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# 4-Phenylpyridinium 3-carboxy-2,3-dihydroxypropanoate dihydrate

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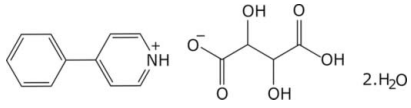
Key indicators: single-crystal X-ray study; $T$ = 290 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.045; $wR$ factor = 0.119; data-to-parameter ratio = 10.0.

In the title compound, $C_{11}H_{10}N^+\cdot C_4H_5O_6^-\cdot 2H_2O$, hydrogen tartrate anions and water molecules are linked by strong O—H···O hydrogen bonds to form corrugated layers. The 4-phenylpyridinium cation decorates the layer from both sides, being hydrogen bonded to the water molecule only. The three-dimensional packing of the complex layers is accomplished by strong $\pi$–$\pi$ interactions of 3.668 (2) Å between the centroids of the benzyl and pyridine rings related by the symmetry operator $(x-\frac{1}{2}, -y+\frac{1}{2}, -z)$.

## Related literature

For related literature, see: Akeroy & Hitchcock (1993); Alyar *et al.* (2006); Dastidar *et al.* (1993); Farrell *et al.* (2002); Guru Row (1999); Kolev *et al.* (1997, 2004, 2005); Turkington *et al.* (2005); Zyss *et al.* (1993).




## Experimental

### Crystal data

$C_{11}H_{10}N^+\cdot C_4H_5O_6^-\cdot 2H_2O$
$M_r$ = 341.31
Orthorhombic, $P2_12_12_1$
$a$ = 7.3051 (16) Å
$b$ = 11.850 (2) Å
$c$ = 18.165 (3) Å
$V$ = 1572.5 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.12 mm$^{-1}$
$T$ = 290 (2) K
0.20 × 0.13 × 0.13 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
4241 measured reflections
2180 independent reflections
1406 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.048
3 standard reflections
frequency: 120 min
intensity decay: none

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.119
$S$ = 0.94
2180 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N21—H21N···*OW2* | 0.86 | 1.85 | 2.698 (4) | 169 |
| O21—H21···O11 | 0.82 | 2.15 | 2.595 (3) | 114 |
| O21—H21···*OW1* | 0.82 | 2.09 | 2.815 (3) | 147 |
| O31—H31···*OW2* | 0.82 | 2.42 | 2.913 (3) | 119 |
| O41—H41···O12$^{i}$ | 0.82 | 1.68 | 2.472 (3) | 163 |
| *OW1*—*HW1B*···O31$^{ii}$ | 0.85 | 2.20 | 2.901 (3) | 140 |
| *OW1*—*HW1A*···O42$^{iii}$ | 0.93 | 1.86 | 2.750 (4) | 160 |
| *OW2*—*HW2A*···O21$^{iv}$ | 0.82 | 2.00 | 2.762 (3) | 156 |
| *OW2*—*HW2B*···O11$^{v}$ | 0.73 | 1.97 | 2.666 (3) | 161 |

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2365).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, o2511 [ **doi:10.1107/S1600536807017217** ]

# 4-Phenylpyridinium 3-carboxy-2,3-dihydroxypropanoate dihydrate

**T. Kolev, B. Shivachev and R. Petrova**

## Comment

The synthesis and structure determination of the title compound, (I) [systematic name: 4-phenylpyridinium 3-carboxy-2,3-dihydroxypropanoate dihydrate], were carried out as a part of our project dealing with organic compounds with potential nonlinear-optical, photorefractive and electro-optical properties (Kolev *et al.*, 2005, 2004, 1997).

Compound (I) is attractive from a crystal engineering and supramolecular chemistry point of view because it posseses a non-centrosymmetric structure and large dipole moments (Zyss *et al.*, 1993). Recent theoretical calculations for torsional barriers and nonlinear-optical properties of phenylpyridines (Alyar *et al.*, 2006) revealed that such molecules posses very weak nonlinear optical properties. However, the second-harmonic generation (SHG) of crystalline materials depends on both the magnitude of the molecular hyperpolarizability and the orientation of the molecules in the crystal lattice. Owing to its ability to form multidirectional hydrogen bonds, L-tartaric acid builds acentric crystalline salts with many organic bases (Turkington *et al.*, 2005; Farrell *et al.*, 2002; Guru Row, 1999; Akeroy & Hitchcock, 1993). Moreover, a number of salts of L-tartaric acid and substituted pyridines have been prepared and quantitative measurements showed that those materials are SHG active (Dastidar *et al.*, 1993).

Crystallization from $H_2O$–methanol solutions of an equimolar mixture of 4-phenylpyridine (H4PPN) and L-tartaric acid gives the title compound, (I), in which complete transfer of a single H atom from the acid component to the basic component has occurred. The geometric parameters of both organic molecules are comparable with those reported earlier (Kolev *et al.*, 2004, 2005; Zyss *et al.*, 1993; Turkington *et al.*, 2005). The $4PPN^+$ cation exhibits an interplanar angle of 34.15 (1)°, comparable with ones found previously in 4PPN-hydrogensquarate and 4PPN-betaine of squaric acid [31.6 (1)° and 28.6 (1)°, respectively].

An extensive hydrogen-bonding network is observed in the structure of (I) (Table 1). The hydrogentartrate (HT) anions are linked by strong bifurcated O41—H41···.(O11, O12) hydrogen bonds to form chains with graph-set symbol $C(7)/R^2_1(4)$ along the a axis. There are two water molecules of crystallisation in the structure and both act as bridges between neighbouring HT chains through hydrogen bonding. Each of the water solvent molecules holds three symmetry-related HT molecules to form undulating layers infinite in the a and b directions and stacked along the c direction. The 4PPN cation decorates both sides of the layers taking part in the formation of N21—H21···OW2 hydrogen bond.

The same crystal packing was found for L-tartaric acid 4-dimethilaminopyridine dihydrate, (II) (Dastidar *et al.*, 1993). In (I), similar to the 4-dimethylaminopyridinium cation in (II), the 4PPN anions are superimposed with dipoles in opposite orientations to each other, and consequently no resultant second-order susceptibility $\Xi^2$ could be expected. The only difference is that the cation in (II) is hydrogen-bonded to an HT anion and not to a water molecule as in (I). Nevertheless, both structures crystallize in the orthorhombic $P2_12_12_1$ space group with close values for a and b cell parameters [7.305 (2) and 11.850 (2) Å in (I), and 7.321 (1) and 11.846 (1) Å in (II)]. Only the stacking parameter c in (I) is longer, due to the larger cation used [18.165 (3) Å in (I) versus 16.469 (1) Å in (II)]. Taking into consideration the measurements and conclusions

made by Dastidar *et al.*, it could be expected that (I) will show similar values for the nonlinear response parameters as (II). It is possible that strong π–π interactions between neighbouring 4PPN anions will improve the SHG activity of (I) [Cg1···Cg2$^{i}$ = 3.668 (2) Å; symmetry code: (i) x-1/2, -y+1/2, -z; Cg1 and Cg2 are the centroids of the 4PPN benzyl and pyridine rings, respectively].

### Experimental

Equimolecular amounts of 4-phenylpyridine (2.15 mmol, 334 mg) and tartaric acid (324 mg) were mixed in distilled water (20 ml). The reaction mixture was stirred for 6 h at room temperature and monitored by thin-layer chromatography.

After completion of the reaction, the obtained solution was filtered and the filtrate set aside. The deposition of crystals of (I) began after one week. The product was separated by filtration and dried in air.

### Refinement

The water H atoms were located in a difference map. The other H atoms were placed in idealized positions, with O—H = 0.82 Å, C—H = 0.93 Å and N—H = 0.86 Å. All H atoms were refined as riding, with $U_{iso}$(H) = 1.2$U_{eq}$(C or N) or 1.5$U_{eq}$(O).

### Figures

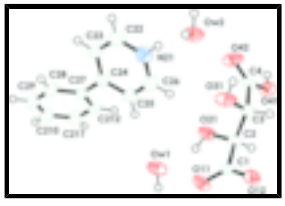

Fig. 1. A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

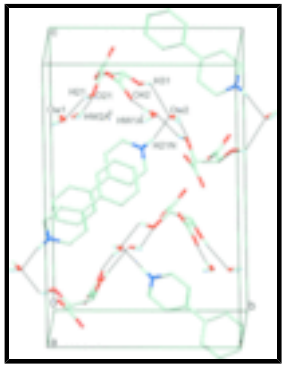

Fig. 2. A view of the molecular packing in (I). Hydrogen bonds are represented by dotted lines. All H atoms except those involved in hydrogen-bond interactions have been omitted. [Symmetry codes: (i) -x+1, y-1/2, -z+3/2; (ii) -x+1, y+1/2, -z+3/2.]

### 4-Phenylpyridinium 3-carboxy-2,3-dihydroxypropanoate dihydrate

*Crystal data*

$C_{11}H_{10}N^{+}·C_4H_5O_6^{-}·2H_2O$

$M_r$ = 341.31

$F_{000}$ = 720

$D_x$ = 1.442 Mg m$^{-3}$

$D_m$ = not meaured Mg m$^{-3}$

$D_m$ measured by none

| | |
|---|---|
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 22 reflections |
| $a = 7.3051$ (16) Å | $\theta = 18.1–19.5°$ |
| $b = 11.850$ (2) Å | $\mu = 0.12$ mm$^{-1}$ |
| $c = 18.165$ (3) Å | $T = 290$ (2) K |
| $V = 1572.5$ (5) Å$^3$ | Prism, brown |
| $Z = 4$ | 0.20 × 0.13 × 0.13 mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.048$ |
| Radiation source: fine-focus sealed tube | $\theta_{max} = 28.0°$ |
| Monochromator: graphite | $\theta_{min} = 2.1°$ |
| $T = 290(2)$ K | $h = 0 \rightarrow 9$ |
| nonprofiled $\omega/2\theta$ scans | $k = 0 \rightarrow 15$ |
| Absorption correction: none | $l = -23 \rightarrow 23$ |
| 4241 measured reflections | 3 standard reflections |
| 2180 independent reflections | every 120 min |
| 1406 reflections with $I > 2\sigma(I)$ | intensity decay: none |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.3826P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $wR(F^2) = 0.119$ | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |
| $S = 0.94$ | $\Delta\rho_{min} = -0.20$ e Å$^{-3}$ |
| 2180 reflections | Extinction correction: none |
| 217 parameters | |
| Primary atom site location: structure-invariant direct methods | |
| Secondary atom site location: difference Fourier map | |
| Hydrogen site location: inferred from neighbouring sites | |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing 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 ($Å^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | −0.0051 (4) | 0.2771 (3) | 0.86282 (19) | 0.0299 (7) |
| C2 | 0.2041 (4) | 0.2727 (3) | 0.86494 (19) | 0.0316 (7) |
| H2 | 0.2412 | 0.2212 | 0.9044 | 0.038* |
| C3 | 0.2900 (4) | 0.3865 (3) | 0.87922 (19) | 0.0321 (8) |
| H3 | 0.2611 | 0.4094 | 0.9297 | 0.039* |
| C4 | 0.4989 (4) | 0.3800 (3) | 0.8712 (2) | 0.0314 (8) |
| C212 | 0.4524 (5) | 0.1070 (3) | 0.4994 (2) | 0.0425 (9) |
| H212 | 0.4797 | 0.0937 | 0.5487 | 0.051* |
| C211 | 0.4563 (6) | 0.0194 (3) | 0.4502 (2) | 0.0475 (10) |
| H211 | 0.4901 | −0.0523 | 0.4658 | 0.057* |
| C210 | 0.4095 (6) | 0.0378 (4) | 0.3768 (2) | 0.0513 (10) |
| H210 | 0.4093 | −0.0218 | 0.3435 | 0.062* |
| C29 | 0.3640 (6) | 0.1439 (3) | 0.3542 (2) | 0.0495 (11) |
| H29 | 0.3332 | 0.1561 | 0.3052 | 0.059* |
| C28 | 0.3629 (5) | 0.2332 (3) | 0.4027 (2) | 0.0422 (9) |
| H28 | 0.3321 | 0.3052 | 0.3864 | 0.051* |
| C27 | 0.4084 (5) | 0.2152 (3) | 0.47646 (18) | 0.0372 (8) |
| C24 | 0.4095 (5) | 0.3097 (3) | 0.52912 (18) | 0.0361 (8) |
| C23 | 0.4631 (5) | 0.4188 (3) | 0.5084 (2) | 0.0415 (9) |
| H23 | 0.5000 | 0.4327 | 0.4603 | 0.050* |
| C22 | 0.4616 (5) | 0.5052 (3) | 0.5587 (2) | 0.0469 (10) |
| H22 | 0.4957 | 0.5777 | 0.5447 | 0.056* |
| C26 | 0.3556 (6) | 0.3821 (4) | 0.6505 (2) | 0.0497 (10) |
| H26 | 0.3179 | 0.3716 | 0.6989 | 0.060* |
| C25 | 0.3547 (5) | 0.2934 (4) | 0.6024 (2) | 0.0453 (10) |
| H25 | 0.3178 | 0.2223 | 0.6182 | 0.054* |
| N21 | 0.4108 (5) | 0.4841 (3) | 0.62782 (18) | 0.0476 (8) |
| H21N | 0.4137 | 0.5384 | 0.6592 | 0.057* |
| O11 | −0.0810 (3) | 0.2321 (2) | 0.81114 (14) | 0.0473 (7) |
| O12 | −0.0837 (3) | 0.3244 (2) | 0.91785 (12) | 0.0418 (6) |
| O21 | 0.2725 (3) | 0.2304 (2) | 0.79728 (14) | 0.0447 (7) |
| H21 | 0.1936 | 0.1919 | 0.7773 | 0.067* |
| O31 | 0.2197 (3) | 0.4688 (2) | 0.83042 (15) | 0.0454 (7) |
| H31 | 0.2690 | 0.5297 | 0.8386 | 0.068* |
| O41 | 0.5784 (3) | 0.3136 (2) | 0.91606 (13) | 0.0426 (6) |
| H41 | 0.6889 | 0.3138 | 0.9080 | 0.064* |
| O42 | 0.5708 (3) | 0.4383 (2) | 0.82451 (16) | 0.0525 (7) |
| OW1 | 0.1312 (4) | 0.0776 (2) | 0.69310 (15) | 0.0504 (7) |
| HW1A | 0.2112 | 0.0176 | 0.6874 | 0.060* |
| HW1B | 0.0527 | 0.0275 | 0.7042 | 0.060* |
| OW2 | 0.3906 (3) | 0.63832 (19) | 0.73677 (14) | 0.0460 (7) |
| HW2A | 0.4742 | 0.6829 | 0.7300 | 0.055* |

| | | | | |
|---|---|---|---|---|
| HW2B | 0.3184 | 0.6762 | 0.7245 | 0.055* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0153 (14) | 0.0318 (17) | 0.0427 (19) | −0.0011 (13) | −0.0001 (13) | 0.0067 (16) |
| C2 | 0.0168 (14) | 0.0358 (18) | 0.0424 (19) | 0.0002 (14) | 0.0010 (14) | 0.0014 (16) |
| C3 | 0.0159 (15) | 0.0396 (18) | 0.0408 (18) | −0.0001 (14) | −0.0007 (14) | −0.0035 (17) |
| C4 | 0.0161 (14) | 0.0349 (18) | 0.0433 (19) | −0.0030 (14) | 0.0006 (14) | −0.0080 (17) |
| C212 | 0.041 (2) | 0.0417 (19) | 0.045 (2) | −0.0032 (17) | −0.0082 (17) | 0.0096 (17) |
| C211 | 0.045 (2) | 0.041 (2) | 0.057 (2) | 0.0001 (19) | −0.0054 (19) | 0.0081 (19) |
| C210 | 0.052 (2) | 0.052 (2) | 0.050 (2) | −0.007 (2) | 0.002 (2) | −0.0044 (19) |
| C29 | 0.056 (3) | 0.055 (2) | 0.038 (2) | −0.001 (2) | −0.0018 (19) | 0.0077 (19) |
| C28 | 0.039 (2) | 0.044 (2) | 0.044 (2) | 0.0032 (18) | −0.0016 (16) | 0.0094 (18) |
| C27 | 0.0274 (17) | 0.0424 (19) | 0.0417 (19) | −0.0042 (17) | 0.0001 (16) | 0.0105 (16) |
| C24 | 0.0255 (17) | 0.0429 (19) | 0.0398 (18) | 0.0030 (17) | −0.0019 (17) | 0.0047 (16) |
| C23 | 0.034 (2) | 0.048 (2) | 0.042 (2) | −0.0019 (17) | 0.0020 (16) | 0.0096 (18) |
| C22 | 0.036 (2) | 0.048 (2) | 0.056 (2) | −0.0040 (19) | −0.0011 (18) | 0.004 (2) |
| C26 | 0.044 (2) | 0.061 (3) | 0.044 (2) | −0.001 (2) | 0.0032 (18) | 0.004 (2) |
| C25 | 0.041 (2) | 0.050 (2) | 0.045 (2) | −0.0041 (18) | 0.0029 (17) | 0.0106 (19) |
| N21 | 0.0381 (17) | 0.0514 (19) | 0.053 (2) | −0.0016 (17) | −0.0016 (17) | −0.0049 (16) |
| O11 | 0.0208 (12) | 0.0649 (17) | 0.0562 (15) | −0.0020 (13) | −0.0027 (12) | −0.0196 (14) |
| O12 | 0.0170 (12) | 0.0671 (17) | 0.0412 (13) | −0.0001 (12) | 0.0002 (11) | −0.0073 (13) |
| O21 | 0.0234 (12) | 0.0513 (15) | 0.0594 (15) | −0.0046 (12) | 0.0067 (12) | −0.0217 (14) |
| O31 | 0.0244 (13) | 0.0331 (13) | 0.0786 (19) | 0.0017 (11) | −0.0014 (13) | 0.0088 (13) |
| O41 | 0.0146 (11) | 0.0641 (16) | 0.0491 (14) | 0.0010 (12) | 0.0007 (11) | 0.0057 (13) |
| O42 | 0.0233 (13) | 0.0605 (17) | 0.0738 (19) | −0.0047 (13) | 0.0049 (13) | 0.0210 (15) |
| OW1 | 0.0327 (14) | 0.0416 (14) | 0.0770 (18) | 0.0004 (12) | 0.0008 (13) | −0.0104 (14) |
| OW2 | 0.0281 (12) | 0.0384 (13) | 0.0716 (17) | −0.0010 (11) | −0.0035 (13) | 0.0132 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—O11 | 1.213 (4) | C28—H28 | 0.9300 |
| C1—O12 | 1.282 (4) | C27—C24 | 1.473 (5) |
| C1—C2 | 1.530 (4) | C24—C23 | 1.402 (5) |
| C2—O21 | 1.419 (4) | C24—C25 | 1.403 (5) |
| C2—C3 | 1.510 (5) | C23—C22 | 1.372 (5) |
| C2—H2 | 0.9800 | C23—H23 | 0.9300 |
| C3—O31 | 1.415 (4) | C22—N21 | 1.333 (5) |
| C3—C4 | 1.535 (4) | C22—H22 | 0.9300 |
| C3—H3 | 0.9800 | C26—N21 | 1.339 (5) |
| C4—O42 | 1.213 (4) | C26—C25 | 1.367 (5) |
| C4—O41 | 1.273 (4) | C26—H26 | 0.9300 |
| C212—C211 | 1.370 (6) | C25—H25 | 0.9300 |
| C212—C27 | 1.386 (5) | N21—H21N | 0.8600 |
| C212—H212 | 0.9300 | O21—H21 | 0.8200 |
| C211—C210 | 1.394 (6) | O31—H31 | 0.8200 |
| C211—H211 | 0.9300 | O41—H41 | 0.8200 |
| C210—C29 | 1.363 (6) | OW1—HW1A | 0.9258 |

| | | | |
|---|---|---|---|
| C210—H210 | 0.9300 | OW1—HW1B | 0.8495 |
| C29—C28 | 1.377 (5) | OW2—HW2A | 0.8170 |
| C29—H29 | 0.9300 | OW2—HW2B | 0.7278 |
| C28—C27 | 1.398 (5) | | |
| O11—C1—O12 | 126.2 (3) | C29—C28—C27 | 119.6 (4) |
| O11—C1—C2 | 117.4 (3) | C29—C28—H28 | 120.2 |
| O12—C1—C2 | 116.3 (3) | C27—C28—H28 | 120.2 |
| O21—C2—C3 | 108.6 (3) | C212—C27—C28 | 119.0 (4) |
| O21—C2—C1 | 110.0 (3) | C212—C27—C24 | 120.5 (3) |
| C3—C2—C1 | 112.9 (3) | C28—C27—C24 | 120.5 (3) |
| O21—C2—H2 | 108.4 | C23—C24—C25 | 117.5 (3) |
| C3—C2—H2 | 108.4 | C23—C24—C27 | 121.9 (3) |
| C1—C2—H2 | 108.4 | C25—C24—C27 | 120.6 (3) |
| O31—C3—C2 | 110.9 (3) | C22—C23—C24 | 120.5 (3) |
| O31—C3—C4 | 109.6 (3) | C22—C23—H23 | 119.7 |
| C2—C3—C4 | 110.6 (3) | C24—C23—H23 | 119.7 |
| O31—C3—H3 | 108.5 | N21—C22—C23 | 119.3 (4) |
| C2—C3—H3 | 108.5 | N21—C22—H22 | 120.4 |
| C4—C3—H3 | 108.5 | C23—C22—H22 | 120.4 |
| O42—C4—O41 | 127.0 (3) | N21—C26—C25 | 119.9 (4) |
| O42—C4—C3 | 118.0 (3) | N21—C26—H26 | 120.1 |
| O41—C4—C3 | 115.0 (3) | C25—C26—H26 | 120.1 |
| C211—C212—C27 | 120.6 (3) | C26—C25—C24 | 120.0 (4) |
| C211—C212—H212 | 119.7 | C26—C25—H25 | 120.0 |
| C27—C212—H212 | 119.7 | C24—C25—H25 | 120.0 |
| C212—C211—C210 | 120.1 (4) | C22—N21—C26 | 122.9 (4) |
| C212—C211—H211 | 120.0 | C22—N21—H21N | 118.6 |
| C210—C211—H211 | 120.0 | C26—N21—H21N | 118.6 |
| C29—C210—C211 | 119.4 (4) | C2—O21—H21 | 109.5 |
| C29—C210—H210 | 120.3 | C3—O31—H31 | 109.5 |
| C211—C210—H210 | 120.3 | C4—O41—H41 | 109.5 |
| C210—C29—C28 | 121.3 (4) | HW1A—OW1—HW1B | 85.2 |
| C210—C29—H29 | 119.4 | HW2A—OW2—HW2B | 95.5 |
| C28—C29—H29 | 119.4 | | |
| C23—C22—N21—C26 | −1.9 (6) | C29—C210—C211—C212 | 1.5 (7) |
| N21—C22—C23—C24 | 0.9 (6) | C210—C211—C212—C27 | −2.2 (6) |
| C22—C23—C24—C25 | 0.1 (5) | C211—C212—C27—C24 | −178.3 (3) |
| C22—C23—C24—C27 | 179.6 (3) | C211—C212—C27—C28 | 1.7 (6) |
| C23—C24—C25—C26 | −0.2 (5) | O11—C1—C2—O21 | 9.5 (5) |
| C27—C24—C25—C26 | −179.7 (4) | O11—C1—C2—C3 | 130.9 (3) |
| C23—C24—C27—C28 | −34.9 (6) | O12—C1—C2—O21 | −173.3 (3) |
| C23—C24—C27—C212 | 145.1 (4) | O12—C1—C2—C3 | −51.8 (4) |
| C25—C24—C27—C28 | 144.6 (4) | O21—C2—C3—O31 | 71.2 (3) |
| C25—C24—C27—C212 | −35.4 (6) | O21—C2—C3—C4 | −50.6 (4) |
| C24—C25—C26—N21 | −0.8 (6) | C1—C2—C3—O31 | −51.0 (4) |
| C25—C26—N21—C22 | 1.9 (6) | C1—C2—C3—C4 | −172.9 (3) |
| C24—C27—C28—C29 | 179.5 (4) | O31—C3—C4—O41 | 175.6 (3) |
| C212—C27—C28—C29 | −0.5 (6) | O31—C3—C4—O42 | −3.4 (5) |

| | | | |
|---|---|---|---|
| C27—C28—C29—C210 | −0.3 (6) | C2—C3—C4—O41 | −61.8 (4) |
| C211—C210—C29—C28 | −0.2 (7) | C2—C3—C4—O42 | 119.2 (3) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N21—H21N···OW2 | 0.86 | 1.85 | 2.698 (4) | 169 |
| O21—H21···O11 | 0.82 | 2.15 | 2.595 (3) | 114 |
| O21—H21···OW1 | 0.82 | 2.09 | 2.815 (3) | 147 |
| O31—H31···OW2 | 0.82 | 2.42 | 2.913 (3) | 119 |
| O41—H41···O12$^{i}$ | 0.82 | 1.68 | 2.472 (3) | 163 |
| OW1—HW1B···O31$^{ii}$ | 0.85 | 2.20 | 2.901 (3) | 140 |
| OW1—HW1A···O42$^{iii}$ | 0.93 | 1.86 | 2.750 (4) | 160 |
| OW2—HW2A···O21$^{iv}$ | 0.82 | 2.00 | 2.762 (3) | 156 |
| OW2—HW2B···O11$^{v}$ | 0.73 | 1.97 | 2.666 (3) | 161 |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*, *y*−1/2, −*z*+3/2; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) −*x*+1, *y*+1/2, −*z*+3/2; (v) −*x*, *y*+1/2, −*z*+3/2.

**Fig. 1**

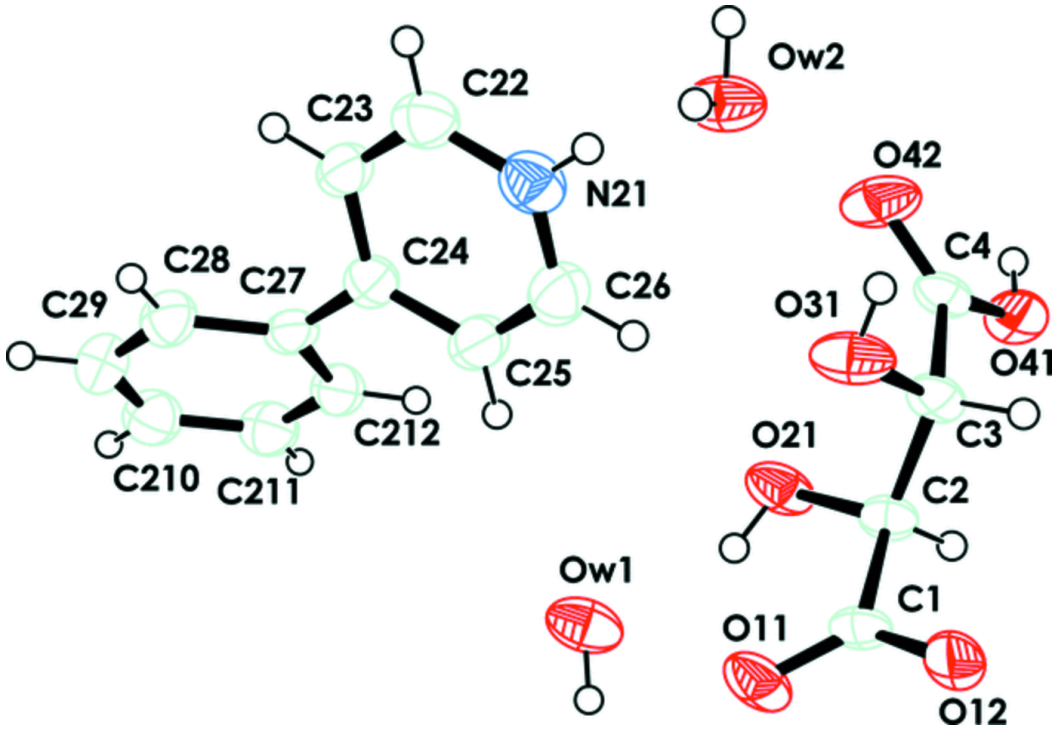
Ow2
C22
C23
N21
O42
C4
C24
C28
C27
C26
O31
O41
C29
C25
C3
O21
C212
C2
C210
C211
Ow1
C1
O11
O12

**Fig. 2**