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4,4'-(Ethene-1,2-diyl)dipyridinium bis(2-hydroxy-3-methoxybenzoate)

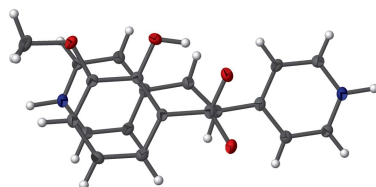
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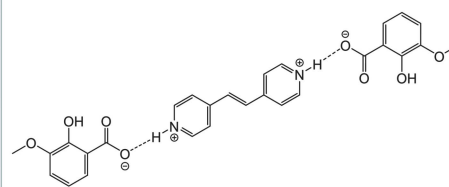
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In the title double proton-transfer salt, $C_{12}H_{12}N_2^{2+} \cdot 2C_8H_7O_4^-$, consisting of a 1:2 ratio of 4,4'-(ethene-1,2-diyl)dipyridinium cations (*trans* bipyridinium ethylene) to 2-hydroxy-3-methoxybenzoate anions (*o*-vanillate), the complete cation is generated by crystallographic inversion symmetry and it is linked to adjacent *o*-vanillate anions by $N-H \cdots O$ hydrogen bonds, forming trimolecular assemblies. The trimers are linked by $C-H \cdots O$ hydrogen bonds as well as aromatic $\pi-\pi$ stacking interactions into a three-dimensional network. The anion features an intramolecular $O-H \cdots O$ hydrogen bond.

3D view



Chemical scheme



Structure description

2-Hydroxy-3-methoxybenzoic acid (*o*-vanillic acid, $C_7H_8O_4$) is similar in nature to its isomeric counterpart 4-hydroxy-3-methoxybenzoic acid (*p*-vanillic acid), with the exception of the hydroxyl-group positioning. Much like its counterpart, *o*-vanillic acid is being investigated for its medicinal benefits, such as its anti-allergic inflammatory effects (Kim *et al.*, 2017). Despite its potential usage for medicinal purposes, there is a significant lack of structural data on this compound and its salts. As such it is beneficial to study the solid-state forms of *o*-vanillic acid and its salts to better understand its interactions. To achieve this, bipyridine ethylene ($C_{12}H_{10}N_2$) was selected due to its demonstrated ability to form both simple and complex hydrogen-bonded networks (MacGillivray *et al.*, 2000; Wang *et al.*, 2007). In addition, as the ΔpK_a value between *o*-vanillic acid ($pK_a = 2.5$) and bipyridine ethylene ($pK_a = 5.5$) is approximately 3, the observed salt formation can reasonably be expected due to the acid–base crystalline complexes ΔpK_a rule (Cruz-Cabeza, 2012).

The structure of the resulting bipyridinium ethylene bis-*o*-vanillate molecular salt, $C_{12}H_{12}N_2^{2+} \cdot 2C_8H_7O_4^-$, exhibits monoclinic ($P2_1/c$) symmetry at 90 K: the complete cation is generated by crystallographic inversion symmetry. A trimolecular unit consisting



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Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O4^i$	1.09 (2)	1.45 (2)	2.5402 (15)	178 (2)
$O2-H2\cdots O3$	0.96 (2)	1.64 (2)	2.5270 (14)	150 (2)
$C13-H13\cdots O2^{ii}$	0.95	2.52	3.1831 (16)	127
$C13-H13\cdots O3^i$	0.95	2.57	3.2092 (17)	125
$C12-H12\cdots O1^{ii}$	0.95	2.46	3.3591 (17)	159

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

of one bipyridinium ethylene cation (BPyE) with two *o*-vanillate anions, each of which accepts an $N1-H1\cdots O4$ hydrogen bond from the pyridinium N atoms of the cation is observed, in which the $H1\cdots O4$ distance of 1.45 (2) Å and the $N1\cdots O4$ separation of 2.5402 (15) Å are notably short. The cation–anion bonding is consolidated by a $C13-H13\cdots O3$ link and within the anion, an $S(6)$ intramolecular $O2-H2\cdots O3$ hydrogen bond is observed between the hydroxyl group and the O atom of the carboxyl group (Fig. 1, Table 1). These trimolecular units (Fig. 2) then stack through aromatic π – π interactions [shortest centroid–centroid separation =

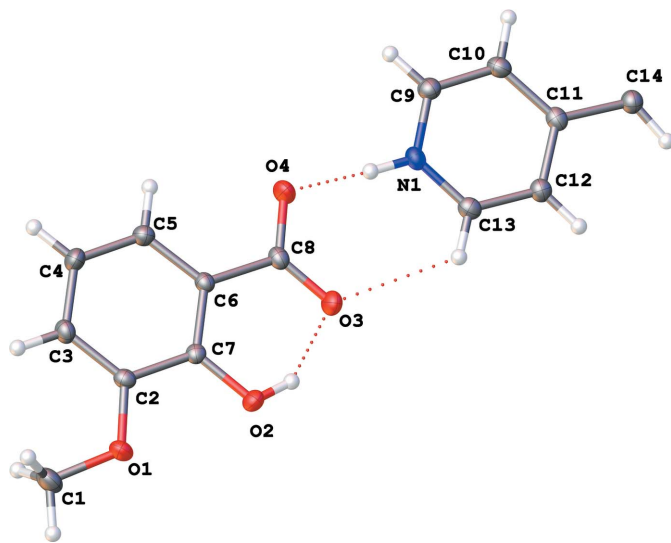


Figure 1

The asymmetric unit of the title molecular salt showing 50% displacement ellipsoids.

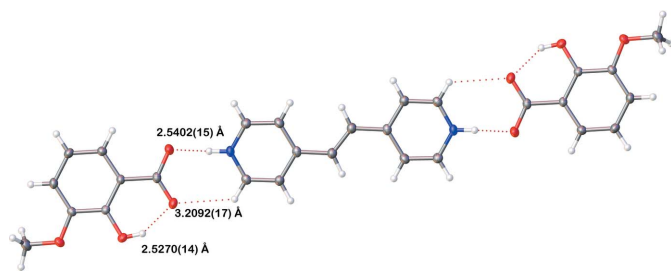


Figure 2

A trimolecular unit of the synthesized salt consisting of two *o*-vanillate anions and one bipyridinium ethylene cation. Hydrogen-bonding interactions are shown as red dashed lines with distances displayed between interacting heteroatoms.

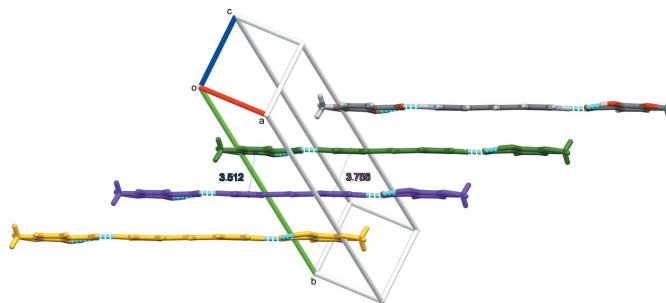


Figure 3

Side on view of the π -stacked trimolecular units. Offset units are shown in different colors. Distances, in Å, are shown between interacting ring centroids.

3.5125 (11) Å between the $N1/C9-C13$ and $C2-C7$ rings] with an approximately one third unit offset (Figs. 3 and 4). The stacks then sit aside of an alternating stack of units and are cross-linked through $C-H\cdots O$ type hydrogen bonds (Fig. 5). When viewed down [101], the slipped stacks can be seen running along [101], with alternating domains parallel to [010] (Fig. 6).

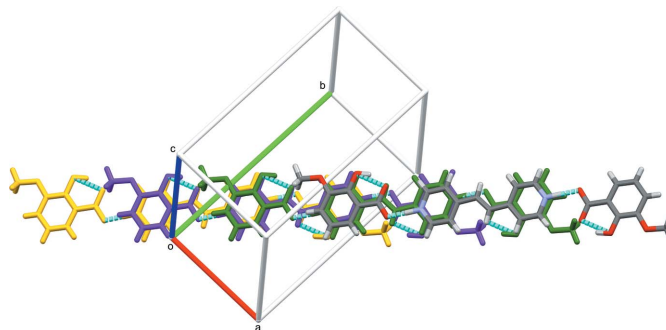


Figure 4

Top down view of the π -stacked trimolecular units. Offset units are shown in different colors.

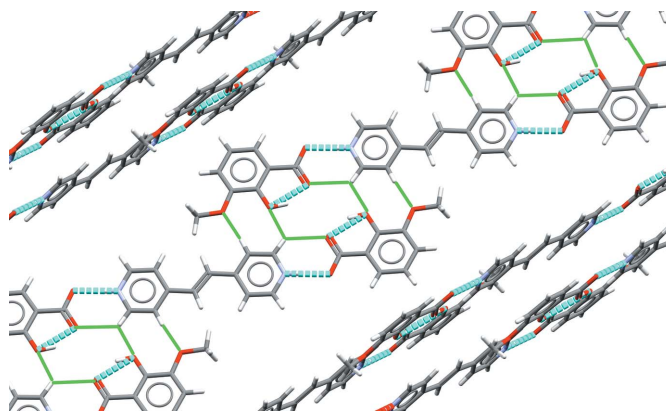


Figure 5

A single layer of the side by side trimolecular unit interactions are shown. Hydrogen-bonding interactions are shown as dashed blue lines; $C-H\cdots O$ type hydrogen-bonding interactions are shown as solid green lines.

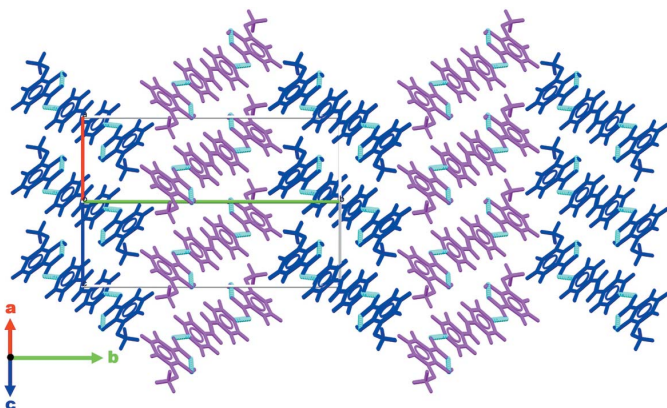


Figure 6

View down [101] showing slipped stacks running along [101] with alternating domains parallel to [010] being highlighted in pink and blue. Hydrogen-bonding interactions are shown as blue dashed lines.

Synthesis and crystallization

A 1:2 molar ratio of bipyridine ethylene (182.2 mg, 1 mmol) and *o*-vanillic acid (336.2 mg, 2 mmol) were dissolved into a vial of excess methanol. The resulting solution was vortexed for 30 s at 3,000 rpm on a VWR Mini Vortexer MV I. The solution was then stored in the dark uncapped to allow for crystal formation while the solvent slowly evaporated.

Refinement

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

Funding information

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Table 2

Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{12}N_2^{2+} \cdot 2C_8H_7O_4^-$
M_r	518.51
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	90
a, b, c (Å)	8.543 (2), 20.729 (5), 7.7061 (17)
β (°)	114.898 (4)
V (Å ³)	1237.8 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.10
Crystal size (mm)	0.58 × 0.25 × 0.02
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)
T_{min}, T_{max}	0.552, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20958, 3650, 2905
R_{int}	0.066
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.132, 1.03
No. of reflections	3650
No. of parameters	181
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.53, -0.22

Computer programs: APEX2 and SAINT (Bruker, 2016), olex2.solve (Bourhis *et al.*, 2015), SHELXL (Sheldrick, 2008), and OLEX2 (Dolomanov *et al.*, 2009).

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full crystallographic data

IUCrData (2022). 7, x220510 [https://doi.org/10.1107/S2414314622005107]

4,4'-(Ethene-1,2-diyl)dipyridinium bis(2-hydroxy-3-methoxybenzoate)

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4,4'-(Ethene-1,2-diyl)dipyridinium bis(2-hydroxy-3-methoxybenzoate)

Crystal data

$C_{12}H_{12}N_2^{2+} \cdot 2C_8H_7O_4^-$

$M_r = 518.51$

Monoclinic, $P2_1/c$

$a = 8.543$ (2) Å

$b = 20.729$ (5) Å

$c = 7.7061$ (17) Å

$\beta = 114.898$ (4)°

$V = 1237.8$ (5) Å³

$Z = 2$

$F(000) = 544$

$D_x = 1.391$ Mg m⁻³

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

Cell parameters from 4917 reflections

$\theta = 2.6$ – 30.2 °

$\mu = 0.10$ mm⁻¹

$T = 90$ K

Plate, clear colourless

$0.58 \times 0.25 \times 0.02$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2016)

$T_{\min} = 0.552$, $T_{\max} = 0.746$

20958 measured reflections

3650 independent reflections

2905 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\max} = 30.2$ °, $\theta_{\min} = 2.0$ °

$h = -11 \rightarrow 12$

$k = -29 \rightarrow 29$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.132$

$S = 1.03$

3650 reflections

181 parameters

0 restraints

Primary atom site location: iterative

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.4983P]$

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

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

$\Delta\rho_{\max} = 0.53$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ 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.

Refinement. H atoms attached to heteroatoms were freely refined isotropically. H atoms connected to carbon atoms were placed geometrically (C—H = 0.95 Å) and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.24089 (12)	0.42238 (4)	0.25115 (13)	0.0198 (2)
O3	0.56630 (12)	0.41986 (5)	0.42339 (13)	0.0225 (2)
O1	−0.04982 (12)	0.36590 (4)	0.01841 (14)	0.0217 (2)
O4	0.71834 (12)	0.35219 (5)	0.32767 (15)	0.0254 (2)
N1	−0.02080 (14)	0.41143 (5)	−0.43034 (15)	0.0171 (2)
C6	0.41360 (15)	0.34659 (6)	0.17054 (16)	0.0147 (2)
C7	0.25353 (15)	0.37113 (5)	0.14897 (16)	0.0145 (2)
C2	0.09975 (15)	0.34088 (6)	0.02102 (17)	0.0158 (2)
C11	0.26852 (16)	0.47304 (6)	−0.16647 (17)	0.0173 (2)
C8	0.57618 (16)	0.37522 (6)	0.31710 (17)	0.0175 (2)
C5	0.41996 (16)	0.29391 (6)	0.06001 (18)	0.0185 (2)
H5	0.528263	0.277301	0.073926	0.022*
C13	−0.03901 (16)	0.45885 (6)	−0.32230 (18)	0.0179 (2)
H13	−0.151365	0.470811	−0.337355	0.022*
C9	0.13651 (17)	0.39427 (6)	−0.41449 (18)	0.0194 (2)
H9	0.146696	0.360930	−0.493684	0.023*
C3	0.10839 (16)	0.28915 (6)	−0.08833 (18)	0.0190 (2)
H3	0.005280	0.269293	−0.176397	0.023*
C14	0.41779 (16)	0.50517 (6)	−0.01775 (18)	0.0198 (2)
H14	0.395078	0.536024	0.059892	0.024*
C12	0.10275 (16)	0.49066 (6)	−0.18939 (18)	0.0188 (2)
H12	0.087893	0.524298	−0.113955	0.023*
C10	0.28331 (16)	0.42435 (6)	−0.28499 (18)	0.0194 (2)
H10	0.393602	0.412167	−0.276192	0.023*
C4	0.26890 (17)	0.26605 (6)	−0.06931 (18)	0.0207 (3)
H4	0.273946	0.230930	−0.145981	0.025*
C1	−0.20613 (18)	0.33220 (7)	−0.0933 (2)	0.0270 (3)
H1A	−0.233819	0.337474	−0.229464	0.041*
H1B	−0.300275	0.349769	−0.066656	0.041*
H1C	−0.191431	0.286266	−0.060228	0.041*
H2	0.357 (3)	0.4327 (11)	0.340 (3)	0.055 (6)*
H1	−0.131 (3)	0.3851 (10)	−0.532 (3)	0.056 (6)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0201 (5)	0.0218 (4)	0.0187 (4)	−0.0005 (3)	0.0094 (4)	−0.0056 (3)
O3	0.0197 (5)	0.0270 (5)	0.0186 (4)	−0.0036 (4)	0.0060 (4)	−0.0076 (4)
O1	0.0138 (4)	0.0248 (5)	0.0271 (5)	−0.0010 (3)	0.0092 (4)	−0.0032 (4)
O4	0.0142 (4)	0.0300 (5)	0.0291 (5)	−0.0030 (4)	0.0063 (4)	−0.0096 (4)
N1	0.0155 (5)	0.0192 (5)	0.0148 (5)	−0.0025 (4)	0.0047 (4)	0.0013 (4)
C6	0.0138 (5)	0.0171 (5)	0.0130 (5)	−0.0019 (4)	0.0055 (4)	0.0002 (4)
C7	0.0163 (5)	0.0159 (5)	0.0123 (5)	−0.0012 (4)	0.0068 (4)	0.0005 (4)
C2	0.0144 (5)	0.0185 (5)	0.0150 (5)	0.0002 (4)	0.0067 (4)	0.0022 (4)
C11	0.0168 (6)	0.0190 (5)	0.0144 (5)	−0.0017 (4)	0.0049 (4)	0.0029 (4)

C8	0.0160 (6)	0.0205 (6)	0.0150 (5)	−0.0035 (4)	0.0056 (4)	0.0002 (4)
C5	0.0162 (6)	0.0202 (6)	0.0195 (6)	0.0001 (4)	0.0080 (5)	−0.0016 (4)
C13	0.0163 (6)	0.0192 (5)	0.0177 (6)	0.0010 (4)	0.0066 (5)	0.0026 (4)
C9	0.0193 (6)	0.0223 (6)	0.0176 (6)	−0.0007 (5)	0.0088 (5)	−0.0008 (4)
C3	0.0163 (6)	0.0214 (6)	0.0170 (6)	−0.0031 (4)	0.0046 (5)	−0.0021 (4)
C14	0.0189 (6)	0.0209 (6)	0.0190 (6)	−0.0017 (4)	0.0074 (5)	−0.0016 (5)
C12	0.0183 (6)	0.0186 (5)	0.0186 (6)	−0.0010 (4)	0.0070 (5)	−0.0002 (4)
C10	0.0153 (6)	0.0242 (6)	0.0194 (6)	−0.0002 (4)	0.0079 (5)	0.0010 (5)
C4	0.0213 (6)	0.0204 (6)	0.0207 (6)	−0.0021 (5)	0.0092 (5)	−0.0063 (5)
C1	0.0159 (6)	0.0304 (7)	0.0335 (7)	−0.0028 (5)	0.0090 (6)	−0.0009 (6)

Geometric parameters (Å, °)

O2—C7	1.3535 (14)	C5—H5	0.9500
O2—H2	0.96 (2)	C5—C4	1.3818 (18)
O3—C8	1.2618 (15)	C13—H13	0.9500
O1—C2	1.3713 (15)	C13—C12	1.3806 (17)
O1—C1	1.4297 (16)	C9—H9	0.9500
O4—C8	1.2753 (16)	C9—C10	1.3797 (18)
N1—C13	1.3389 (16)	C3—H3	0.9500
N1—C9	1.3451 (17)	C3—C4	1.4005 (18)
N1—H1	1.09 (2)	C14—C14 ⁱ	1.330 (3)
C6—C7	1.4018 (16)	C14—H14	0.9500
C6—C8	1.4954 (16)	C12—H12	0.9500
C6—C5	1.3999 (16)	C10—H10	0.9500
C7—C2	1.4144 (17)	C4—H4	0.9500
C2—C3	1.3849 (17)	C1—H1A	0.9800
C11—C14	1.4672 (17)	C1—H1B	0.9800
C11—C12	1.3998 (18)	C1—H1C	0.9800
C11—C10	1.4020 (17)		
C7—O2—H2	105.9 (13)	C12—C13—H13	119.4
C2—O1—C1	116.90 (10)	N1—C9—H9	119.5
C13—N1—C9	120.72 (11)	N1—C9—C10	121.02 (11)
C13—N1—H1	121.6 (12)	C10—C9—H9	119.5
C9—N1—H1	117.7 (12)	C2—C3—H3	119.9
C7—C6—C8	119.67 (10)	C2—C3—C4	120.11 (11)
C5—C6—C7	119.79 (11)	C4—C3—H3	119.9
C5—C6—C8	120.50 (11)	C11—C14—H14	117.2
O2—C7—C6	121.91 (10)	C14 ⁱ —C14—C11	125.64 (15)
O2—C7—C2	118.38 (10)	C14 ⁱ —C14—H14	117.2
C6—C7—C2	119.68 (11)	C11—C12—H12	120.2
O1—C2—C7	115.39 (10)	C13—C12—C11	119.60 (12)
O1—C2—C3	124.89 (11)	C13—C12—H12	120.2
C3—C2—C7	119.71 (11)	C11—C10—H10	120.2
C12—C11—C14	118.72 (11)	C9—C10—C11	119.52 (11)
C12—C11—C10	118.00 (11)	C9—C10—H10	120.2
C10—C11—C14	123.27 (11)	C5—C4—C3	120.57 (12)

O3—C8—O4	123.73 (11)	C5—C4—H4	119.7
O3—C8—C6	119.12 (11)	C3—C4—H4	119.7
O4—C8—C6	117.15 (11)	O1—C1—H1A	109.5
C6—C5—H5	120.0	O1—C1—H1B	109.5
C4—C5—C6	120.07 (11)	O1—C1—H1C	109.5
C4—C5—H5	120.0	H1A—C1—H1B	109.5
N1—C13—H13	119.4	H1A—C1—H1C	109.5
N1—C13—C12	121.11 (11)	H1B—C1—H1C	109.5
O2—C7—C2—O1	−2.15 (15)	C8—C6—C5—C4	177.25 (11)
O2—C7—C2—C3	178.70 (11)	C5—C6—C7—O2	−179.29 (11)
O1—C2—C3—C4	−177.73 (11)	C5—C6—C7—C2	2.46 (17)
N1—C13—C12—C11	−0.18 (18)	C5—C6—C8—O3	−175.32 (11)
N1—C9—C10—C11	0.76 (18)	C5—C6—C8—O4	4.15 (17)
C6—C7—C2—O1	176.16 (10)	C13—N1—C9—C10	0.90 (18)
C6—C7—C2—C3	−2.99 (17)	C9—N1—C13—C12	−1.20 (18)
C6—C5—C4—C3	−1.40 (19)	C14—C11—C12—C13	−176.93 (11)
C7—C6—C8—O3	2.21 (17)	C14—C11—C10—C9	176.58 (11)
C7—C6—C8—O4	−178.32 (11)	C12—C11—C14—C14 ⁱ	−178.18 (16)
C7—C6—C5—C4	−0.28 (18)	C12—C11—C10—C9	−2.06 (18)
C7—C2—C3—C4	1.34 (18)	C10—C11—C14—C14 ⁱ	3.2 (2)
C2—C3—C4—C5	0.9 (2)	C10—C11—C12—C13	1.78 (18)
C8—C6—C7—O2	3.16 (17)	C1—O1—C2—C7	−173.35 (11)
C8—C6—C7—C2	−175.09 (10)	C1—O1—C2—C3	5.75 (18)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O4 ⁱⁱ	1.09 (2)	1.45 (2)	2.5402 (15)	178 (2)
O2—H2 $\cdots$ O3	0.96 (2)	1.64 (2)	2.5270 (14)	150 (2)
C13—H13 $\cdots$ O2 ⁱⁱⁱ	0.95	2.52	3.1831 (16)	127
C13—H13 $\cdots$ O3 ⁱⁱ	0.95	2.57	3.2092 (17)	125
C12—H12 $\cdots$ O1 ⁱⁱⁱ	0.95	2.46	3.3591 (17)	159

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