

Methyl 2-[(4-hydroxyphenyl)(methoxycarbonylmethyl)aminocarbonyl]ethanoate hemihydrate

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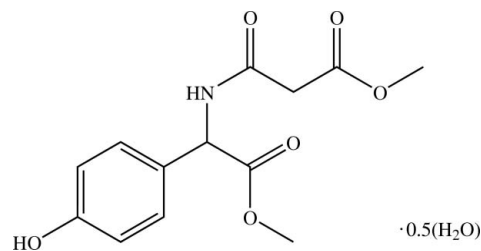
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.040; wR factor = 0.091; data-to-parameter ratio = 11.2.

In the structure of the title compound, $\text{C}_{13}\text{H}_{15}\text{NO}_6 \cdot 0.5\text{H}_2\text{O}$, the water O atom lies on a twofold rotation axis. The methoxycarbonylmethyl and amino groups are essentially coplanar and the methoxycarbonylmethyl group makes a dihedral angle of $79.73(10)^\circ$ with the mean plane of the hydroxyphenyl ring. The amino and methoxycarbonylmethyl groups are involved in an intramolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond which generates an $S(5)$ ring motif. In the crystal structure, molecules are linked *via* $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds and weak $\text{C}-\text{H} \cdots \text{O}$ interactions into a two-dimensional network parallel to the $(\bar{2}01)$ plane. The crystal structure is further stabilized by $\text{C}-\text{H} \cdots \pi$ interactions.

Related literature

For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For details of the biological properties of compounds containing tetramic acid, see for example: Iida *et al.* (1986); Matkhalikova *et al.* (1969); Reddy & Rao (2006); Reiner (2007); Royles (1996). For the syntheses of compounds containing tetramic acid units, see for example: Steglich (1989); Royles (1996).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{15}\text{NO}_6 \cdot 0.5\text{H}_2\text{O}$
 $M_r = 290.27$
Monoclinic, $C2$
 $a = 22.7764(12)$ Å
 $b = 5.3046(3)$ Å
 $c = 13.0686(6)$ Å
 $\beta = 117.612(3)^\circ$

$V = 1399.11(13)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 100.0(1)$ K
 $0.41 \times 0.19 \times 0.04$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.956$, $T_{\max} = 0.996$

9426 measured reflections
2248 independent reflections
1884 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.090$
 $S = 1.06$
2248 reflections
200 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.39$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{O1W}-\text{H1W} \cdots \text{O1}^i$ | 0.95 (4) | 1.86 (3) | 2.803 (3) | 170 (3) |
| $\text{N1}-\text{H1N1} \cdots \text{O1W}$ | 0.91 (3) | 2.14 (3) | 3.002 (3) | 157 (2) |
| $\text{N1}-\text{H1N1} \cdots \text{O3}$ | 0.91 (3) | 2.28 (3) | 2.669 (3) | 105 (2) |
| $\text{O6}-\text{H1O6} \cdots \text{O2}^{ii}$ | 0.89 (4) | 1.75 (3) | 2.638 (2) | 171 (3) |
| $\text{C2}-\text{H2A} \cdots \text{O1W}$ | 0.97 | 2.49 | 3.363 (3) | 150 |
| $\text{C2}-\text{H2B} \cdots \text{O6}^{ii}$ | 0.97 | 2.34 | 3.146 (3) | 140 |
| $\text{C6}-\text{H6B} \cdots \text{O6}^{iii}$ | 0.96 | 2.49 | 3.420 (3) | 162 |
| $\text{C7}-\text{H7B} \cdots \text{Cg1}^{iv}$ | 0.96 | 2.68 | 3.574 (3) | 155 |
| $\text{C10}-\text{H10} \cdots \text{Cg1}^{ii}$ | 0.93 | 3.01 | 3.717 (2) | 134 |

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iii) $x, y, z + 1$; (iv) $-x + 1, y, -z$. Cg1 is the centroid of the C8–C13 phenyl ring.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2467).

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supporting information

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Methyl 2-[[[(4-hydroxyphenyl)(methoxycarbonyl)methyl]aminocarbonyl]ethanoate hemihydrate

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S1. Comment

Natural products containing tetramic acid groups continue to attract the interest of chemists and biologists due to their challenging structures and remarkable biological properties (Iida *et al.*, 1986; Matkhalikova *et al.*, 1969; Reddy & Rao, 2006; Reiner, 2007; Royles, 1996). Among these, tetramic acids carrying an aromatic substituent on the ring are rarely found in nature (Reddy & Rao, 2006). The title compound, C₁₃H₁₅NO₆, can act as an essential intermediate in the synthesis of compounds responsible for the orange-yellow colour of plasmodia from *Leocarpus fragilis* (Steglich, 1989; Royles, 1995). We have synthesized the title compound and its structure is reported here.

The asymmetric unit of the title compound contains one molecule of C₁₃H₁₅NO₆ and half an H₂O molecule with the O1W atom lying on a twofold rotation axis, (Fig. 1). The methoxycarbonylmethyl [C4/C5/C7/O3/O5] and the C3/N1/C4 amino sections of the molecule are essentially coplanar with a dihedral angle of 3.12 (10)° between them. An intramolecular N1—H1N1···O3 hydrogen bond (Fig. 1) generates an S(5) ring motif (Bernstein *et al.*, 1995) and contributes to this planarity.

In the 3-oxopropanoate moiety [C1—C3/C6/O1/O2/O4], atoms C1, C2, C6, O1 and O4 lie on the same plane with C1 deviating by a maximum of -0.017 (2) Å. Similarly atoms C3, O2, C4, C5, N1 and O3 lie on the same plane with the maximum deviation -0.058 (2) Å for C4. The dihedral angle between these two planes is 70.29 (11) Å. The methoxycarbonylmethyl moiety makes a dihedral angle of 79.73 (10) Å with the hydroxyphenyl ring. The water molecule links with the C₁₃H₁₅NO₆ molecule *via* an N1—H1N1···O1W hydrogen bond (Fig. 1). All bond lengths and angles show normal values (Allen *et al.*, 1987).

In the crystal packing (Fig. 2), the molecules are stacked down both the [010] and [102] directions forming a two dimensional network parallel to the (-2 0 1) plane *via* N—H···O, O—H···O hydrogen bonds and weak C—H···O interactions (Table 1). The crystal is further stabilized by C—H···π interactions (Table 1); Cg₁ is the centroid of the C8–C13 phenyl ring.

S2. Experimental

The title compound was synthesized *via* condensation between an equimolar amount of hydroxyphenylglycine methyl-ester (10.0 g, 60 mmol) and methylmalonate potassium salt (9.4 g, 60 mmol) in acetonitrile/water (140:40 ml) at 273 K. The mixture was stirred for 2 h in the presence of dicyclohexylcarbodiimide, which acted as a catalyst and a peptide-coupling agent. The white precipitate formed during the reaction was filtered and washed thoroughly with dichloromethane. The filtrate and the dichloromethane were combined and evaporated. The resulting crude product was partitioned between water and dichloromethane, and the dichloromethane extract was dried over anhydrous magnesium

sulfate and evaporated. Colorless needle-shaped single crystals suitable for *X*-ray structure determination were obtained by slow evaporation of dichloromethane/petroleum ether (5:1 *v/v*) solution after several days (10.93 g, 65%).

S3. Refinement

The amino, hydroxyl and water hydrogen atoms were located in a difference map and refined isotropically. Hydrogen atoms attached to the carbon atoms were constrained in a riding motion approximation with $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic, 0.98 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for CH , 0.97 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for CH_2 , 0.96 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for CH_3 atoms. A rotating group model was used for the methyl groups. In the absence of significant anomalous scattering effects, a total of 1388 Friedel pairs were merged before final refinement.

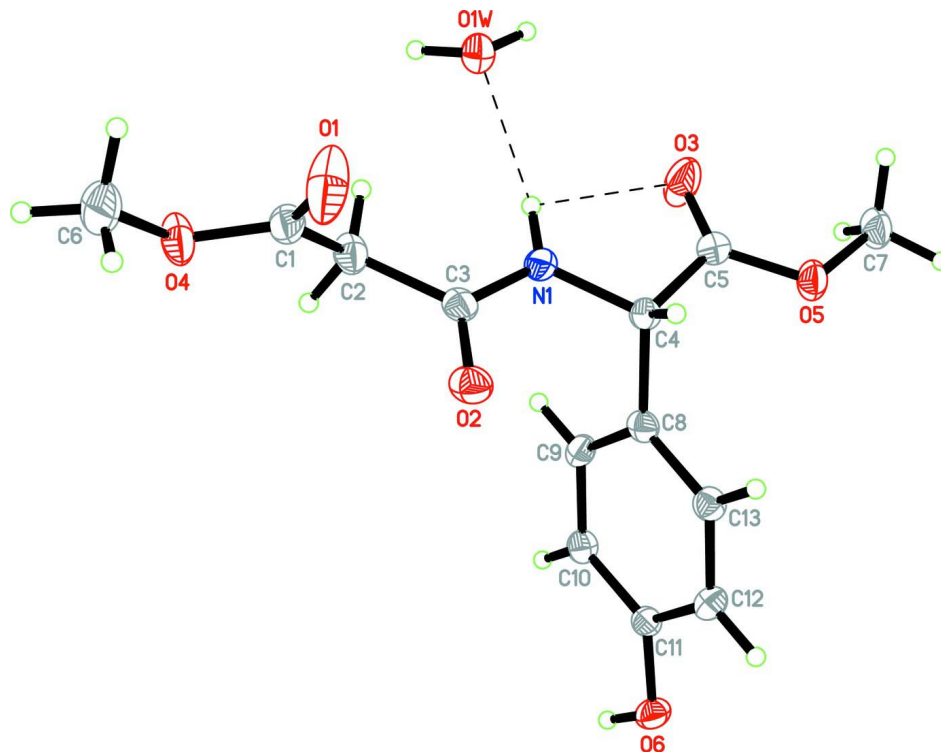


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. N—H \cdots O hydrogen bonds are drawn as dashed lines.

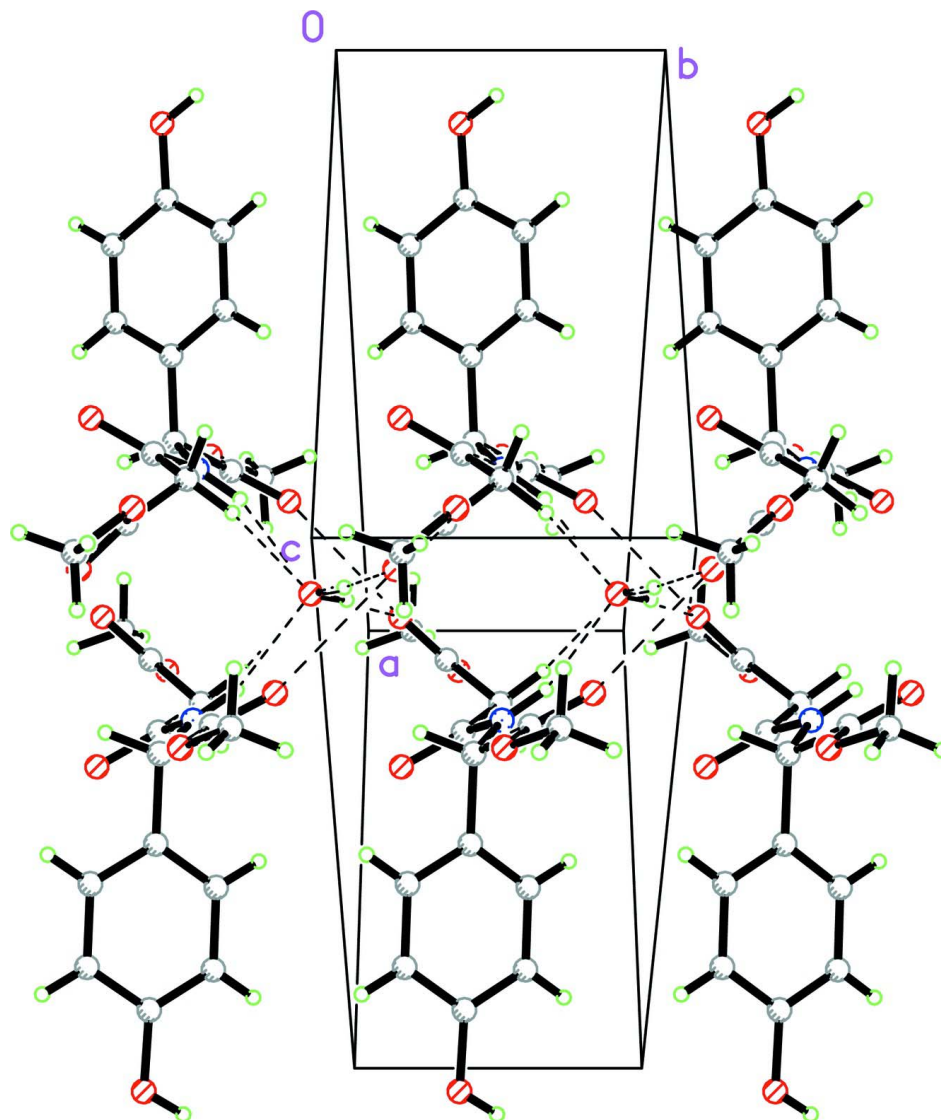


Figure 2

The crystal packing of (I), viewed along the [102] direction. Hydrogen bonds are drawn as dashed lines.

Methyl 2-[(4-hydroxyphenyl)(methoxycarbonyl)methyl]aminocarbonyl]ethanoate hemihydrate

Crystal data

$C_{13}H_{15}NO_6 \cdot 0.5H_2O$

$M_r = 290.27$

Monoclinic, $C2$

Hall symbol: $C 2y$

$a = 22.7764$ (12) Å

$b = 5.3046$ (3) Å

$c = 13.0686$ (6) Å

$\beta = 117.612$ (3)°

$V = 1399.11$ (13) Å³

$Z = 4$

$F(000) = 612$

$D_x = 1.378$ Mg m⁻³

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

Cell parameters from 2248 reflections

$\theta = 1.8$ – 30.0 °

$\mu = 0.11$ mm⁻¹

$T = 100$ K

Needle, colorless

$0.41 \times 0.19 \times 0.04$ mm

Data collection

Bruker SMART APEX2 CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.956$, $T_{\max} = 0.996$

9426 measured reflections

2248 independent reflections

1884 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -29 \rightarrow 31$

$k = -7 \rightarrow 7$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.090$

$S = 1.06$

2248 reflections

200 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.4523P]$

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

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

$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|------------|---------------|----------------------------------|
| O1W | 0.5000 | 0.8858 (5) | 0.5000 | 0.0242 (5) |
| H1W | 0.4734 (14) | 0.998 (7) | 0.518 (2) | 0.058 (9)* |
| O1 | 0.41331 (9) | 0.1694 (5) | 0.55170 (15) | 0.0512 (6) |
| O2 | 0.36387 (7) | 0.1785 (3) | 0.28492 (11) | 0.0255 (3) |
| O3 | 0.51628 (9) | 0.7925 (4) | 0.27318 (16) | 0.0435 (5) |
| O4 | 0.32338 (7) | 0.3629 (4) | 0.53519 (12) | 0.0311 (4) |
| O5 | 0.52565 (7) | 0.5121 (3) | 0.15432 (12) | 0.0250 (3) |
| O6 | 0.23720 (7) | 0.3718 (3) | -0.23284 (11) | 0.0232 (3) |
| H1O6 | 0.2058 (14) | 0.488 (7) | -0.250 (2) | 0.046 (8)* |
| N1 | 0.43133 (8) | 0.5081 (4) | 0.31026 (13) | 0.0196 (4) |
| H1N1 | 0.4513 (13) | 0.650 (6) | 0.351 (2) | 0.039 (7)* |
| C1 | 0.37123 (10) | 0.3244 (4) | 0.50613 (16) | 0.0231 (5) |
| C2 | 0.36758 (10) | 0.5050 (5) | 0.41546 (17) | 0.0239 (4) |
| H2A | 0.3963 | 0.6477 | 0.4522 | 0.029* |

| | | | | |
|-----|--------------|------------|---------------|------------|
| H2B | 0.3226 | 0.5676 | 0.3728 | 0.029* |
| C3 | 0.38810 (9) | 0.3812 (5) | 0.33240 (15) | 0.0201 (4) |
| C4 | 0.44916 (9) | 0.4168 (4) | 0.22326 (14) | 0.0178 (4) |
| H4 | 0.4684 | 0.2479 | 0.2450 | 0.021* |
| C5 | 0.50120 (10) | 0.5952 (4) | 0.22279 (16) | 0.0213 (4) |
| C6 | 0.32471 (12) | 0.1992 (6) | 0.62502 (18) | 0.0382 (6) |
| H6A | 0.3150 | 0.0295 | 0.5966 | 0.057* |
| H6B | 0.2921 | 0.2546 | 0.6473 | 0.057* |
| H6C | 0.3678 | 0.2051 | 0.6907 | 0.057* |
| C7 | 0.57232 (10) | 0.6792 (5) | 0.14299 (18) | 0.0275 (5) |
| H7A | 0.5530 | 0.8438 | 0.1209 | 0.041* |
| H7B | 0.5831 | 0.6152 | 0.0850 | 0.041* |
| H7C | 0.6119 | 0.6897 | 0.2155 | 0.041* |
| C8 | 0.39035 (9) | 0.4061 (4) | 0.10253 (14) | 0.0173 (4) |
| C9 | 0.34208 (9) | 0.5916 (4) | 0.06352 (15) | 0.0185 (4) |
| H9 | 0.3447 | 0.7234 | 0.1124 | 0.022* |
| C10 | 0.28956 (9) | 0.5828 (4) | -0.04846 (15) | 0.0186 (4) |
| H10 | 0.2571 | 0.7071 | -0.0738 | 0.022* |
| C11 | 0.28619 (9) | 0.3874 (4) | -0.12164 (14) | 0.0171 (4) |
| C12 | 0.33391 (9) | 0.1994 (4) | -0.08248 (15) | 0.0202 (4) |
| H12 | 0.3312 | 0.0669 | -0.1311 | 0.024* |
| C13 | 0.38579 (9) | 0.2087 (4) | 0.02927 (15) | 0.0189 (4) |
| H13 | 0.4177 | 0.0820 | 0.0552 | 0.023* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1W | 0.0252 (10) | 0.0249 (12) | 0.0262 (9) | 0.000 | 0.0151 (9) | 0.000 |
| O1 | 0.0576 (11) | 0.0695 (15) | 0.0432 (9) | 0.0427 (12) | 0.0373 (9) | 0.0351 (11) |
| O2 | 0.0250 (7) | 0.0272 (8) | 0.0224 (6) | -0.0058 (7) | 0.0094 (6) | 0.0016 (7) |
| O3 | 0.0540 (11) | 0.0432 (12) | 0.0547 (11) | -0.0279 (9) | 0.0432 (10) | -0.0289 (9) |
| O4 | 0.0244 (7) | 0.0455 (11) | 0.0303 (7) | 0.0075 (8) | 0.0185 (6) | 0.0128 (8) |
| O5 | 0.0257 (7) | 0.0254 (8) | 0.0320 (7) | -0.0051 (7) | 0.0204 (6) | -0.0065 (7) |
| O6 | 0.0202 (7) | 0.0268 (9) | 0.0176 (6) | 0.0031 (7) | 0.0046 (5) | -0.0047 (6) |
| N1 | 0.0196 (8) | 0.0240 (9) | 0.0163 (7) | -0.0034 (8) | 0.0093 (6) | -0.0012 (7) |
| C1 | 0.0205 (10) | 0.0301 (13) | 0.0188 (8) | 0.0034 (9) | 0.0093 (7) | 0.0033 (8) |
| C2 | 0.0220 (9) | 0.0286 (11) | 0.0240 (9) | 0.0026 (9) | 0.0132 (8) | 0.0046 (9) |
| C3 | 0.0159 (8) | 0.0270 (11) | 0.0148 (7) | 0.0007 (9) | 0.0048 (7) | 0.0048 (9) |
| C4 | 0.0174 (8) | 0.0200 (10) | 0.0166 (7) | -0.0016 (8) | 0.0083 (7) | -0.0003 (8) |
| C5 | 0.0200 (9) | 0.0237 (11) | 0.0199 (8) | -0.0016 (9) | 0.0091 (7) | -0.0025 (9) |
| C6 | 0.0391 (13) | 0.0542 (17) | 0.0285 (10) | -0.0056 (14) | 0.0218 (10) | 0.0085 (13) |
| C7 | 0.0255 (10) | 0.0311 (12) | 0.0337 (10) | -0.0055 (10) | 0.0203 (9) | -0.0048 (10) |
| C8 | 0.0175 (8) | 0.0181 (10) | 0.0175 (7) | -0.0034 (8) | 0.0091 (7) | 0.0017 (8) |
| C9 | 0.0218 (9) | 0.0178 (10) | 0.0184 (8) | -0.0006 (8) | 0.0115 (7) | -0.0022 (8) |
| C10 | 0.0191 (9) | 0.0168 (10) | 0.0208 (8) | 0.0018 (8) | 0.0099 (7) | 0.0011 (8) |
| C11 | 0.0157 (8) | 0.0187 (10) | 0.0168 (7) | -0.0006 (8) | 0.0074 (7) | 0.0003 (8) |
| C12 | 0.0233 (10) | 0.0183 (10) | 0.0196 (8) | -0.0002 (9) | 0.0105 (8) | -0.0030 (8) |
| C13 | 0.0182 (9) | 0.0174 (10) | 0.0211 (8) | 0.0011 (8) | 0.0092 (7) | 0.0000 (8) |

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|-------------|-------------|
| O1W—H1W | 0.95 (3) | C4—C8 | 1.526 (2) |
| O1—C1 | 1.192 (3) | C4—H4 | 0.9800 |
| O2—C3 | 1.236 (3) | C6—H6A | 0.9600 |
| O3—C5 | 1.199 (3) | C6—H6B | 0.9600 |
| O4—C1 | 1.326 (2) | C6—H6C | 0.9600 |
| O4—C6 | 1.449 (3) | C7—H7A | 0.9600 |
| O5—C5 | 1.329 (3) | C7—H7B | 0.9600 |
| O5—C7 | 1.443 (3) | C7—H7C | 0.9600 |
| O6—C11 | 1.364 (2) | C8—C9 | 1.385 (3) |
| O6—H1O6 | 0.89 (3) | C8—C13 | 1.390 (3) |
| N1—C3 | 1.331 (3) | C9—C10 | 1.397 (2) |
| N1—C4 | 1.456 (2) | C9—H9 | 0.9300 |
| N1—H1N1 | 0.91 (3) | C10—C11 | 1.388 (3) |
| C1—C2 | 1.496 (3) | C10—H10 | 0.9300 |
| C2—C3 | 1.516 (3) | C11—C12 | 1.386 (3) |
| C2—H2A | 0.9700 | C12—C13 | 1.390 (2) |
| C2—H2B | 0.9700 | C12—H12 | 0.9300 |
| C4—C5 | 1.519 (3) | C13—H13 | 0.9300 |
| | | | |
| C1—O4—C6 | 115.36 (18) | H6A—C6—H6B | 109.5 |
| C5—O5—C7 | 115.06 (18) | O4—C6—H6C | 109.5 |
| C11—O6—H1O6 | 112.7 (18) | H6A—C6—H6C | 109.5 |
| C3—N1—C4 | 120.25 (18) | H6B—C6—H6C | 109.5 |
| C3—N1—H1N1 | 120.7 (17) | O5—C7—H7A | 109.5 |
| C4—N1—H1N1 | 119.0 (17) | O5—C7—H7B | 109.5 |
| O1—C1—O4 | 122.7 (2) | H7A—C7—H7B | 109.5 |
| O1—C1—C2 | 125.06 (19) | O5—C7—H7C | 109.5 |
| O4—C1—C2 | 112.13 (18) | H7A—C7—H7C | 109.5 |
| C1—C2—C3 | 111.5 (2) | H7B—C7—H7C | 109.5 |
| C1—C2—H2A | 109.3 | C9—C8—C13 | 119.26 (16) |
| C3—C2—H2A | 109.3 | C9—C8—C4 | 121.39 (18) |
| C1—C2—H2B | 109.3 | C13—C8—C4 | 119.34 (18) |
| C3—C2—H2B | 109.3 | C8—C9—C10 | 120.66 (18) |
| H2A—C2—H2B | 108.0 | C8—C9—H9 | 119.7 |
| O2—C3—N1 | 122.28 (19) | C10—C9—H9 | 119.7 |
| O2—C3—C2 | 121.48 (19) | C11—C10—C9 | 119.58 (18) |
| N1—C3—C2 | 116.2 (2) | C11—C10—H10 | 120.2 |
| N1—C4—C5 | 107.25 (16) | C9—C10—H10 | 120.2 |
| N1—C4—C8 | 113.02 (16) | O6—C11—C12 | 117.66 (18) |
| C5—C4—C8 | 109.38 (15) | O6—C11—C10 | 122.39 (18) |
| N1—C4—H4 | 109.0 | C12—C11—C10 | 119.95 (16) |
| C5—C4—H4 | 109.0 | C11—C12—C13 | 120.13 (19) |
| C8—C4—H4 | 109.0 | C11—C12—H12 | 119.9 |
| O3—C5—O5 | 123.8 (2) | C13—C12—H12 | 119.9 |
| O3—C5—C4 | 124.54 (19) | C12—C13—C8 | 120.40 (19) |
| O5—C5—C4 | 111.55 (18) | C12—C13—H13 | 119.8 |

| | | | |
|-------------|--------------|-----------------|--------------|
| O4—C6—H6A | 109.5 | C8—C13—H13 | 119.8 |
| O4—C6—H6B | 109.5 | | |
| C6—O4—C1—O1 | -1.3 (3) | C8—C4—C5—O5 | -63.6 (2) |
| C6—O4—C1—C2 | -178.40 (19) | N1—C4—C8—C9 | 38.6 (3) |
| O1—C1—C2—C3 | 38.6 (3) | C5—C4—C8—C9 | -80.8 (2) |
| O4—C1—C2—C3 | -144.42 (18) | N1—C4—C8—C13 | -142.68 (19) |
| C4—N1—C3—O2 | 3.3 (3) | C5—C4—C8—C13 | 97.9 (2) |
| C4—N1—C3—C2 | -174.03 (16) | C13—C8—C9—C10 | -0.5 (3) |
| C1—C2—C3—O2 | 50.6 (2) | C4—C8—C9—C10 | 178.14 (18) |
| C1—C2—C3—N1 | -132.06 (19) | C8—C9—C10—C11 | -0.7 (3) |
| C3—N1—C4—C5 | -177.48 (17) | C9—C10—C11—O6 | -178.20 (18) |
| C3—N1—C4—C8 | 61.9 (2) | C9—C10—C11—C12 | 1.5 (3) |
| C7—O5—C5—O3 | -0.6 (3) | O6—C11—C12—C13 | 178.59 (19) |
| C7—O5—C5—C4 | 176.08 (16) | C10—C11—C12—C13 | -1.2 (3) |
| N1—C4—C5—O3 | -10.0 (3) | C11—C12—C13—C8 | -0.1 (3) |
| C8—C4—C5—O3 | 113.0 (2) | C9—C8—C13—C12 | 0.9 (3) |
| N1—C4—C5—O5 | 173.45 (16) | C4—C8—C13—C12 | -177.78 (18) |

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

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|---|-------------|---------------------|----------------------------|-------------------------------|
| O1 <i>W</i> —H1 <i>W</i> \cdots O1 ⁱ | 0.95 (4) | 1.86 (3) | 2.803 (3) | 170 (3) |
| N1—H1 <i>M</i> \cdots O1 <i>W</i> | 0.91 (3) | 2.14 (3) | 3.002 (3) | 157 (2) |
| N1—H1 <i>M</i> \cdots O3 | 0.91 (3) | 2.28 (3) | 2.669 (3) | 105 (2) |
| O6—H1 <i>O</i> \cdots O2 ⁱⁱ | 0.89 (4) | 1.75 (3) | 2.638 (2) | 171 (3) |
| C2—H2 <i>A</i> \cdots O1 <i>W</i> | 0.97 | 2.49 | 3.363 (3) | 150 |
| C2—H2 <i>B</i> \cdots O6 ⁱⁱ | 0.97 | 2.34 | 3.146 (3) | 140 |
| C6—H6 <i>B</i> \cdots O6 ⁱⁱⁱ | 0.96 | 2.49 | 3.420 (3) | 162 |
| C7—H7 <i>B</i> \cdots Cg1 ^{iv} | 0.96 | 2.68 | 3.574 (3) | 155 |
| C10—H10 \cdots Cg1 ⁱⁱ | 0.93 | 3.01 | 3.717 (2) | 134 |

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