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Hydrogen-bonding and carbonyl–carbonyl interactions in violuric acid methanol solvate

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

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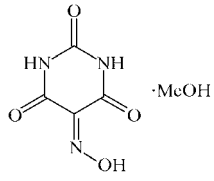
Violuric acid [systematic name: pyrimidine-2,4,5,6(1*H*,3*H*)-tetrone 5-oxime] crystallizes from a methanol solution stored at approximately 278 K as a monosolvate, $C_4H_3N_3O_4\cdot CH_3OH$, in the form of very small and fragile needles. Synchrotron radiation was needed to collect an adequate data set. Analysis of the crystal structure reveals that the isonitroso group of violuric acid is disordered over two positions with refined occupancies of approximately 3:1 for the major and minor disorder components. This fact has some important consequences for the hydrogen-bonding motifs found in the crystal packing, which are different for each component, although the overall packing pattern does not change. The crystal packing consists of closely stacked hydrogen-bonded sheets. Between the sheets are found carbonyl–carbonyl dipolar interactions, which are the principal intermolecular forces holding the sheets together.

Comment

We have been interested in *s*-block metal complexes of cyanuric acid, barbituric acid and other related ligands for some time. Violuric acid is a derivative of barbituric acid, having a C=N—OH substituent at the 5-position on the barbiturate ring. This substituent allows extra coordination and hydrogen-bonding possibilities compared with barbituric acid itself. Many transition metal complexes of violuric acid are known (Abraham *et al.*, 1980; Hamelin, 1972; Tamaki & Okabe, 1996; Faus *et al.*, 1996), along with some *s*-block metal complexes (Gillier, 1965; Hamelin, 1976). We have sought to plug the gaps in the literature, and also to look again at those reported structures (some of which are many years old) in order to evaluate trends in the coordination and hydrogen bonding of violuric acid with *s*-block metals.

For a reliable comparison of the molecular structure of coordinated *versus* free violuric acid, we sought to determine the crystal structure of violuric acid in the absence of any other molecule. Although the crystal structure of violuric acid monohydrate has been known for many years (Craven & Mascarenhas, 1964; Craven & Takei, 1964), we recently redetermined it in order to resolve several issues in the original reports (Nichol & Clegg, 2005). However, we still wished to obtain the structure of unsolvated violuric acid. We thought that crystallization from a methanol solution might achieve our goal. As this report shows, this was not the case. What the result does allow us to do, however, is observe the effect of changing the solvent on the resulting hydrogen-bonding motifs found within the structure.



(I)

Unlike the straightforward crystallization from aqueous solutions, violuric acid does not readily crystallize from methanol. Storage of a methanol solution at 278 K for around one month resulted in only a few very delicate needle crystals. These were taken to Station 9.8, SRS, Daresbury Laboratory, in an ice-box and data were collected *via* the EPSRC-funded UK National Crystallography Service.

The molecular structure of violuric acid methanol solvate, (I), is shown in Fig. 1. As is clear from the figure, the isonitroso group is disordered over two positions, with relative occupancies of approximately 3:1 for the major and minor components. This disorder is not uncommon and is something that we have observed in violurate–metal complexes, although it is not observed at all in violuric acid monohydrate. Although this disorder has little bearing on the molecular structure, it is of great importance to the crystal packing. Other than this disorder, the molecular dimensions (Table 1) are largely unexceptional and the rest of the violuric acid molecule appears to be well ordered; the exocyclic angles at atom C4 deviate somewhat from the ideal trigonal value of 120° because of steric interaction between the isonitroso group and adjacent ring substituents.

The most elegant aspect of the analysis is to be found not in the molecular structure but in the crystal packing. In essence, this is rather simple and consists of three basic hydrogen-bonding (Table 2) graph-set motifs (Bernstein *et al.*, 1995). Firstly, there is the very common $R_2^2(8)$ motif – found in almost all barbiturate crystal structures – involving two N—H···O

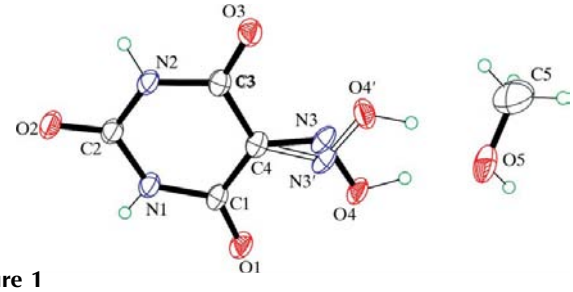


Figure 1
The asymmetric unit of (I), with 50% probability displacement ellipsoids. Open bonds show the minor disorder component.

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hydrogen bonds; this is located about a crystallographic inversion centre and connects the violuric acid molecules into tapes, which run parallel to the *ac* diagonal. Secondly – and ignoring the minor disorder component for the moment – the methanol molecule is connected to the violuric acid molecule by a more unusual but not uncommon $R_1^2(6)$ motif, involving the methanol O-bound H atom acting as a bifurcated donor to one carbonyl O atom and the O atom of the isonitroso group. Finally, an $R_4^4(8)$ motif links the aforementioned methanol and isonitroso atoms together with their symmetry equivalents about a crystallographic inversion centre. It is this final link that joins the tapes together to form a two-dimensional network sheet structure, as shown in Fig. 2.

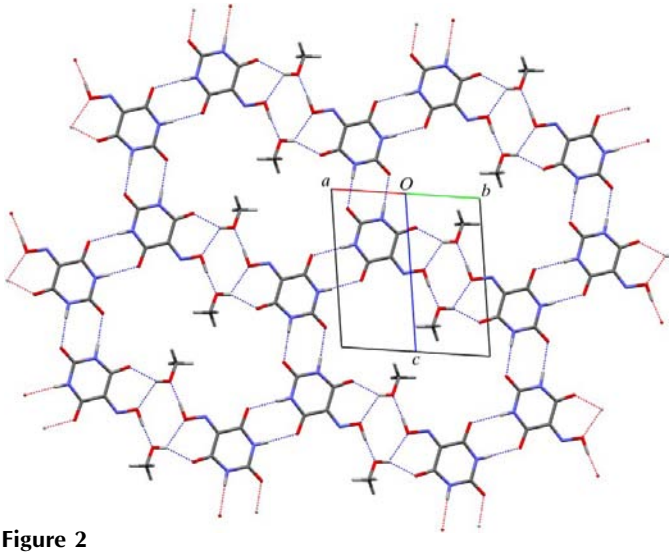

Figure 2
The hydrogen-bonded sheet structure in (I), viewed along the *ab* diagonal; the minor disorder component has been ignored. Dashed lines represent hydrogen bonds and the continuation of hydrogen bonding.

Given that the minor disorder component is present in around one-quarter of the crystal structures, we cannot simply ignore how it affects the crystal packing. Whilst the $R_2^2(8)$ tapes are unaffected by this disorder, the way they are linked together is very much at the heart of the disorder analysis. Fig. 3 gives two views of the methanol–violuric acid interactions, with the major and minor disorder components shown separately. At the top is the major component, with the two hydrogen-bonding motifs already discussed clearly visible. At the bottom is the hydrogen bonding involving the minor component of the disorder only. Although the only atoms displaced are those of the isonitroso substituent (the methanol molecule is not significantly disordered, despite the large ellipsoids which suggest that this might be a possibility), the difference in the hydrogen-bonding motifs is quite striking. The methanol O-bound H atom can now no longer act as a bifurcated donor; were it to form an O—H···N interaction, the H···*A* distance would be an unacceptably long 2.86 Å. We therefore have a single large $R_4^4(16)$ connection between the violuric acid tapes, which themselves are unaffected by the disorder. The effect on the overall form of the crystal packing is only slight; Fig. 4 shows the crystal packing involving the minor component only and the patterns formed are still the same.

Whilst there is extensive hydrogen bonding within each sheet, there are no hydrogen-bonding interactions linking different sheets together. The distance between adjacent sheets is around 3 Å, which is very close and is less than the sum of the van der Waals radii of the respective atoms. As a result, what we see are many dipolar carbonyl–carbonyl

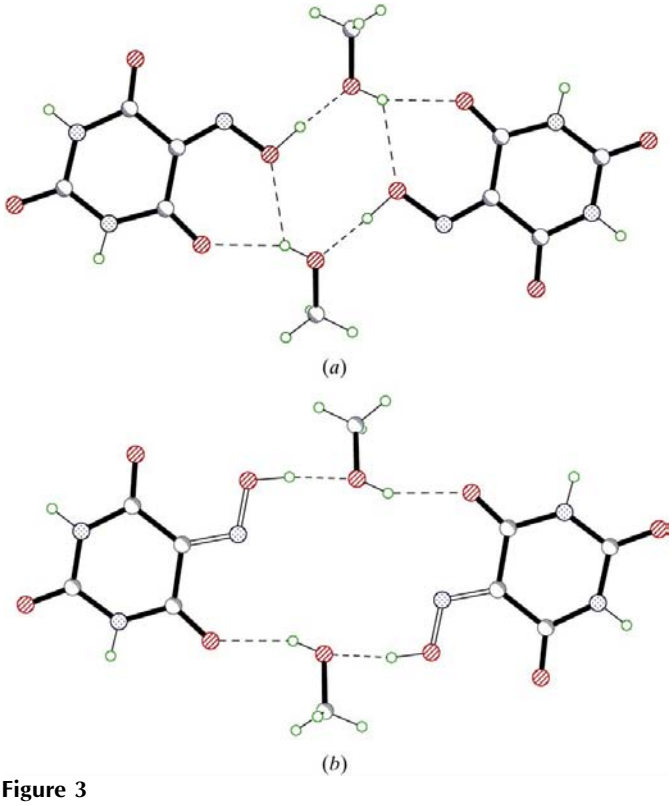

Figure 3
A representation of how the disorder affects the hydrogen-bonding motifs. (*a*) The hydrogen bonding involving the major component and (*b*) the hydrogen bonding involving the minor component.

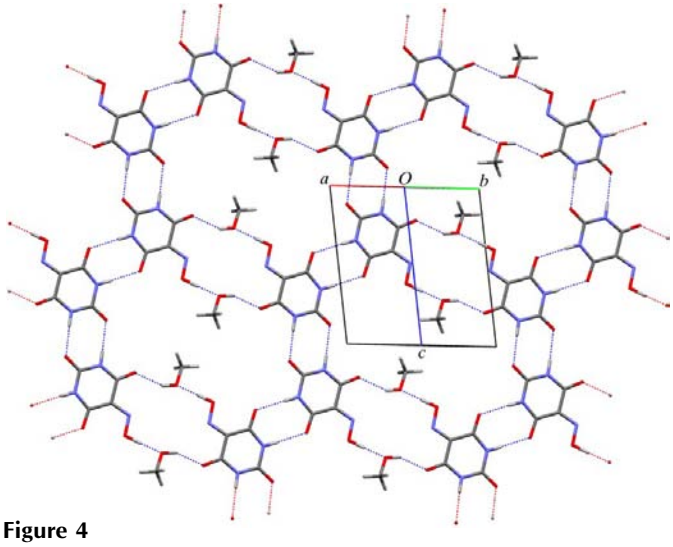

Figure 4
The hydrogen-bonded sheet structure in (I), viewed along the *ab* diagonal; the major disorder component has been ignored. Dashed lines are as in Fig. 2.

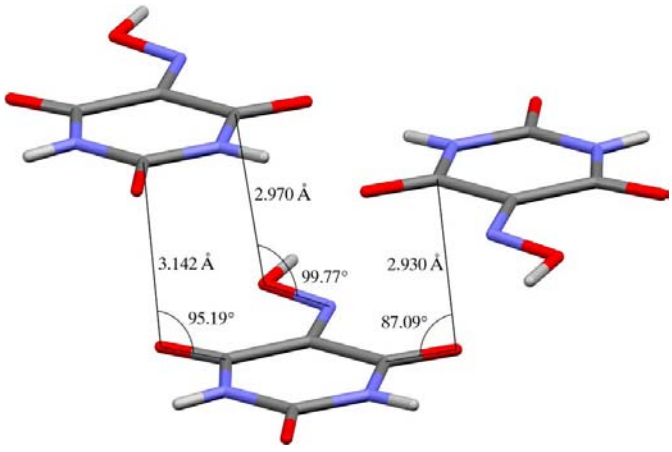

Figure 5
Some highlighted carbonyl–carbonyl interactions within the crystal packing of (I).

interactions (Allen *et al.*, 1998) between the tightly packed sheets (Fig. 5). Multipolar interactions have often been overlooked when considering those interactions that play a significant role in crystal packing. However, with the development of information-rich structural databases and powerful search algorithms, the subject has received increasing attention in recent years, in both small-molecule and macromolecular crystallography, so much so that a review has been published recently (Paulini *et al.*, 2005). The present structure offers a further example of one in which dipolar interactions are vital to the integrity of the crystal packing. Despite this, the difficulty with which the crystals grew and their relative instability once formed suggests that the attractive strength of these purely electrostatic interactions cannot be relied upon as the basis of controllable crystal growth in the same manner as hydrogen bonds are now widely considered.

Experimental

Violuric acid (0.17 g, 1 mmol) was dissolved in methanol (10 ml) with gentle heating. Storage for around one month at 278 K resulted in the growth of very small and fragile feather-like crystal agglomerations.

Crystal data

$C_4H_3N_3O_4\cdot CH_4O$
M_r = 189.14
Triclinic, $P\overline{1}$
a = 4.9650 (9) Å
b = 8.6208 (17) Å
c = 10.2613 (17) Å
α = 100.474 (2)°
β = 102.939 (2)°
γ = 99.823 (2)°
V = 410.56 (13) Å^3
Z = 2
D_x = 1.530 Mg m^{-3}
Synchrotron radiation
λ = 0.6751 Å
Cell parameters from 1809 reflections
θ = 4.0–28.8°
μ = 0.14 mm^{-1}
T = 120 (2) K
Needle, colourless
0.17 × 0.06 × 0.04 mm

Data collection

Bruker APEX-2 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.950, T_{max} = 0.995
3107 measured reflections
1462 independent reflections
1290 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 24.0°
$h = -5 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.113
S = 1.08
1462 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.1629P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.218 (2)	N1—C1	1.376 (2)
O2—C2	1.2202 (19)	N1—C2	1.374 (2)
O3—C3	1.2218 (19)	N2—C2	1.372 (2)
O4—N3	1.361 (3)	N2—C3	1.369 (2)
N3—C4	1.293 (4)	C1—C4	1.490 (2)
O4′—N3′	1.299 (13)	C3—C4	1.490 (2)
N3′—C4	1.349 (16)	O5—C5	1.395 (3)
O4—N3—C4	114.6 (2)	N2—C3—C4	115.32 (14)
O4′—N3′—C4	111.7 (8)	N3—C4—C1	129.00 (17)
C1—N1—C2	126.63 (15)	N3—C4—C3	111.45 (17)
C2—N2—C3	126.80 (14)	N3′—C4—C1	109.4 (5)
N1—C1—C4	115.10 (14)	N3′—C4—C3	131.1 (5)
N1—C2—N2	116.56 (14)	C1—C4—C3	119.53 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O5	0.98 (4)	1.59 (4)	2.567 (2)	174 (3)
O4′—H4′···O5	1.01 (12)	1.64 (12)	2.574 (5)	152 (9)
O5—H5···O1^{i}	0.84 (3)	1.98 (3)	2.7361 (18)	150 (2)
O5—H5···O4^{i}	0.84 (3)	2.21 (3)	2.761 (2)	124 (2)
N1—H1N···O2^{ii}	0.86 (2)	1.97 (2)	2.8322 (19)	178 (2)
N2—H2N···O3^{iii}	0.88 (2)	1.98 (2)	2.8519 (18)	172 (2)

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

The NOH group was refined as disordered, with a refined occupancy of 0.749 (4) for the major component. The anisotropic displacement parameters of atoms N3 and N3′ were constrained to be equal. All H atoms were located in a difference electron-density map and, with the exception of the methyl H atoms, were freely refined. Methyl H atoms were refined using a riding model, with U_{iso}(H) values of 1.5U_{eq}(C) and a C—H distance of 0.98 Å. There is a short H···H contact between this methyl group and the H atom of the minor component of the disordered isonitroso group; this indicates that the methyl group is also disordered by rotation about the C—O bond, but the minor component was not included in the refinement.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL* and *MERCURY* (Bruno *et al.*, 2002); 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: SK1883). Services for accessing these data are described at the back of the journal.

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