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4,4'-([4,4'-Bipyridine]-1,1'-dium-1,1'-diyl)dibenzoate dihydrate

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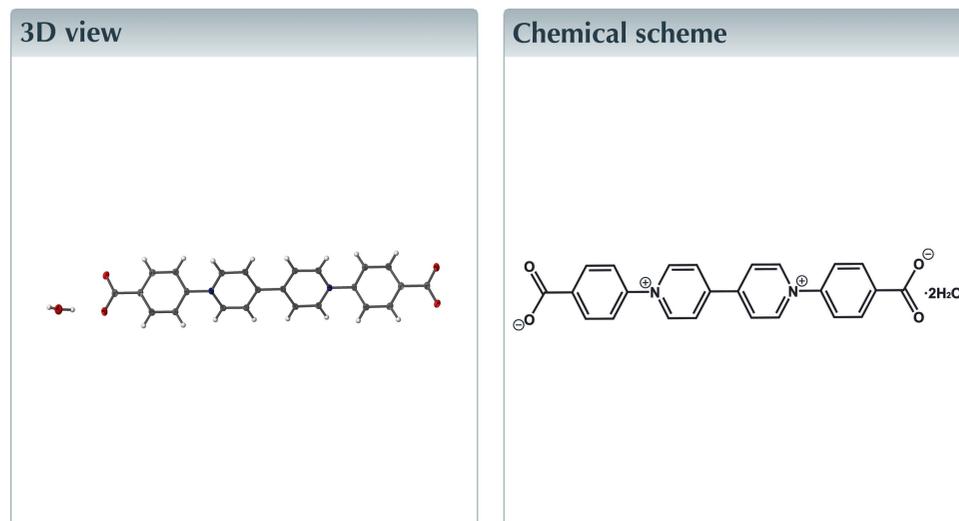
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Keywords: crystal structure; zwitterion; hydrogen bonding; bipyridinium; π - π stacking.

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Structural data: full structural data are available from iucrdata.iucr.org

We report here the synthesis of a neutral viologen derivative, $C_{24}H_{16}N_2O_4 \cdot 2H_2O$. The non-solvent portion of the structure (*Z*-Lig) is a zwitterion, consisting of two positively charged pyridinium cations and two negatively charged carboxylate anions. The carboxylate group is almost coplanar [dihedral angle = $2.04(11)^\circ$] with the benzene ring, whereas the dihedral angle between pyridine and benzene rings is $46.28(5)^\circ$. The *Z*-Lig molecule is positioned on a center of inversion (Fig. 1). The presence of the twofold axis perpendicular to the *c*-glide plane in space group *C2/c* generates a screw-axis parallel to the *b* axis that is shifted from the origin by $1/4$ in the *a* and *c* directions. This screw-axis replicates the molecule (and solvent water molecules) through space. The *Z*-Lig molecule links to adjacent molecules *via* O—H \cdots O hydrogen bonds involving solvent water molecules as well as intermolecular C—H \cdots O interactions. There are also π - π interactions between benzene rings on adjacent molecules.



Structure description

The title compound, $C_{24}H_{16}N_2O_4 \cdot 2H_2O$, (Fig. 1), includes both the ligand molecule 4,4'-([4,4'-bipyridine]-1,1'-dium-1,1'-diyl)dibenzoate (*Z*-Lig) and two solvent water molecules. The *Z*-Lig molecule is of great interest due to its zwitterionic properties. Zwitterions have been used for the construction of coordination polymers with built-in charged surfaces. Such polymers could be employed in gas sorption, separation, and electrochemical applications (*e.g.* see Aulakh *et al.*, 2015).

The *Z*-Lig molecule is positioned on a center of inversion (Fig. 1). The presence of the twofold axis perpendicular to the *c*-glide plane in space group *C2/c* generates a screw-axis

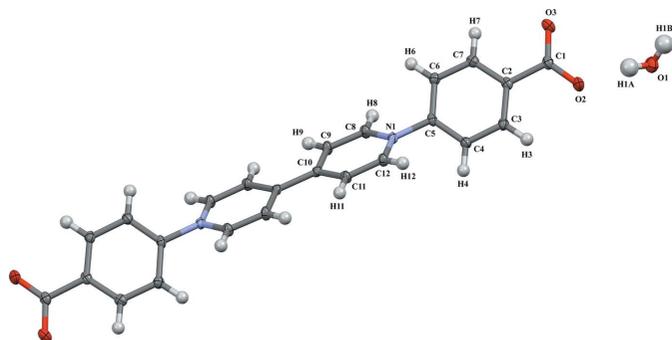


Figure 1

The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids for non-H atoms. Only one of the solvent water molecules is shown. Symmetry-equivalent atoms are generated by inversion ($\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$).

parallel to the *b* axis that is shifted from the origin by 1/4 in the *a* and *c* directions. This screw-axis replicates the molecule (and solvent water molecules) through space. The solvent water molecules serve to link the *Z*-Lig molecules *via* hydrogen bonding to neighboring *Z*-Lig molecules. The hydrogen bonding of the *Z*-Lig molecules is complex (Table 1 and Fig. 2). The carboxylate group, with atoms O2 and O3, forms a bond to a neighboring *Z*-Lig molecule *via* O2···H11 and O3···H12 bonds. Note that these bonds link to atoms C11 and C12 that are part of the same neighboring molecule. This is illustrated by the O2 and O3 atoms showing linkage to these same H11 and H12 atoms, respectively, along the backbone of the *Z*-Lig molecule [distances of 3.0641 (15) Å for O3···C12 and 3.3980 (16) Å for O2···C11, Fig. 2]. This linkage demands that some of the *Z*-Lig molecules link at near 90° orientations to one another. This bonding is more easily accommodated by the tilt of the inner (pyridyl) rings of the *Z*-Lig molecule about the N atoms above and below the plane formed by the carboxylate and the outer (benzene) rings.

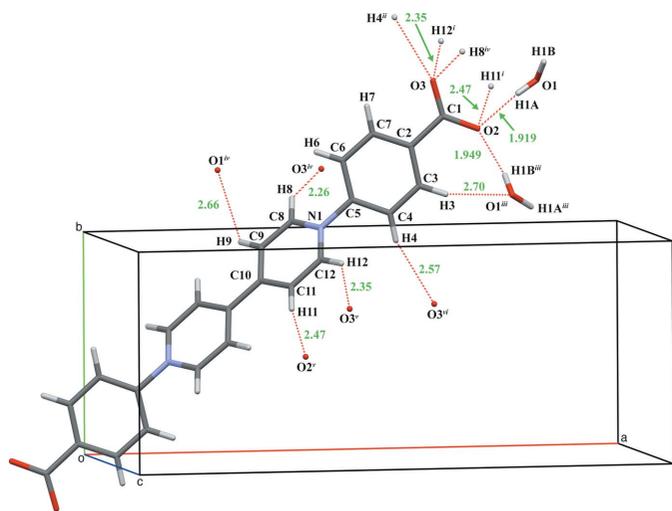


Figure 2

Molecule of *Z*-Lig showing hydrogen bonding to nearby solvent water and neighboring molecules. Distances are given in Å. Symmetry codes: (i) $1 - x, 1 + y, \frac{3}{2} - z$; (ii) $x, 1 + y, z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (iv) $1 - x, 3 - y, 1 - z$; (v) $1 - x, -1 + y, \frac{3}{2} - z$; (vi) $x, -1 + y, z$. Distance cutoff = 2.7 Å.

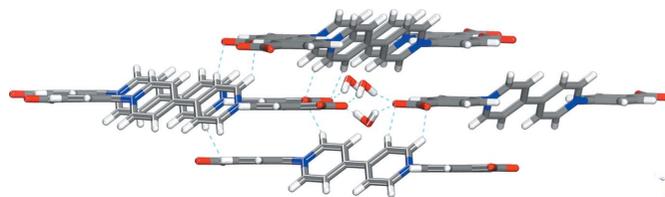


Figure 3

Packing diagram showing hydrogen bonding between *Z*-Lig molecules and water along with other intermolecular interactions. See text for details.

The carboxylate O2 atom is hydrogen bonded to the solvent water molecule. Each O2 atom interacts with both the H1A and H1B atoms of different solvent water molecules, as shown in Fig. 2. The simultaneous bonding of O2 to two water molecules designates it as a bifurcated acceptor. The O3 atom of the carboxylate does not directly interact with the solvent water molecule; instead it makes linkages to atoms H8 and H4 of neighboring molecules. Note that these O3···H8 and O3···H4 bonds are not to the same neighboring molecule. There is another interaction between the O1 atom to the H9 atom located near the midway point along the *Z*-Lig backbone. A packing diagram of *Z*-Lig molecules shown in Fig. 3 highlights the linking of molecules *via* the solvent water molecule, as well as the bonding of the carboxylate to the neighboring molecule *via* the linkage with both O2···H11 and O3···H12. Fig. 4 illustrates an important π - π stacking interaction between *Z*-Lig molecules related *via* $(1 - x, y, \frac{3}{2} - z)$, in which the centroid-centroid distance is 3.514 (2) Å.

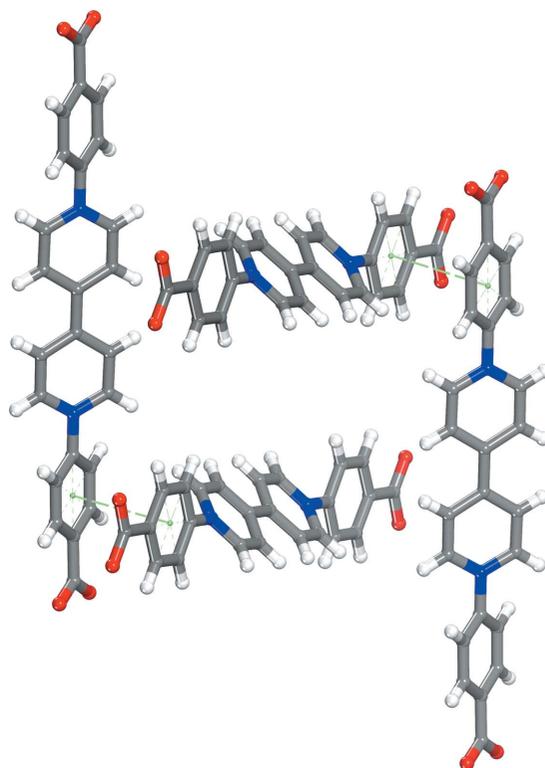


Figure 4

Illustration of the π - π interaction between adjacent *Z*-Lig molecules in the structure.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12 \cdots O3 ⁱ	0.95	2.35	3.0641 (15)	132
C11—H11 \cdots O2 ⁱ	0.95	2.47	3.3980 (16)	165
C4—H4 \cdots O3 ⁱⁱ	0.95	2.57	3.4735 (16)	159
O1—H1B \cdots O2 ⁱⁱⁱ	0.90 (2)	1.95 (2)	2.7997 (15)	158 (2)
O1—H1A \cdots O2	0.89 (2)	1.92 (2)	2.7893 (15)	165 (2)
C8—H8 \cdots O3 ^{iv}	0.95	2.26	3.0834 (16)	145
C9—H9 \cdots O1 ^{iv}	0.95	2.66	3.2673 (17)	122

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

Similar structures to *Z*-Lig have been published by Gutov *et al.* (2009) for a hexahydrate as well as a protonated form of *Z*-Lig with Cl[−] counter-ions and solvent water. An Eu-based metal–organic framework compound synthesized with *Z*-Lig has been documented by Liu *et al.* (2015). For a related structure with similar C—H \cdots O intermolecular interactions, see Fun *et al.* (2010).

Synthesis and crystallization

The title compound, *Z*-Lig, was synthesized in a two-step process as detailed below.

Step one: synthesis of H₂L. A mixture of 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride (1.00 g, 1.8 mmol)

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₄ H ₁₆ N ₂ O ₄ ·2H ₂ O
M_r	432.43
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
a, b, c (Å)	19.1437 (6), 7.6420 (3), 13.2619 (4)
β (°)	97.369 (1)
V (Å ³)	1924.14 (11)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ^{−1})	0.90
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	CMOS area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
T_{\min}, T_{\max}	0.86, 0.91
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9869, 1933, 1782
R_{int}	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.139, 1.12
No. of reflections	1933
No. of parameters	153
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.26, −0.38

Computer programs: *SAINT* and *SHELXS* (Sheldrick, 2008) in *APEX2* (Bruker, 2014), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *Materials Studio* (Accelrys, 2013).

and 4-aminobenzoic acid (0.51 g, 3.7 mmol) in 20 ml of ethanol was stirred and heated at 368 K overnight. The reaction was cooled to room temperature, followed by addition of 50 ml of dichloromethane. The intermediate product was collected by filtration, then further triturated using dichloromethane to obtain 536 mg (64%) of the final product hereafter known as H₂L (the protonated version of the title compound, with two chloride anions balancing the overall charge) as a light-brown solid.

¹H NMR (500 MHz, [D₆]DMSO): δ 8.09–8.11 ($d, J = 8.0$ Hz, 4H 4 × CH_{Ar}), 8.31–8.32 ($d, J = 8.0$ Hz, 4H 4 × CH_{Ar}), 9.01–9.10 ($d, J = 6.0$ Hz, 4H 4 × CH_{Ar}), 9.74–9.75 ($d, J = 6.0$ Hz, 4H 4 × CH_{Ar}) p.p.m.

Step two: Synthesis of the title compound *Z*-Lig. The reaction mixture containing Co(NO₃)₂·6H₂O (0.0045 g, 0.0154 mmol) and the above product H₂L (0.003 g, 0.0075 mmol) in 0.75 ml DMF, 0.75 ml H₂O and 1 drop concentrated HNO₃ was placed in a convection oven at 348 K for 24 h (heating rate 1.5 K/min and cooling rate of 1 K min^{−1}), yielding large orange rod-shaped single crystals (70%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160966 [doi:10.1107/S2414314616009664]

4,4'-([4,4'-Bipyridine]-1,1'-diium-1,1'-diyl)dibenzoate dihydrate

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4,4'-([4,4'-Bipyridine]-1,1'-diium-1,1'-diyl)dibenzoate dihydrate

Crystal data

$C_{24}H_{16}N_2O_4 \cdot 2H_2O$

$M_r = 432.43$

Monoclinic, $C2/c$

$a = 19.1437$ (6) Å

$b = 7.6420$ (3) Å

$c = 13.2619$ (4) Å

$\beta = 97.369$ (1)°

$V = 1924.14$ (11) Å³

$Z = 4$

$F(000) = 904$

$D_x = 1.493$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 200 reflections

$\theta = 4.7$ – 74.4 °

$\mu = 0.90$ mm⁻¹

$T = 100$ K

Block, orange

$0.20 \times 0.15 \times 0.10$ mm

Data collection

CMOS area detector
diffractometer

Radiation source: microfocus

ω and ϕ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.86$, $T_{\max} = 0.91$

9869 measured reflections

1933 independent reflections

1782 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 74.4$ °, $\theta_{\min} = 4.7$ °

$h = -23 \rightarrow 23$

$k = -9 \rightarrow 9$

$l = -16 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.139$

$S = 1.12$

1933 reflections

153 parameters

2 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5868P]$

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

$(\Delta/\sigma)_{\max} = 0.009$

$\Delta\rho_{\max} = 0.26$ e Å⁻³

$\Delta\rho_{\min} = -0.38$ e Å⁻³

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.78102 (5)	1.70456 (15)	0.67740 (8)	0.0281 (3)
H1A	0.7441 (9)	1.649 (3)	0.6973 (15)	0.040 (5)*
H1B	0.7896 (11)	1.788 (2)	0.7251 (14)	0.042 (6)*
O2	0.66644 (5)	1.49477 (13)	0.70827 (8)	0.0257 (3)
O3	0.58676 (5)	1.70850 (12)	0.67687 (7)	0.0196 (3)
N1	0.38723 (5)	1.04952 (14)	0.56125 (8)	0.0137 (3)
C1	0.60486 (7)	1.55138 (17)	0.67957 (9)	0.0168 (3)
C2	0.54808 (7)	1.41649 (17)	0.64604 (9)	0.0149 (3)
C3	0.56309 (6)	1.23826 (18)	0.64965 (10)	0.0163 (3)
H3	0.6097	1.2000	0.6721	0.020*
C4	0.51070 (7)	1.11543 (17)	0.62088 (10)	0.0161 (3)
H4	0.5209	0.9937	0.6233	0.019*
C5	0.44304 (6)	1.17558 (17)	0.58849 (9)	0.0140 (3)
C6	0.42649 (7)	1.35231 (17)	0.58328 (9)	0.0161 (3)
H6	0.3799	1.3903	0.5604	0.019*
C7	0.47989 (7)	1.47252 (17)	0.61249 (9)	0.0162 (3)
H7	0.4697	1.5942	0.6095	0.019*
C8	0.34121 (7)	1.07409 (17)	0.47631 (9)	0.0164 (3)
H8	0.3465	1.1719	0.4337	0.020*
C9	0.28684 (7)	0.95821 (17)	0.45133 (9)	0.0167 (3)
H9	0.2546	0.9765	0.3916	0.020*
C10	0.27881 (6)	0.81375 (16)	0.51321 (9)	0.0136 (3)
C11	0.32705 (6)	0.79378 (17)	0.60111 (10)	0.0162 (3)
H11	0.3230	0.6971	0.6450	0.019*
C12	0.38017 (7)	0.91350 (17)	0.62417 (9)	0.0163 (3)
H12	0.4121	0.9006	0.6847	0.020*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0223 (6)	0.0283 (6)	0.0353 (6)	−0.0051 (4)	0.0098 (5)	−0.0033 (4)
O2	0.0163 (5)	0.0204 (6)	0.0395 (6)	−0.0046 (4)	0.0005 (4)	−0.0017 (4)
O3	0.0243 (5)	0.0157 (5)	0.0185 (5)	−0.0052 (4)	0.0019 (4)	−0.0006 (3)
N1	0.0114 (5)	0.0150 (6)	0.0149 (5)	−0.0022 (4)	0.0027 (4)	−0.0008 (4)
C1	0.0170 (6)	0.0193 (7)	0.0146 (6)	−0.0040 (5)	0.0045 (5)	−0.0007 (5)
C2	0.0168 (6)	0.0170 (7)	0.0116 (6)	−0.0040 (5)	0.0052 (5)	−0.0015 (4)
C3	0.0130 (6)	0.0194 (7)	0.0168 (6)	−0.0013 (5)	0.0031 (5)	−0.0017 (5)
C4	0.0161 (7)	0.0154 (6)	0.0171 (6)	−0.0016 (5)	0.0028 (5)	−0.0015 (5)
C5	0.0132 (6)	0.0174 (7)	0.0118 (6)	−0.0045 (5)	0.0026 (4)	−0.0008 (4)
C6	0.0147 (6)	0.0176 (7)	0.0161 (6)	−0.0006 (5)	0.0027 (5)	0.0001 (5)
C7	0.0192 (7)	0.0158 (7)	0.0142 (6)	−0.0016 (5)	0.0047 (5)	−0.0001 (5)
C8	0.0165 (6)	0.0166 (6)	0.0159 (6)	−0.0026 (5)	0.0016 (5)	0.0027 (5)
C9	0.0153 (6)	0.0189 (7)	0.0152 (6)	−0.0023 (5)	−0.0012 (5)	0.0030 (5)
C10	0.0110 (6)	0.0154 (7)	0.0151 (6)	0.0000 (5)	0.0034 (5)	−0.0007 (5)
C11	0.0163 (6)	0.0152 (6)	0.0169 (6)	−0.0019 (5)	0.0010 (5)	0.0029 (5)

C12 0.0151 (6) 0.0175 (7) 0.0156 (6) -0.0013 (5) -0.0002 (5) 0.0016 (5)

Geometric parameters (Å, °)

O1—H1A	0.892 (16)	C5—C6	1.3869 (19)
O1—H1B	0.898 (16)	C6—C7	1.3919 (18)
O2—C1	1.2674 (16)	C6—H6	0.9500
O3—C1	1.2490 (17)	C7—H7	0.9500
N1—C12	1.3506 (17)	C8—C9	1.3743 (18)
N1—C8	1.3513 (16)	C8—H8	0.9500
N1—C5	1.4495 (15)	C9—C10	1.3957 (18)
C1—C2	1.5226 (17)	C9—H9	0.9500
C2—C3	1.3916 (19)	C10—C11	1.3996 (17)
C2—C7	1.3916 (18)	C10—C10 ⁱ	1.480 (2)
C3—C4	1.3908 (17)	C11—C12	1.3730 (17)
C3—H3	0.9500	C11—H11	0.9500
C4—C5	1.3895 (18)	C12—H12	0.9500
C4—H4	0.9500		
H1A—O1—H1B	101.9 (19)	C5—C6—H6	120.9
C12—N1—C8	121.05 (11)	C7—C6—H6	120.9
C12—N1—C5	119.11 (10)	C2—C7—C6	120.75 (12)
C8—N1—C5	119.76 (11)	C2—C7—H7	119.6
O3—C1—O2	125.50 (12)	C6—C7—H7	119.6
O3—C1—C2	117.22 (11)	N1—C8—C9	120.27 (12)
O2—C1—C2	117.28 (12)	N1—C8—H8	119.9
C3—C2—C7	119.56 (12)	C9—C8—H8	119.9
C3—C2—C1	121.07 (11)	C8—C9—C10	120.33 (11)
C7—C2—C1	119.37 (11)	C8—C9—H9	119.8
C4—C3—C2	120.84 (12)	C10—C9—H9	119.8
C4—C3—H3	119.6	C9—C10—C11	117.73 (11)
C2—C3—H3	119.6	C9—C10—C10 ⁱ	121.10 (14)
C5—C4—C3	118.19 (12)	C11—C10—C10 ⁱ	121.17 (14)
C5—C4—H4	120.9	C12—C11—C10	120.24 (11)
C3—C4—H4	120.9	C12—C11—H11	119.9
C6—C5—C4	122.38 (12)	C10—C11—H11	119.9
C6—C5—N1	118.58 (11)	N1—C12—C11	120.35 (11)
C4—C5—N1	119.03 (11)	N1—C12—H12	119.8
C5—C6—C7	118.29 (12)	C11—C12—H12	119.8

Symmetry code: (i) $-x+1/2, -y+3/2, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C12—H12...O3 ⁱⁱ	0.95	2.35	3.0641 (15)	132
C11—H11...O2 ⁱⁱ	0.95	2.47	3.3980 (16)	165
C4—H4...O3 ⁱⁱⁱ	0.95	2.57	3.4735 (16)	159
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O1—H1A···O2	0.89 (2)	1.92 (2)	2.7893 (15)	165 (2)
C8—H8···O3 ^v	0.95	2.26	3.0834 (16)	145
C9—H9···O1 ^v	0.95	2.66	3.2673 (17)	122

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