ—H5Aⁱⁱ...O3ⁱⁱ and N2ⁱⁱ—H2ⁱⁱ...O5 generate a centrosymmetric $R_4^4(12)$ motif; (vi) finally, N2—H2...O5ⁱⁱ and O5^v—H5B...O2 (equivalent to O5—H5B...O2^{iv}), together with their inversion-related equivalents N2^{vi}—H2^{vi}...O5^v and O5ⁱⁱ—H5Bⁱⁱ...O2^{vi} [symmetry codes: (v) $x, 1 + y, z$; (vi) $2 - x, 2 - y, 1 - z$], generate another centrosymmetric $R_4^4(12)$ motif, with both of these larger ring motifs containing two water and two violuric acid molecules. Hydrogen bonds formed exclusively by violuric acid molecules link these molecules into ribbons along the *b* axis, and the larger ring motifs involving water molecules provide lateral connections between the ribbons, forming the overall sheet structure shown in Fig. 3.

The bond lengths and angles in the two polymorphs are essentially the same.

Experimental

Small colourless block-shaped crystals were obtained from an aqueous solution prepared by adding one equivalent of barbituric acid to three equivalents of violuric acid and one equivalent of magnesium sulfate in water, in an attempt to prepare a complex containing both ligands. The solution was stirred and boiled to reduce its volume to 40% of the original, and then allowed to cool slowly to room temperature. Crystals appeared after approximately three weeks.

Crystal data

$C_4H_3N_3O_4 \cdot H_2O$
 $M_r = 175.11$
 Monoclinic, $P2_1/n$
 $a = 7.862$ (5) Å
 $b = 8.869$ (5) Å
 $c = 9.479$ (5) Å
 $\beta = 100.25$ (3)°

$V = 650.4$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.17$ mm⁻¹
 $T = 150$ (2) K
 $0.30 \times 0.20 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2006)
 $T_{min} = 0.960$, $T_{max} = 0.985$

7836 measured reflections
 1266 independent reflections
 864 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.118$
 $S = 1.05$
 1266 reflections

129 parameters
 All H-atom parameters refined
 $\Delta\rho_{max} = 0.21$ e Å⁻³
 $\Delta\rho_{min} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1^i$	0.89 (3)	2.27 (3)	3.077 (3)	151 (2)
$N1-H1 \cdots N3^i$	0.89 (3)	2.38 (2)	3.124 (3)	141 (2)
$N2-H2 \cdots O5^{ii}$	0.83 (3)	2.02 (3)	2.828 (3)	164 (2)
$O4-H4 \cdots O1^{iii}$	0.96 (3)	1.85 (3)	2.722 (2)	150 (3)
$O4-H4 \cdots O2^{iv}$	0.96 (3)	2.30 (3)	2.817 (2)	113 (2)
$O5-H5A \cdots O3$	0.83 (3)	2.17 (3)	2.988 (3)	168 (3)
$O5-H5A \cdots O4$	0.83 (3)	2.61 (3)	3.087 (3)	118 (2)
$O5-H5B \cdots O2^{iv}$	0.93 (4)	2.00 (4)	2.907 (3)	163 (3)

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

All H atoms were located in a difference Fourier map and were freely refined.

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: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3032). Services for accessing these data are described at the back of the journal.

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