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ISSN 2414-3146

Bis[2-(2-hydroxyphenyl)-1*H*-benzimidazol-3-ium] chloranilate

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Received 27 October 2021
Accepted 31 October 2021

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

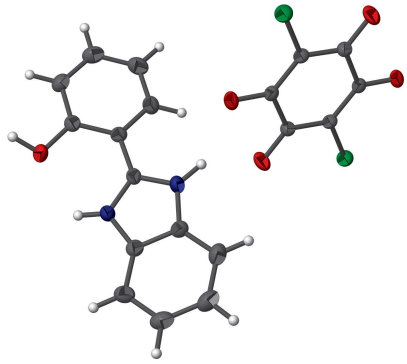
Keywords: crystal structure; chloranilic acid; 2-(2-hydroxyphenyl)-1*H*-benzimidazole; hydrogen bond.

CCDC reference: 2119367

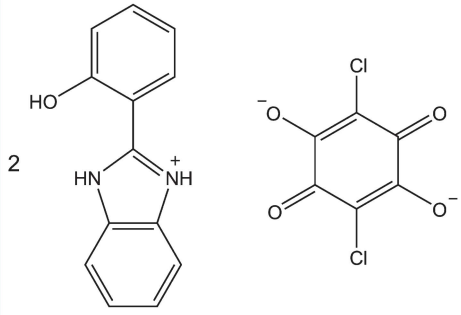
Structural data: full structural data are available from iucrdata.iucr.org

In the crystal of the title molecular salt {systematic name: bis[2-(2-hydroxyphenyl)-1*H*-benzimidazol-3-ium] 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate}, $2C_{13}H_{11}N_2O^+\cdot C_6Cl_2O_4^{2-}$, the chloranilate anion is located on an inversion centre, so that the asymmetric unit contains one cation and one half of the chloranilate anion. In the crystal, the cation and the anion are connected by a bifurcated N—H···(O,O) hydrogen bond, forming a 2:1 unit. The units are linked into a layer lying parallel to ($\bar{1}$01) *via* O—H···O and N—H···Cl hydrogen bonds. Between the layers, a C—Cl···π interaction is observed.

3D view



Chemical scheme



Structure description

We have prepared the title compound in order to continue our studies of *D*—H···*A* hydrogen bonding (*D* = N, O or C; *A* = N, O or Cl) in chloranilic acid–organic base systems (Gotoh & Ishida, 2017*a*,*b*, 2018, and references therein). In the cation, the C4–C9 benzene ring and the C10/N1/C11–C16/N2 benzimidazolium ring system are twisted to each other with a dihedral angle of 17.95 (7)°. An intramolecular N—H···O hydrogen bond (N2—H2···O3; Table 1) is observed. In the crystal, the chloranilate anion is located on an inversion centre, and the cation and the anion are connected by a bifurcated N—H···(O,O) hydrogen bond [N1—H1···(O1^{i},O2); symmetry code as given in Table 1], forming a cation–anion 2:1 unit (Fig. 1). The 2:1 units are further linked into a layer parallel to the ($\bar{1}$01) plane *via* O—H···O and N—H···Cl hydrogen bonds (O3—H3···O1^{iii} and N2—H2···Cl1^{ii}; Fig. 2, Table 1). A C—Cl···π interaction [C2—Cl1···*Cg*3^{iv}; Cl1···*Cg*3^{iv} = 3.6539 (10) Å and C2—Cl1···*Cg*3^{iv} = 139.21 (5)°; symmetry code: (iv) *x*, *y*, *z* − 1] is observed between the layers, where *Cg*3 is the centroid of the C11–C16 ring.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.91 (3)	2.01 (3)	2.7635 (18)	139 (3)
N1—H1···O1^{i}	0.91 (3)	2.16 (3)	2.9336 (18)	142 (3)
N2—H2···O3	0.878 (18)	2.138 (19)	2.6704 (19)	118.4 (15)
N2—H2···Cl1^{ii}	0.878 (18)	2.823 (18)	3.5907 (14)	146.9 (16)
O3—H3···O1^{iii}	0.94 (3)	1.73 (3)	2.6524 (18)	165 (3)

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

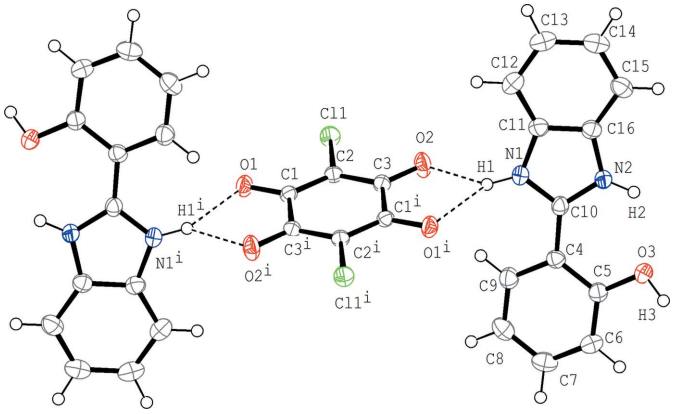


Figure 1
Molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the bifurcated N—H···(O,O) hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_{13}H_{11}N_2O^+\cdot C_6Cl_2O_4^{2-}$
M_r	629.45
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	180
a, b, c (Å)	8.6694 (11), 9.1751 (13), 10.0313 (14)
α, β, γ (°)	113.654 (4), 95.963 (5), 105.579 (4)
V (Å^3)	683.47 (17)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.23 × 0.17 × 0.06
Data collection	
Diffractometer	Rigaku R-AXIS RAPIDII
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.871, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14095, 3980, 3105
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.704
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.101, 1.10
No. of reflections	3980
No. of parameters	211
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.26

Computer programs: *PROCESS-AUTO* (Rigaku, 2006), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020), *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2020).

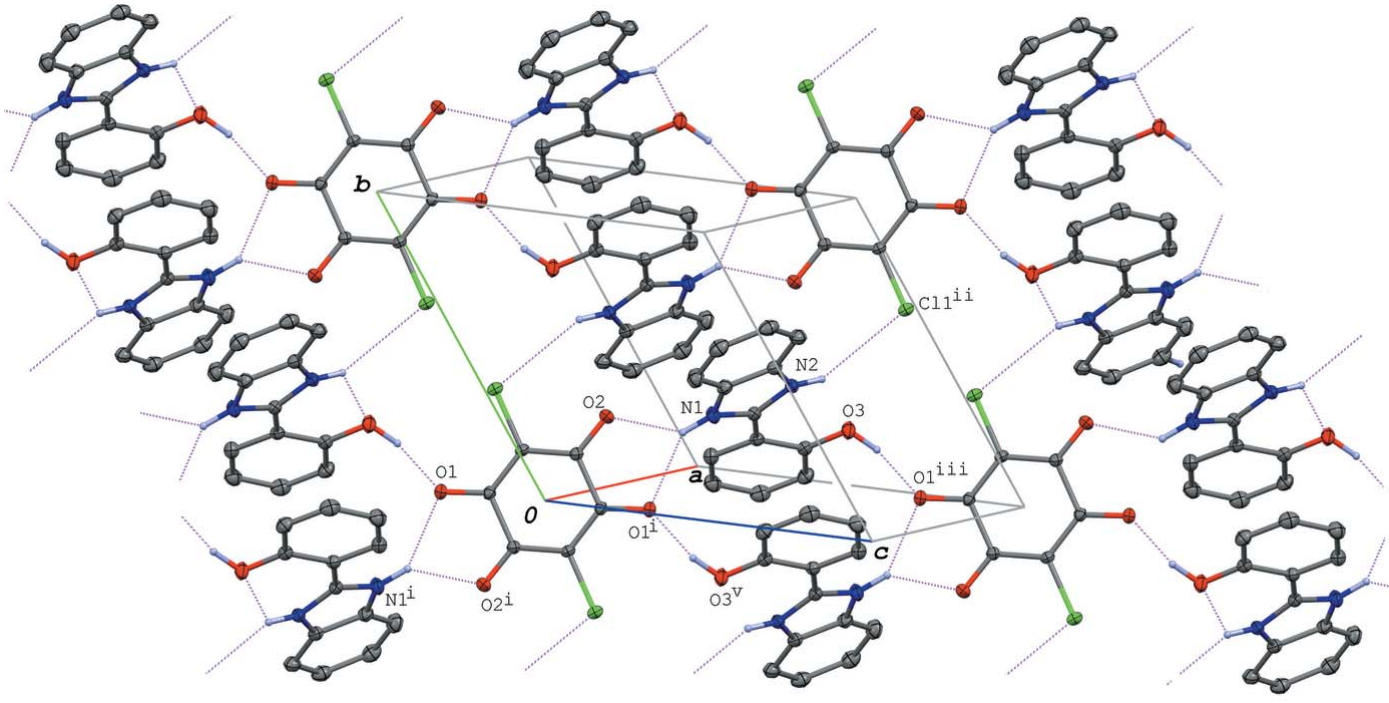


Figure 2
A packing diagram of the title compound, showing the hydrogen-bonded layer structure formed *via* the N—H···O, O—H···O and N—H···Cl hydrogen bonds (magenta dotted lines). H atoms not involved in the hydrogen bonds are omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x+1, y, z+1$; (v) $-x+1, -y, -z+1$.]

Synthesis and crystallization

Single crystals of the title salt were obtained by slow evaporation from a methanol solution of chloranilic acid with 2-(2-hydroxyphenyl)-1*H*-benzimidazole in a *ca* 1:1 molar ratio at room temperature [150 ml methanol solution of chloranilic acid (0.45 g) and 2-(2-hydroxyphenyl)-1*H*-benzimidazole (0.45 g)].

Refinement

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

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full crystallographic data

IUCrData (2021). **6**, x211150 [https://doi.org/10.1107/S2414314621011500]

Bis[2-(2-hydroxyphenyl)-1*H*-benzimidazol-3-ium] chloranilate

Hiroyuki Ishida

Bis[2-(2-hydroxyphenyl)-1*H*-benzimidazol-3-ium] 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate

Crystal data

$2C_{13}H_{11}N_2O^+\cdot C_6Cl_2O_4^{2-}$
M_r = 629.45
Triclinic, $P\overline{1}$
a = 8.6694 (11) Å
b = 9.1751 (13) Å
c = 10.0313 (14) Å
α = 113.654 (4)°
β = 95.963 (5)°
γ = 105.579 (4)°
V = 683.47 (17) Å^3
Z = 1
$F(000)$ = 324.00
D_x = 1.529 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 10316 reflections
θ = 3.4–30.1°
μ = 0.29 mm^{-1}
T = 180 K
Block, brown
0.23 × 0.17 × 0.06 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.871, T_{max} = 0.983
14095 measured reflections
3980 independent reflections
3105 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 30.0°, θ_{min} = 3.4°
h = −12→11
k = −12→12
l = −14→14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.101
S = 1.10
3980 reflections
211 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.2103P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. _reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.09994 (4)	0.34752 (4)	−0.02027 (4)	0.02882 (10)
O1	−0.14183 (13)	0.01196 (13)	−0.24683 (11)	0.0289 (2)
O2	0.21238 (14)	0.27933 (13)	0.23324 (12)	0.0346 (3)
O3	0.75991 (14)	0.23427 (14)	0.69412 (12)	0.0329 (2)
N1	0.35863 (16)	0.30308 (17)	0.50287 (14)	0.0295 (3)
N2	0.55002 (15)	0.40290 (15)	0.70561 (13)	0.0254 (2)
C1	−0.07044 (16)	0.01567 (16)	−0.12934 (14)	0.0209 (3)
C2	0.04335 (16)	0.15741 (16)	−0.00910 (15)	0.0215 (3)
C3	0.11500 (16)	0.15402 (16)	0.12180 (15)	0.0220 (3)
C4	0.59135 (17)	0.19499 (17)	0.47216 (15)	0.0243 (3)
C5	0.71650 (18)	0.16090 (17)	0.54313 (16)	0.0257 (3)
C6	0.7897 (2)	0.0516 (2)	0.45539 (18)	0.0322 (3)
H6	0.873099	0.026322	0.502062	0.039*
C7	0.7424 (2)	−0.0201 (2)	0.30162 (19)	0.0358 (3)
H7	0.792239	−0.095973	0.242994	0.043*
C8	0.6224 (2)	0.0171 (2)	0.23097 (18)	0.0361 (3)
H8	0.592107	−0.031076	0.124678	0.043*
C9	0.54818 (19)	0.12356 (19)	0.31562 (17)	0.0305 (3)
H9	0.466344	0.149222	0.267406	0.037*
C10	0.50320 (17)	0.29865 (17)	0.55883 (15)	0.0240 (3)
C11	0.31061 (19)	0.41400 (18)	0.61747 (16)	0.0283 (3)
C12	0.1694 (2)	0.4589 (2)	0.6176 (2)	0.0384 (4)
H12	0.084527	0.412181	0.529115	0.046*
C13	0.1595 (2)	0.5750 (2)	0.7532 (2)	0.0386 (4)
H13	0.065121	0.609007	0.758876	0.046*
C14	0.2855 (2)	0.6435 (2)	0.88216 (19)	0.0362 (4)
H14	0.275017	0.724559	0.973058	0.043*
C15	0.4247 (2)	0.59789 (19)	0.88273 (18)	0.0330 (3)
H15	0.509383	0.644482	0.971298	0.040*
C16	0.43388 (18)	0.48016 (17)	0.74661 (16)	0.0264 (3)
H1	0.299 (3)	0.241 (3)	0.406 (3)	0.076 (8)*
H2	0.644 (2)	0.422 (2)	0.763 (2)	0.041 (5)*
H3	0.812 (3)	0.170 (3)	0.723 (3)	0.065 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0365 (2)	0.01955 (15)	0.03055 (19)	0.00738 (13)	0.00309 (14)	0.01391 (13)
O1	0.0337 (6)	0.0260 (5)	0.0248 (5)	0.0086 (4)	−0.0031 (4)	0.0128 (4)
O2	0.0404 (6)	0.0222 (5)	0.0279 (6)	0.0001 (4)	−0.0093 (4)	0.0094 (4)
O3	0.0398 (6)	0.0352 (6)	0.0259 (5)	0.0201 (5)	0.0016 (4)	0.0128 (5)

N1	0.0285 (6)	0.0326 (6)	0.0233 (6)	0.0135 (5)	−0.0001 (5)	0.0083 (5)
N2	0.0262 (6)	0.0227 (5)	0.0233 (6)	0.0085 (5)	0.0008 (5)	0.0078 (5)
C1	0.0220 (6)	0.0210 (6)	0.0222 (6)	0.0094 (5)	0.0053 (5)	0.0106 (5)
C2	0.0252 (6)	0.0166 (6)	0.0238 (6)	0.0073 (5)	0.0047 (5)	0.0103 (5)
C3	0.0225 (6)	0.0191 (6)	0.0228 (6)	0.0066 (5)	0.0034 (5)	0.0088 (5)
C4	0.0267 (7)	0.0201 (6)	0.0255 (7)	0.0072 (5)	0.0057 (5)	0.0101 (5)
C5	0.0278 (7)	0.0233 (6)	0.0261 (7)	0.0076 (5)	0.0050 (5)	0.0123 (5)
C6	0.0327 (8)	0.0328 (8)	0.0378 (8)	0.0170 (6)	0.0107 (6)	0.0179 (7)
C7	0.0404 (9)	0.0329 (8)	0.0387 (9)	0.0167 (7)	0.0202 (7)	0.0151 (7)
C8	0.0443 (9)	0.0342 (8)	0.0264 (8)	0.0119 (7)	0.0110 (7)	0.0106 (6)
C9	0.0322 (8)	0.0313 (7)	0.0273 (7)	0.0102 (6)	0.0039 (6)	0.0137 (6)
C10	0.0256 (7)	0.0215 (6)	0.0238 (7)	0.0063 (5)	0.0019 (5)	0.0112 (5)
C11	0.0321 (8)	0.0264 (7)	0.0286 (7)	0.0132 (6)	0.0073 (6)	0.0123 (6)
C12	0.0353 (8)	0.0438 (9)	0.0406 (9)	0.0198 (7)	0.0058 (7)	0.0199 (8)
C13	0.0389 (9)	0.0401 (9)	0.0498 (10)	0.0230 (7)	0.0190 (8)	0.0243 (8)
C14	0.0462 (9)	0.0297 (7)	0.0392 (9)	0.0176 (7)	0.0202 (7)	0.0163 (7)
C15	0.0407 (9)	0.0257 (7)	0.0302 (8)	0.0110 (6)	0.0090 (6)	0.0105 (6)
C16	0.0284 (7)	0.0225 (6)	0.0289 (7)	0.0085 (5)	0.0064 (5)	0.0122 (6)

Geometric parameters (Å, º)

Cl1—C2	1.7333 (13)	C6—C7	1.375 (2)
O1—C1	1.2562 (15)	C6—H6	0.9500
O2—C3	1.2392 (16)	C7—C8	1.390 (2)
O3—C5	1.3477 (18)	C7—H7	0.9500
O3—H3	0.95 (2)	C8—C9	1.370 (2)
N1—C10	1.3368 (18)	C8—H8	0.9500
N1—C11	1.3851 (19)	C9—H9	0.9500
N1—H1	0.91 (3)	C11—C16	1.386 (2)
N2—C10	1.3359 (18)	C11—C12	1.393 (2)
N2—C16	1.3860 (19)	C12—C13	1.379 (2)
N2—H2	0.88 (2)	C12—H12	0.9500
C1—C2	1.3872 (18)	C13—C14	1.396 (3)
C1—C3^{i}	1.5351 (18)	C13—H13	0.9500
C2—C3	1.4088 (18)	C14—C15	1.379 (2)
C4—C9	1.399 (2)	C14—H14	0.9500
C4—C5	1.4079 (19)	C15—C16	1.387 (2)
C4—C10	1.452 (2)	C15—H15	0.9500
C5—C6	1.390 (2)		

C5—O3—H3	107.6 (14)	C9—C8—C7	119.56 (15)
C10—N1—C11	108.93 (12)	C9—C8—H8	120.2
C10—N1—H1	125.9 (17)	C7—C8—H8	120.2
C11—N1—H1	125.2 (17)	C8—C9—C4	120.82 (14)
C10—N2—C16	109.44 (12)	C8—C9—H9	119.6
C10—N2—H2	123.2 (13)	C4—C9—H9	119.6
C16—N2—H2	127.3 (13)	N2—C10—N1	108.68 (13)
O1—C1—C2	125.88 (12)	N2—C10—C4	126.61 (13)

O1—C1—C3^{i}	115.72 (11)	N1—C10—C4	124.71 (13)
C2—C1—C3^{i}	118.39 (11)	N1—C11—C16	106.88 (13)
C1—C2—C3	123.02 (11)	N1—C11—C12	131.05 (15)
C1—C2—Cl1	118.52 (10)	C16—C11—C12	122.06 (15)
C3—C2—Cl1	118.46 (10)	C13—C12—C11	116.36 (15)
O2—C3—C2	124.66 (12)	C13—C12—H12	121.8
O2—C3—C1^{i}	116.80 (11)	C11—C12—H12	121.8
C2—C3—C1^{i}	118.54 (11)	C12—C13—C14	121.24 (15)
C9—C4—C5	119.33 (13)	C12—C13—H13	119.4
C9—C4—C10	119.64 (13)	C14—C13—H13	119.4
C5—C4—C10	121.00 (13)	C15—C14—C13	122.52 (15)
O3—C5—C6	122.30 (13)	C15—C14—H14	118.7
O3—C5—C4	118.68 (13)	C13—C14—H14	118.7
C6—C5—C4	119.02 (13)	C14—C15—C16	116.18 (15)
C7—C6—C5	120.51 (14)	C14—C15—H15	121.9
C7—C6—H6	119.7	C16—C15—H15	121.9
C5—C6—H6	119.7	N2—C16—C11	106.04 (12)
C6—C7—C8	120.71 (15)	N2—C16—C15	132.34 (14)
C6—C7—H7	119.6	C11—C16—C15	121.61 (14)
C8—C7—H7	119.6		

O1—C1—C2—C3	177.85 (13)	C11—N1—C10—N2	0.01 (17)
C3^{i}—C1—C2—C3	−2.5 (2)	C11—N1—C10—C4	179.39 (13)
O1—C1—C2—Cl1	−2.1 (2)	C9—C4—C10—N2	−164.99 (14)
C3^{i}—C1—C2—Cl1	177.54 (9)	C5—C4—C10—N2	17.0 (2)
C1—C2—C3—O2	−177.30 (14)	C9—C4—C10—N1	15.7 (2)
Cl1—C2—C3—O2	2.7 (2)	C5—C4—C10—N1	−162.30 (14)
C1—C2—C3—C1^{i}	2.5 (2)	C10—N1—C11—C16	0.99 (17)
Cl1—C2—C3—C1^{i}	−177.54 (9)	C10—N1—C11—C12	−178.19 (16)
C9—C4—C5—O3	178.22 (13)	N1—C11—C12—C13	179.91 (16)
C10—C4—C5—O3	−3.7 (2)	C16—C11—C12—C13	0.8 (2)
C9—C4—C5—C6	−2.4 (2)	C11—C12—C13—C14	0.4 (3)
C10—C4—C5—C6	175.59 (13)	C12—C13—C14—C15	−1.1 (3)
O3—C5—C6—C7	−179.73 (14)	C13—C14—C15—C16	0.5 (2)
C4—C5—C6—C7	1.0 (2)	C10—N2—C16—C11	1.60 (16)
C5—C6—C7—C8	1.0 (2)	C10—N2—C16—C15	−179.40 (15)
C6—C7—C8—C9	−1.4 (3)	N1—C11—C16—N2	−1.55 (16)
C7—C8—C9—C4	−0.1 (2)	C12—C11—C16—N2	177.72 (14)
C5—C4—C9—C8	2.1 (2)	N1—C11—C16—C15	179.32 (13)
C10—C4—C9—C8	−176.01 (14)	C12—C11—C16—C15	−1.4 (2)
C16—N2—C10—N1	−1.01 (16)	C14—C15—C16—N2	−178.19 (15)
C16—N2—C10—C4	179.62 (13)	C14—C15—C16—C11	0.7 (2)

Symmetry code: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.91 (3)	2.01 (3)	2.7635 (18)	139 (3)

N1—H1···O1^{i}	0.91 (3)	2.16 (3)	2.9336 (18)	142 (3)
N2—H2···O3	0.878 (18)	2.138 (19)	2.6704 (19)	118.4 (15)
N2—H2···Cl1^{ii}	0.878 (18)	2.823 (18)	3.5907 (14)	146.9 (16)
O3—H3···O1^{iii}	0.94 (3)	1.73 (3)	2.6524 (18)	165 (3)

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