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Short N···O hydrogen bonds in the 1:1 adduct of 4,4′-bipyridyl and oxalic acid

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Oxalic acid, $C_2O_4H_2$, and 4,4′-bipyridyl, $C_{10}H_8N_2$, crystallize in a 1:1 ratio. The asymmetric unit consists of one oxalic acid (OXA) molecule and one 4,4'bipyridyl (BPY) molecule in general positions, together with one half-OXA molecule and one half-BPY molecule; the latter two molecules are centrosymmetric. The molecules are linked in two parallel independent chains by strong O—H···N hydrogen bonds. In one chain there is one independent O—H···N hydrogen bond [N···O = 2.557 (3) Å] and the molecules lie on centres of symmetry and are therefore constrained to have planar central portions. The second chain contains two independent O—H···N hydrogen bonds [O···N = 2.549 (3) and 2.581 (3) Å] and both molecules are twisted about their central bonds.

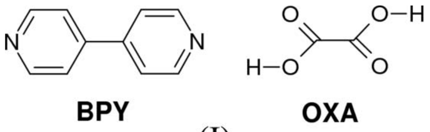
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.070
wR factor = 0.193
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Temperature-dependent proton migration has recently been observed in short N···O hydrogen bonds between carboxylic acid and pyridyl groups (Cowan *et al.*, 2003, 2005). It occurred to us that 4,4′-bipyridyl (BPY) and oxalic acid (OXA) would be likely to co-crystallize in the same intermolecular configuration, but hopefully with only one independent N—H···O hydrogen bond in the asymmetric unit. We present here the crystal structure of the title 1:1 adduct of BPY and OXA, (I).



(I)

The asymmetric unit of (I) consists of one oxalic acid (OXA) molecule and one 4,4′-bipyridyl (BPY) molecule in general positions, together with one half-OXA molecule and one half-BPY molecule; the latter two molecules are centrosymmetric. BPY and OXA crystallize to form two similar independent one-dimensional chains. In both chains the OXA and BPY molecules are linked together by strong O—H···N hydrogen bonds in concert with C—H···O hydrogen bonds (Table 1). A similar configuration is often observed in co-crystals of BPY and carboxylic acids, for example in the co-crystals of BPY with fumaric acid (Chatterjee *et al.*, 1998), phosphonoacetic acid (Bowes *et al.*, 2003) and malonic acid (Pedireddi *et al.*, 1998). That one-dimensional tapes are formed is unsurprising considering the co-crystals of BPY with 2,5-dihydroxybenzoquinone (Cowan *et al.*, 2001), squaric acid (Reetz *et al.*, 1994) and 2,5-dichloro-3,6-dihydroxybenzoquinone (Zaman *et al.*, 1999), which all have a similar

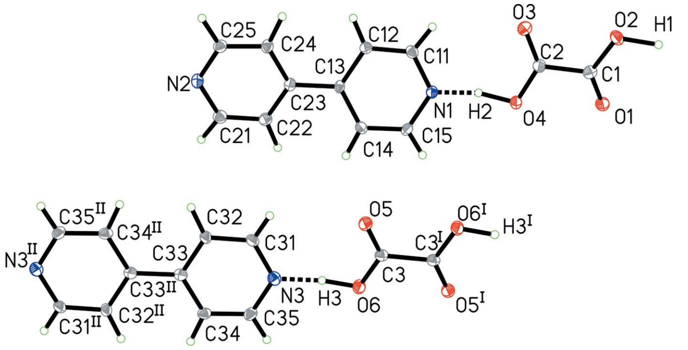


Figure 1

The structures of segments of both independent chain, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (I) $2 - x$, $2 - y$, $1 - z$; (II) $3 - x$, $1 - y$, $1 - z$.]

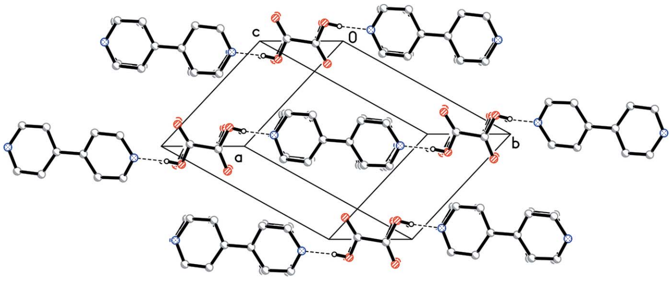


Figure 2

A packing diagram for (I), illustrating the molecular chains. All H atoms, except those involved in strong hydrogen bonds, have been omitted for clarity.

arrangement of O atoms to OXA and which all form one-dimensional tapes.

The two types of chains are distinguished by the twists within the molecules. In one chain, the planes of the pyridyl rings of the BPY molecule are twisted by 23.75 (6)° with respect to each other and there is a twist of 5.35 (11)° between the carboxylic acid groups of the OXA molecule, while in the other chain, the OXA and BPY molecules lie on centres of symmetry and are consequently both have planar central portions. Both chains lie in the *ab* plane and propagate in the [1$\bar{1}$0] direction (Fig. 2). The chains are linked by C—H···O hydrogen bonds into parallel planes. One set of planes consists of only flat molecules and the other consists of only twisted molecules. The only significant interaction linking the planes is a C—H···O hydrogen bond (C11···O3) between adjacent planes of twisted molecules.

There are three similar O—H···N hydrogen bonds in the structure of (I). Although the H-atom positions were constrained in the final refinement, O—H distances between 1.15 and 1.25 Å in earlier free refinements hint that the true H-atom positions may be close to the centres of the hydrogen bonds. The graph produced by Steiner (2002) from neutron diffraction data of N···O hydrogen bonds suggests that the O—H distance becomes significantly elongated when the N—O distance is below ~2.6 Å. Although not as short as the hydrogen bonds in which temperature-dependent proton migration has been observed, the N···O distances in the three hydrogen bonds in (I) are all below ~2.6 Å. Therefore, a large elongation of the O—H bond is expected and the H-atom position may be temperature-dependent. Neutron diffraction is required for accurate H-atom positions.

Experimental

Equimolar quantities of BPY and OXA were dissolved in methanol. Crystals of (I) suitable for X-ray structure determination were prepared by slow evaporation of the solvent at room temperature.

Crystal data

$C_{10}H_8N_2{\cdot}C_2H_2O_4$
$M_r = 246.22$
Triclinic, $P\bar{1}$
$a = 8.7365$ (18) Å
$b = 9.9154$ (19) Å
$c = 10.380$ (2) Å
$\alpha = 100.253$ (10)°
$\beta = 105.349$ (11)°
$\gamma = 107.569$ (10)°
$V = 793.5$ (3) Å^3
$Z = 3$
$D_x = 1.546$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 100$ (2) K
Block, brown
0.3 × 0.2 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
8434 measured reflections
3601 independent reflections
2523 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\rm max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.193$
$S = 1.09$
3601 reflections
259 parameters
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.9233P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.53$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···N2$^{\rm i}$	0.82	1.77	2.586 (3)	174
O4—H2···N1	0.82	1.74	2.553 (3)	174
O6—H3···N3	0.82	1.74	2.560 (3)	174
C11—H11···O3$^{\rm ii}$	0.93	2.59	3.270 (4)	130
C22—H22···O3$^{\rm iii}$	0.93	2.45	3.375 (3)	172
C24—H24···O1$^{\rm iv}$	0.93	2.40	3.326 (4)	171
C25—H25···O4$^{\rm iv}$	0.93	2.48	3.216 (3)	136
C32—H32···O5$^{\rm v}$	0.93	2.56	3.418 (3)	153
C34—H34···O5$^{\rm iii}$	0.93	2.52	3.373 (3)	153
C35—H35···O6$^{\rm vi}$	0.93	2.57	3.207 (3)	126

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

All H atoms were located in a difference Fourier map and then repositioned in idealized locations, with O—H = 0.82 Å and C—H = 0.93 Å. They were refined with their coordinates, but not their isotropic displacement parameters, riding on their parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL97*.

References

Bowes, K. F., Ferguson, G., Lough, A. J., Zakaria, C. M. & Glidewell, C. (2003). *Acta Cryst.* B**59**, 87–99.

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chatterjee, S., Pedireddi, V. R. & Rao, C. N. R. (1998). *Tetrahedron Lett.* **39**, 2843–2846.

Cowan, J. A., Howard, J. A. K. & Leech, M. A. (2001). *Acta Cryst.* C**57**, 302–303.

Cowan, J. A., Howard, J. A. K., McIntyre, G. J., Lo, S. M.-F. & Williams, I. D. (2003). *Acta Cryst.* B**59**, 794–801.

Cowan, J. A., Howard, J. A. K., McIntyre, G. J., Lo, S. M.-F. & Williams, I. D. (2005). *Acta Cryst.* B**61**, 724–730.

Pedireddi, V. R., Chatterjee, S., Ranganathan, A. & Rao, C. N. R. (1998). *Tetrahedron*, **54**, 9457–9474.

Reetz, M. T., Höger, S. & Harms, K. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 181–183.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 5.10 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.

Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.

Zaman, M. B., Tomura, M. & Yamashita, Y. (1999). *Chem. Commun.* pp. 999–1000.

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supporting information

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Short N···O hydrogen bonds in the 1:1 adduct of 4,4′-bipyridyl and oxalic acid

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4,4′-bipyridyl–oxalic acid (1/1)

Crystal data

$C_{10}H_8N_2{\cdot}C_2H_2O_4$
$M_r = 246.22$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.7365$ (18) Å
$b = 9.9154$ (19) Å
$c = 10.380$ (2) Å
$\alpha = 100.253$ (10)°
$\beta = 105.349$ (11)°
$\gamma = 107.569$ (10)°
$V = 793.5$ (3) Å^3
$Z = 3$
$F(000) = 384$
$D_x = 1.546$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 874 reflections
$\theta = 10.1$–19.0°
$\mu = 0.12$ mm^{-1}
$T = 100$ K
Block, brown
0.3 × 0.2 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
8434 measured reflections
3601 independent reflections
2523 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\rm max} = 27.5°$, $\theta_{\rm min} = 2.1°$
$h = -11 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.193$
$S = 1.09$
3601 reflections
259 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.9233P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.53$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Special details

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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.0631 (4)	0.9499 (3)	0.1702 (3)	0.0157 (6)
O1	0.1464 (3)	1.0696 (2)	0.1636 (2)	0.0204 (5)
O2	−0.0932 (3)	0.9108 (2)	0.1751 (2)	0.0195 (5)
H1	−0.1252	0.9805	0.1745	0.080 (18)*
C2	0.1318 (4)	0.8219 (3)	0.1705 (3)	0.0150 (5)
O3	0.0336 (3)	0.6941 (2)	0.1412 (2)	0.0247 (5)
O4	0.2955 (2)	0.8668 (2)	0.2015 (2)	0.0192 (5)
H2	0.3248	0.7954	0.1933	0.10 (2)*
N1	0.4089 (3)	0.6576 (2)	0.1828 (2)	0.0128 (5)
C11	0.3087 (4)	0.5142 (3)	0.1246 (3)	0.0148 (6)
H11	0.1909	0.4881	0.0909	0.021 (8)*
C12	0.3763 (3)	0.4040 (3)	0.1134 (3)	0.0136 (5)
H12	0.3046	0.3057	0.0731	0.020 (8)*
C13	0.5547 (3)	0.4431 (3)	0.1638 (3)	0.0112 (5)
C14	0.6565 (3)	0.5934 (3)	0.2216 (3)	0.0144 (5)
H14	0.7748	0.6235	0.2536	0.022 (8)*
C15	0.5800 (3)	0.6968 (3)	0.2308 (3)	0.0145 (5)
H15	0.6485	0.7959	0.2712	0.014 (7)*
N2	0.7855 (3)	0.1180 (2)	0.1646 (2)	0.0156 (5)
C21	0.8754 (4)	0.2565 (3)	0.1681 (3)	0.0178 (6)
H21	0.9884	0.2805	0.1721	0.024 (9)*
C22	0.8046 (4)	0.3642 (3)	0.1659 (3)	0.0163 (6)
H22	0.8694	0.4587	0.1680	0.034 (10)*
C23	0.6351 (3)	0.3295 (3)	0.1604 (3)	0.0130 (5)
C24	0.5416 (4)	0.1853 (3)	0.1546 (3)	0.0144 (5)
H24	0.4277	0.1574	0.1485	0.023 (9)*
C25	0.6229 (4)	0.0842 (3)	0.1581 (3)	0.0155 (6)
H25	0.5613	−0.0113	0.1559	0.012 (7)*
C3	1.0356 (3)	0.9366 (3)	0.5023 (3)	0.0142 (5)
O5	0.9471 (2)	0.8154 (2)	0.5031 (2)	0.0185 (4)
O6	1.1925 (2)	0.9765 (2)	0.5046 (2)	0.0192 (5)
H3	1.2232	0.9060	0.5033	0.10 (2)*
N3	1.3099 (3)	0.7691 (2)	0.5027 (2)	0.0155 (5)
C31	1.2128 (4)	0.6253 (3)	0.4680 (3)	0.0160 (6)
H31	1.0951	0.5979	0.4446	0.013 (7)*
C32	1.2821 (3)	0.5163 (3)	0.4658 (3)	0.0154 (6)
H32	1.2116	0.4178	0.4415	0.030 (9)*
C33	1.4596 (3)	0.5564 (3)	0.5007 (3)	0.0132 (5)
C34	1.5585 (3)	0.7073 (3)	0.5373 (3)	0.0143 (5)
H34	1.6765	0.7387	0.5607	0.020 (8)*

C35	1.4788 (4)	0.8091 (3)	0.5382 (3)	0.0161 (6)
H35	1.5457	0.9089	0.5645	0.024 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0173 (14)	0.0156 (13)	0.0141 (12)	0.0053 (11)	0.0061 (11)	0.0040 (9)
O1	0.0169 (11)	0.0149 (9)	0.0321 (11)	0.0053 (8)	0.0114 (9)	0.0095 (8)
O2	0.0149 (10)	0.0191 (10)	0.0285 (11)	0.0085 (8)	0.0098 (9)	0.0088 (8)
C2	0.0159 (14)	0.0146 (13)	0.0163 (12)	0.0063 (11)	0.0069 (11)	0.0051 (10)
O3	0.0185 (11)	0.0137 (10)	0.0411 (13)	0.0053 (8)	0.0090 (9)	0.0081 (8)
O4	0.0143 (10)	0.0122 (9)	0.0330 (11)	0.0064 (8)	0.0096 (8)	0.0056 (8)
N1	0.0131 (12)	0.0116 (10)	0.0169 (11)	0.0049 (9)	0.0083 (9)	0.0064 (8)
C11	0.0129 (14)	0.0167 (13)	0.0164 (12)	0.0061 (10)	0.0048 (11)	0.0075 (10)
C12	0.0135 (13)	0.0116 (12)	0.0163 (12)	0.0041 (10)	0.0060 (10)	0.0047 (9)
C13	0.0141 (13)	0.0111 (12)	0.0131 (11)	0.0069 (10)	0.0081 (10)	0.0054 (9)
C14	0.0117 (13)	0.0150 (12)	0.0167 (13)	0.0056 (10)	0.0043 (10)	0.0049 (10)
C15	0.0150 (14)	0.0102 (12)	0.0180 (13)	0.0043 (10)	0.0064 (11)	0.0027 (9)
N2	0.0175 (12)	0.0154 (11)	0.0170 (11)	0.0081 (9)	0.0074 (9)	0.0063 (8)
C21	0.0161 (14)	0.0178 (13)	0.0191 (13)	0.0046 (11)	0.0062 (11)	0.0066 (10)
C22	0.0158 (14)	0.0137 (12)	0.0199 (13)	0.0046 (11)	0.0068 (11)	0.0065 (10)
C23	0.0156 (13)	0.0140 (12)	0.0099 (11)	0.0071 (10)	0.0033 (10)	0.0035 (9)
C24	0.0153 (14)	0.0143 (12)	0.0171 (12)	0.0070 (10)	0.0076 (10)	0.0068 (10)
C25	0.0157 (14)	0.0131 (12)	0.0174 (13)	0.0038 (10)	0.0065 (11)	0.0045 (10)
C3	0.0132 (13)	0.0140 (13)	0.0146 (12)	0.0041 (10)	0.0046 (10)	0.0035 (9)
O5	0.0151 (10)	0.0131 (9)	0.0279 (11)	0.0043 (8)	0.0079 (8)	0.0076 (8)
O6	0.0143 (10)	0.0138 (9)	0.0319 (11)	0.0053 (8)	0.0113 (9)	0.0065 (8)
N3	0.0156 (12)	0.0176 (11)	0.0150 (11)	0.0073 (9)	0.0063 (9)	0.0047 (8)
C31	0.0109 (13)	0.0164 (13)	0.0197 (13)	0.0045 (11)	0.0033 (11)	0.0067 (10)
C32	0.0121 (13)	0.0127 (12)	0.0220 (13)	0.0045 (10)	0.0043 (11)	0.0089 (10)
C33	0.0137 (13)	0.0148 (12)	0.0108 (11)	0.0033 (10)	0.0038 (10)	0.0064 (9)
C34	0.0111 (13)	0.0135 (12)	0.0159 (12)	0.0021 (10)	0.0058 (10)	0.0009 (9)
C35	0.0165 (14)	0.0117 (12)	0.0201 (13)	0.0038 (10)	0.0079 (11)	0.0047 (10)

Geometric parameters (Å, º)

C1—O1	1.215 (3)	C22—C23	1.399 (4)
C1—O2	1.320 (3)	C22—H22	0.9300
C1—C2	1.559 (4)	C23—C24	1.398 (4)
O2—H1	0.8200	C24—C25	1.393 (4)
C2—O3	1.226 (3)	C24—H24	0.9300
C2—O4	1.292 (3)	C25—H25	0.9300
O4—H2	0.8200	C3—O5	1.220 (3)
N1—C11	1.348 (3)	C3—O6	1.299 (3)
N1—C15	1.349 (3)	C3—C3^{i}	1.563 (5)
C11—C12	1.392 (4)	O6—H3	0.8200
C11—H11	0.9300	N3—C35	1.334 (4)
C12—C13	1.408 (4)	N3—C31	1.344 (3)

C12—H12	0.9300	C31—C32	1.388 (4)
C13—C14	1.404 (3)	C31—H31	0.9300
C13—C23	1.497 (4)	C32—C33	1.406 (4)
C14—C15	1.385 (4)	C32—H32	0.9300
C14—H14	0.9300	C33—C34	1.404 (4)
C15—H15	0.9300	C33—C33^{ii}	1.492 (5)
N2—C25	1.337 (4)	C34—C35	1.389 (4)
N2—C21	1.350 (3)	C34—H34	0.9300
C21—C22	1.386 (4)	C35—H35	0.9300
C21—H21	0.9300		

O1—C1—O2	125.6 (3)	C23—C22—H22	120.3
O1—C1—C2	122.3 (3)	C24—C23—C22	118.3 (2)
O2—C1—C2	112.1 (2)	C24—C23—C13	120.1 (2)
C1—O2—H1	109.5	C22—C23—C13	121.7 (2)
O3—C2—O4	126.4 (3)	C25—C24—C23	118.5 (3)
O3—C2—C1	120.7 (3)	C25—C24—H24	120.8
O4—C2—C1	112.9 (2)	C23—C24—H24	120.8
C2—O4—H2	109.5	N2—C25—C24	123.1 (2)
C11—N1—C15	119.5 (2)	N2—C25—H25	118.4
N1—C11—C12	121.9 (3)	C24—C25—H25	118.4
N1—C11—H11	119.0	O5—C3—O6	126.3 (2)
C12—C11—H11	119.0	O5—C3—C3^{i}	121.0 (3)
C11—C12—C13	119.2 (2)	O6—C3—C3^{i}	112.7 (3)
C11—C12—H12	120.4	C3—O6—H3	109.5
C13—C12—H12	120.4	C35—N3—C31	119.1 (2)
C14—C13—C12	117.8 (2)	N3—C31—C32	122.3 (3)
C14—C13—C23	120.4 (2)	N3—C31—H31	118.9
C12—C13—C23	121.8 (2)	C32—C31—H31	118.9
C15—C14—C13	119.7 (3)	C31—C32—C33	119.4 (2)
C15—C14—H14	120.1	C31—C32—H32	120.3
C13—C14—H14	120.1	C33—C32—H32	120.3
N1—C15—C14	121.8 (2)	C34—C33—C32	117.3 (2)
N1—C15—H15	119.1	C34—C33—C33^{ii}	121.2 (3)
C14—C15—H15	119.1	C32—C33—C33^{ii}	121.5 (3)
C25—N2—C21	118.6 (2)	C35—C34—C33	119.5 (3)
N2—C21—C22	122.1 (3)	C35—C34—H34	120.2
N2—C21—H21	119.0	C33—C34—H34	120.2
C22—C21—H21	119.0	N3—C35—C34	122.4 (2)
C21—C22—C23	119.5 (2)	N3—C35—H35	118.8
C21—C22—H22	120.3	C34—C35—H35	118.8

Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $-x+3, -y+1, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···N2^{iii}	0.82	1.77	2.586 (3)	174

O4—H2···N1	0.82	1.74	2.553 (3)	174
O6—H3···N3	0.82	1.74	2.560 (3)	174
C11—H11···O3^{iv}	0.93	2.59	3.270 (4)	130
C22—H22···O3^{v}	0.93	2.45	3.375 (3)	172
C24—H24···O1^{vi}	0.93	2.40	3.326 (4)	171
C25—H25···O4^{vi}	0.93	2.48	3.216 (3)	136
C32—H32···O5^{vii}	0.93	2.56	3.418 (3)	153
C34—H34···O5^{v}	0.93	2.52	3.373 (3)	153
C35—H35···O6^{viii}	0.93	2.57	3.207 (3)	126

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