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Crystal structure of the co-crystal butylparaben–isonicotinamide (1/1)

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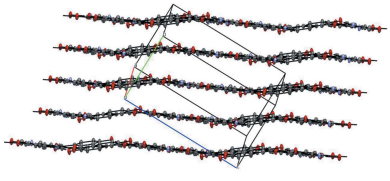
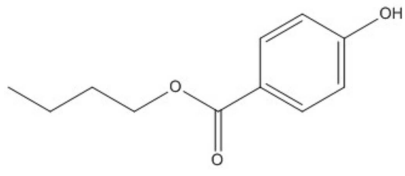
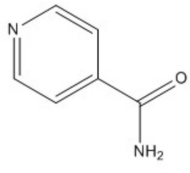
The title 1:1 co-crystal, $C_{11}H_{14}O_3{\cdot}C_6H_6N_2O$ [systematic name: butyl 4-hydroxybenzoate–isonicotinamide (1/1)], crystallizes with one molecule of butylparaben (BPN) and one molecule of isonicotinamide (ISN) in the asymmetric unit. In the crystal, BPN and ISN molecules form hydrogen-bonded (O—H···N and N—H···O) dimers of paired BPN and ISN molecules. These dimers are further connected to each other *via* N—H···O=C hydrogen bonds, creating ribbons in [011] which further stack along the *a* axis to form a layered structure with short C···C contacts of 3.285 (3) Å. Packing interactions within the crystal structure were assessed using PIXEL calculations.

1. Chemical context

Butylparaben (butyl 4-hydroxybenzoate, BPN), a naturally derived preservative, is widely used in pharmaceutical products and cosmetics (Charnock & Finsrud, 2007), and generally considered to be safe (Hossaini *et al.*, 2000). The solubility of BPN has been reported in various solvents (Yang & Rasmuson, 2010; 2012; 2013). Isonicotinamide (ISN) is a widely used coformer (Aakeröy *et al.*, 2003) and is known to form hydrogen-bonded co-crystals with phenolic compounds (Vishweshwar *et al.*, 2003; McKellar *et al.*, 2014). The sample of butyl paraben–isonicotinamide (BPIN) co-crystals was isolated during an experimental co-crystal screening of BPN. The sample was identified as a novel form using multi-sample foil transmission X-ray powder diffraction analysis (Florence *et al.*, 2003). A suitable sample for single crystal X-ray diffraction analysis was obtained from slow evaporation of 1:1 molar solution of BPN with ISN in ethanol at room temperature.







2. Structural commentary

The title co-crystal crystallizes with one molecule of BPN and a molecule of ISN in the asymmetric unit (Fig. 1). In the solid state, the BPN molecule exhibits a planar conformation with a fully extended *trans* zigzag butyl ester group.

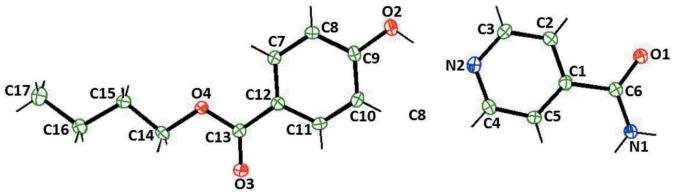


Figure 1
A view of the molecular structure of the asymmetric unit of the title co-crystal, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H3O···N2	0.95 (3)	1.79 (3)	2.721 (2)	165 (2)
N1—H1N···O1^{i}	0.91 (2)	1.97 (2)	2.880 (2)	175.3 (15)
N1—H2N···O3^{ii}	0.94 (2)	2.02 (2)	2.948 (2)	168.3 (18)

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

3. Supramolecular features

The crystal structure is defined by hydrogen-bonded BPN–ISN–ISN–BPN dimers of paired BPN···ISN molecules connected *via* O—H···N hydrogen bonds (Fig. 2*a*). These BPN–ISN–ISN–BPN dimers are further connected to each other *via* N—H···O=C hydrogen-bonds extending the structure to form ribbons in [011]; see Fig. 2*b* and Table 1. These ribbons further stack along *a* axis to produce a layered structure (Fig. 3) which is stabilized by various van der Waals interactions and exhibits short C···C contacts of 3.285 (3) Å. PIXEL (Gavezzotti, 2002; 2003) calculations revealed that the largest contribution to crystal stabilization comes from the dispersion energy (E_d, −98.5 kJ mol^{-1}). The next greatest contribution comes from electrostatic (Coulombic) energy, (E_C, −67.3 kJ mol^{-1}) and then from polarization energy (E_p, −32.2 kJ mol^{-1}).

4. Database survey

The crystal structures of BPN (CSD refcode: UDOMIL) (Yang & Rasmuson, 2013) and its clathrate hydrate (CSD refcode: VOFKIL) have been reported in the literature (de Vries & Caira, 2008). In UDOMIL, the BPN molecule exhibits a planar conformation except for the terminal ethyl moiety of butyl ester group which is in a *cis* orientation with respect to the ester group.

5. Synthesis and crystallization

Plate shaped crystals were grown from the saturated 1:1 molar solution of BPN with ISN in ethanol by isothermal solvent evaporation at 298 K.

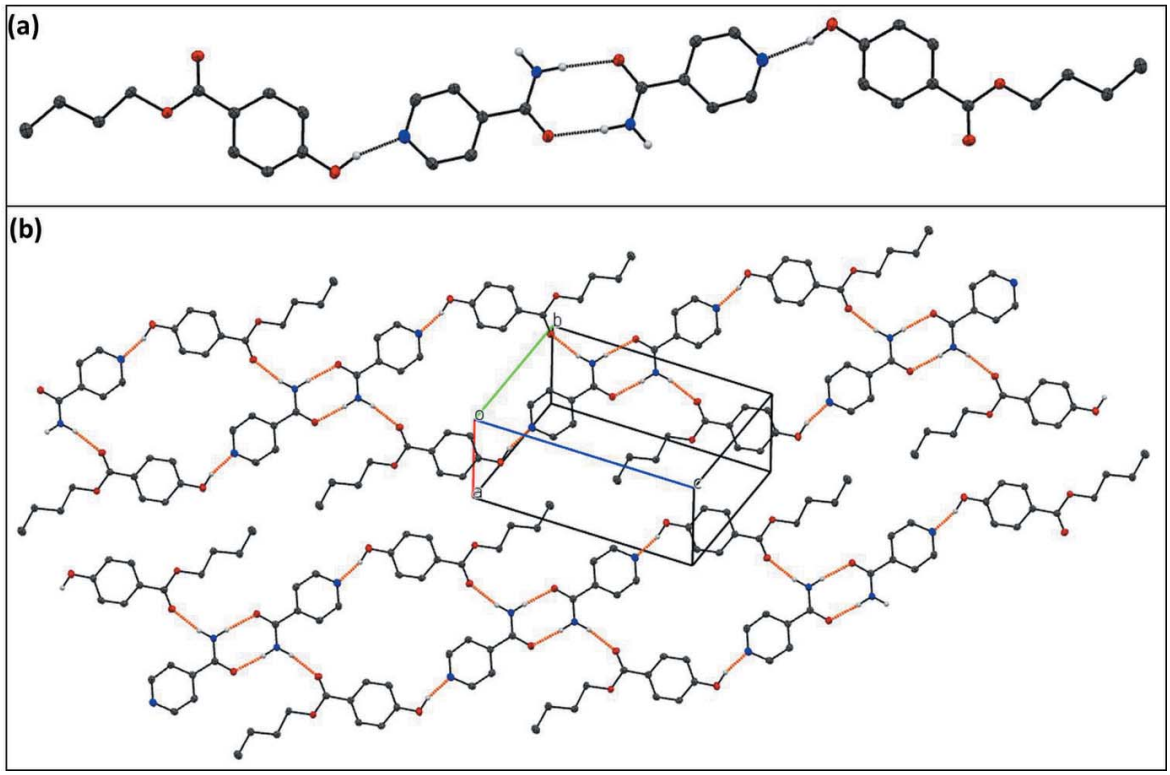


Figure 2
Hydrogen bonds in the title compound: (*a*) hydrogen-bonded (thin grey lines) dimer of paired BPN···ISN molecules; (*b*) hydrogen-bonded (thin orange lines) ribbon of dimers extended in [011]. Atom colour code: C, N, O and H are grey, blue, red and white, respectively. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

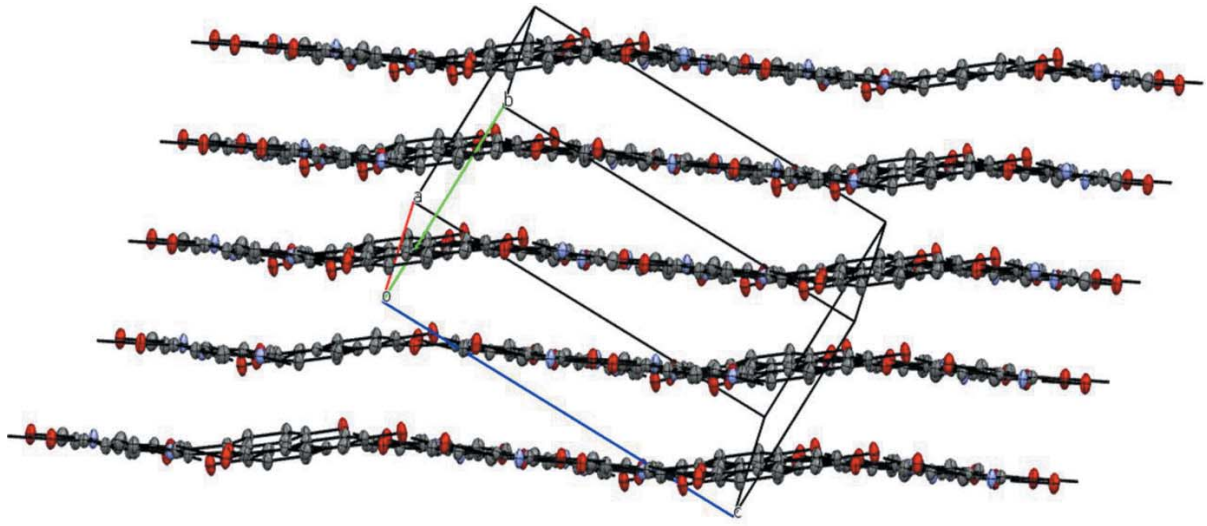


Figure 3
A portion of the crystal packing showing the layered structure of the title co-crystal. H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{14}O_3{\cdot}C_6H_6N_2O$
M_r	316.35
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	5.6257 (6), 9.8661 (11), 14.3979 (15)
α, β, γ (°)	90.834 (7), 91.431 (7), 91.645 (7)
V (Å^3)	798.47 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.45 × 0.36 × 0.21
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.625, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10444, 3225, 2344
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.116, 1.05
No. of reflections	3225
No. of parameters	221
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.27

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N and O bound H atoms were located in a difference Fourier map and isotropically refined. The C-bound H atoms were placed in calculated positions and refined as riding atoms: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and = 1.2U_{eq}(C) for other H atoms.

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

Butyl 4-hydroxybenzoate–isonicotinamide (1/1)

Crystal data

$C_{11}H_{14}O_3{\cdot}C_6H_6N_2O$
M_r = 316.35
Triclinic, $P\overline{1}$
a = 5.6257 (6) Å
b = 9.8661 (11) Å
c = 14.3979 (15) Å
α = 90.834 (7)°
β = 91.431 (7)°
γ = 91.645 (7)°
V = 798.47 (15) Å^3
Z = 2
$F(000)$ = 336
D_x = 1.316 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4038 reflections
θ = 2.5–26.4°
μ = 0.09 mm^{-1}
T = 150 K
Plate, colourless
0.45 × 0.36 × 0.21 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.625, T_{max} = 0.745
10444 measured reflections
3225 independent reflections
2344 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 26.5°, θ_{min} = 2.1°
h = −6→7
k = −12→12
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.116
S = 1.05
3225 reflections
221 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.3682P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H1N	−0.623 (3)	1.480 (2)	1.4226 (13)	0.019 (5)*
H2N	−0.626 (4)	1.399 (2)	1.3256 (16)	0.035 (6)*
H3O	0.140 (5)	0.939 (3)	1.1807 (17)	0.054 (7)*
O4	0.1197 (2)	0.47988 (13)	0.82145 (8)	0.0227 (3)
O1	−0.2641 (2)	1.38157 (14)	1.49057 (9)	0.0275 (3)
N1	−0.5594 (3)	1.41555 (17)	1.38514 (11)	0.0238 (4)
O2	0.2637 (2)	0.88155 (15)	1.16227 (9)	0.0308 (4)
N2	−0.0392 (3)	1.05682 (16)	1.24155 (10)	0.0234 (4)
O3	−0.2134 (2)	0.59634 (14)	0.80166 (9)	0.0297 (3)
C13	−0.0315 (3)	0.57543 (19)	0.84578 (12)	0.0207 (4)
C7	0.2633 (3)	0.63083 (19)	0.97609 (12)	0.0220 (4)
H8	0.3619	0.5641	0.9542	0.026*
C6	−0.3631 (3)	1.35566 (18)	1.41440 (12)	0.0194 (4)
C12	0.0462 (3)	0.65243 (18)	0.93023 (12)	0.0190 (4)
C14	0.0586 (3)	0.40447 (19)	0.73615 (12)	0.0223 (4)
H15A	0.0438	0.4660	0.6845	0.027*
H15B	−0.0918	0.3552	0.7423	0.027*
C8	0.3330 (3)	0.7076 (2)	1.05364 (13)	0.0239 (4)
H9	0.4775	0.6920	1.0839	0.029*
C2	−0.0520 (3)	1.18936 (19)	1.38204 (13)	0.0234 (4)
H2	0.0162	1.2121	1.4399	0.028*
C10	−0.0302 (3)	0.83018 (19)	1.04128 (12)	0.0229 (4)
H11	−0.1290	0.8969	1.0631	0.027*
C16	0.2264 (3)	0.2420 (2)	0.62252 (13)	0.0242 (4)
H17A	0.0722	0.1955	0.6171	0.029*
H17B	0.2306	0.3126	0.5764	0.029*
C5	−0.3533 (3)	1.21153 (19)	1.26476 (12)	0.0213 (4)
H6	−0.4918	1.2498	1.2420	0.026*
C15	0.2548 (3)	0.30708 (19)	0.71924 (12)	0.0220 (4)
H16A	0.2511	0.2370	0.7658	0.026*
H16B	0.4075	0.3551	0.7248	0.026*
C1	−0.2580 (3)	1.25031 (18)	1.35125 (12)	0.0185 (4)
C9	0.1866 (3)	0.80852 (19)	1.08652 (12)	0.0221 (4)
C11	−0.0986 (3)	0.75279 (19)	0.96404 (12)	0.0223 (4)
H12	−0.2437	0.7680	0.9342	0.027*
C3	0.0504 (3)	1.0945 (2)	1.32551 (13)	0.0251 (4)
H3	0.1888	1.0544	1.3467	0.030*
C4	−0.2387 (3)	1.11486 (19)	1.21283 (13)	0.0240 (4)
H5	−0.3042	1.0892	1.1551	0.029*

C17	0.4194 (4)	0.1414 (2)	0.60224 (14)	0.0314 (5)
H18A	0.5725	0.1869	0.6068	0.047*
H18B	0.3946	0.1042	0.5407	0.047*
H18C	0.4130	0.0696	0.6465	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.0233 (7)	0.0256 (7)	0.0192 (7)	0.0096 (6)	−0.0068 (5)	−0.0082 (5)
O1	0.0308 (7)	0.0313 (8)	0.0203 (7)	0.0134 (6)	−0.0072 (6)	−0.0097 (6)
N1	0.0260 (9)	0.0268 (9)	0.0185 (8)	0.0106 (7)	−0.0047 (7)	−0.0089 (7)
O2	0.0272 (7)	0.0367 (8)	0.0279 (7)	0.0099 (6)	−0.0072 (6)	−0.0183 (6)
N2	0.0251 (8)	0.0230 (8)	0.0223 (8)	0.0055 (7)	0.0000 (6)	−0.0049 (7)
O3	0.0284 (7)	0.0376 (8)	0.0229 (7)	0.0145 (6)	−0.0098 (6)	−0.0089 (6)
C13	0.0215 (9)	0.0228 (10)	0.0181 (9)	0.0066 (8)	−0.0013 (7)	−0.0014 (8)
C7	0.0227 (9)	0.0230 (10)	0.0205 (9)	0.0081 (8)	−0.0021 (7)	−0.0043 (8)
C6	0.0209 (9)	0.0199 (9)	0.0173 (9)	0.0022 (8)	−0.0009 (7)	−0.0019 (7)
C12	0.0211 (9)	0.0195 (9)	0.0164 (9)	0.0033 (7)	−0.0010 (7)	−0.0006 (7)
C14	0.0257 (10)	0.0252 (10)	0.0157 (9)	0.0049 (8)	−0.0061 (7)	−0.0061 (8)
C8	0.0190 (9)	0.0311 (11)	0.0215 (9)	0.0076 (8)	−0.0060 (7)	−0.0061 (8)
C2	0.0234 (9)	0.0270 (10)	0.0195 (9)	0.0037 (8)	−0.0046 (7)	−0.0050 (8)
C10	0.0226 (9)	0.0241 (10)	0.0222 (9)	0.0090 (8)	0.0014 (7)	−0.0035 (8)
C16	0.0281 (10)	0.0246 (10)	0.0199 (9)	0.0060 (8)	−0.0034 (8)	−0.0053 (8)
C5	0.0234 (9)	0.0230 (10)	0.0176 (9)	0.0068 (8)	−0.0040 (7)	−0.0013 (8)
C15	0.0233 (9)	0.0232 (10)	0.0194 (9)	0.0062 (8)	−0.0042 (7)	−0.0027 (8)
C1	0.0200 (9)	0.0176 (9)	0.0179 (9)	0.0017 (7)	0.0009 (7)	−0.0015 (7)
C9	0.0239 (10)	0.0239 (10)	0.0184 (9)	0.0031 (8)	−0.0009 (7)	−0.0067 (8)
C11	0.0196 (9)	0.0276 (10)	0.0199 (9)	0.0079 (8)	−0.0037 (7)	−0.0010 (8)
C3	0.0225 (9)	0.0263 (10)	0.0265 (10)	0.0095 (8)	−0.0033 (8)	−0.0059 (8)
C4	0.0277 (10)	0.0269 (11)	0.0173 (9)	0.0055 (8)	−0.0029 (7)	−0.0058 (8)
C17	0.0348 (11)	0.0310 (11)	0.0287 (11)	0.0096 (9)	0.0016 (9)	−0.0062 (9)

Geometric parameters (Å, º)

O4—C13	1.336 (2)	C12—C11	1.391 (2)
O4—C14	1.455 (2)	C14—C15	1.506 (2)
O1—C6	1.238 (2)	C8—C9	1.395 (2)
N1—C6	1.330 (2)	C2—C3	1.379 (2)
O2—C9	1.354 (2)	C2—C1	1.387 (2)
N2—C4	1.334 (2)	C10—C11	1.380 (3)
N2—C3	1.341 (2)	C10—C9	1.392 (3)
O3—C13	1.215 (2)	C16—C17	1.523 (3)
C13—C12	1.475 (2)	C16—C15	1.528 (2)
C7—C8	1.382 (3)	C5—C4	1.387 (2)
C7—C12	1.397 (2)	C5—C1	1.388 (2)
C6—C1	1.514 (2)		
C13—O4—C14	115.95 (13)	C3—C2—C1	118.97 (17)

C4—N2—C3	117.20 (15)	C11—C10—C9	120.08 (16)
O3—C13—O4	122.73 (16)	C17—C16—C15	112.76 (15)
O3—C13—C12	123.99 (16)	C4—C5—C1	118.94 (16)
O4—C13—C12	113.28 (14)	C14—C15—C16	110.66 (15)
C8—C7—C12	120.73 (16)	C2—C1—C5	118.09 (16)
O1—C6—N1	123.13 (16)	C2—C1—C6	117.54 (16)
O1—C6—C1	118.87 (15)	C5—C1—C6	124.37 (15)
N1—C6—C1	117.99 (16)	O2—C9—C10	122.75 (16)
C11—C12—C7	118.73 (16)	O2—C9—C8	117.70 (16)
C11—C12—C13	118.87 (15)	C10—C9—C8	119.55 (16)
C7—C12—C13	122.38 (15)	C10—C11—C12	120.95 (17)
O4—C14—C15	107.55 (14)	N2—C3—C2	123.48 (17)
C7—C8—C9	119.96 (17)	N2—C4—C5	123.31 (17)

C14—O4—C13—O3	2.3 (3)	O1—C6—C1—C2	−1.0 (3)
C14—O4—C13—C12	−177.25 (15)	N1—C6—C1—C2	179.41 (18)
C8—C7—C12—C11	0.0 (3)	O1—C6—C1—C5	179.42 (18)
C8—C7—C12—C13	178.19 (18)	N1—C6—C1—C5	−0.2 (3)
O3—C13—C12—C11	2.0 (3)	C11—C10—C9—O2	179.70 (18)
O4—C13—C12—C11	−178.52 (16)	C11—C10—C9—C8	−0.4 (3)
O3—C13—C12—C7	−176.20 (19)	C7—C8—C9—O2	−179.54 (17)
O4—C13—C12—C7	3.3 (3)	C7—C8—C9—C10	0.6 (3)
C13—O4—C14—C15	177.62 (16)	C9—C10—C11—C12	0.1 (3)
C12—C7—C8—C9	−0.4 (3)	C7—C12—C11—C10	0.1 (3)
O4—C14—C15—C16	−170.00 (15)	C13—C12—C11—C10	−178.09 (17)
C17—C16—C15—C14	−179.45 (17)	C4—N2—C3—C2	−0.4 (3)
C3—C2—C1—C5	0.6 (3)	C1—C2—C3—N2	−0.2 (3)
C3—C2—C1—C6	−179.01 (17)	C3—N2—C4—C5	0.7 (3)
C4—C5—C1—C2	−0.4 (3)	C1—C5—C4—N2	−0.3 (3)
C4—C5—C1—C6	179.21 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H3*O*···N2	0.95 (3)	1.79 (3)	2.721 (2)	165 (2)
N1—H1*N*···O1^{i}	0.91 (2)	1.97 (2)	2.880 (2)	175.3 (15)
N1—H2*N*···O3^{ii}	0.94 (2)	2.02 (2)	2.948 (2)	168.3 (18)

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