Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A monoclinic polymorph of 5-[(1*H*-benzimidazol-1-yl)methyl]benzene-1,3-dicarboxylic acid

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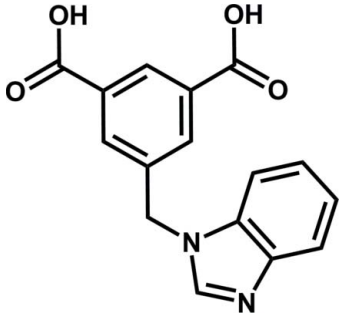
Received 22 September 2012; accepted 29 September 2012

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.152; data-to-parameter ratio = 11.8.

Crystals of the title compound, $C_{16}H_{12}N_2O_4$, were obtained accidentally by the hydrothermal reaction of 5-[(1*H*-benzo[*d*]imidazol-1-yl)methyl]isophthalic acid with manganese chloride tetrahydrate in the presence of KOH as alkaline reagent for the deprotonation. A triclinic polymorph of this structure has been reported previously from a similar reaction [Cheng (2011). *Acta Cryst.* E**67**, o3299]. The benzimidazole ring system is almost planar, with a maximum deviation from the mean plane of 0.020 (4) Å. The benzimidazole unit and benzene ring are inclined at a dihedral angle of 68.17 (4)°, reflecting the axial rotation of the flexible benzimidazolyl arm. In the crystal, pairs of O—H···O hydrogen bonds link adjacent molecules into inversion dimers. O—H···N contacts connect these dimers into zigzag chains along [010].

Related literature

For a triclinic polymorph of the title compound, see: Cheng (2011).



Experimental

Crystal data

$C_{16}H_{12}N_2O_4$
M_r = 296.28
Monoclinic, $P2_1/c$
a = 7.401 (5) Å
b = 16.589 (5) Å
c = 11.762 (4) Å
β = 111.53 (3)°
V = 1343.3 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 K
0.20 × 0.10 × 0.10 mm

Data collection

Bruker Smart APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.979, T_{max} = 0.989
6722 measured reflections
2358 independent reflections
1239 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.152
S = 0.96
2358 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H5···O4^{i}	0.84	1.82	2.649 (3)	171
O1—H4···N1^{ii}	0.84	1.76	2.576 (4)	164

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5265).

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Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
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supporting information

Acta Cryst. (2012). E**68**, o3068 [doi:10.1107/S1600536812041025]

A monoclinic polymorph of 5-[(1*H*-benzimidazol-1-yl)methyl]benzene-1,3-dicarboxylic acid

Hai-Wei Kuai

S1. Comment

5-((1*H*-benzo[*d*]imidazol-1-yl)methyl)isophthalic acid (H_2L), is usually regarded as an excellent candidate for use as a building block in molecular self-assembly engineerings due to its variable conformations and coordination modes. During an attempt to assemble a coordination polymer, we accidentally obtained some single crystals of the title compound, $C_{16}H_{12}N_2O_4$, as a result of the hydrothermal reaction of 5-((1*H*-benzo[*d*]imidazol-1-yl)methyl)isophthalic acid with manganese chloride tetrahydrate at 453 K in the presence of KOH as alkaline reagent for the deprotonation. A triclinic polymorph of this structure has been reported previously (Cheng, 2011) from a very similar hydrothermal reaction involving manganese bromide. The bond distances and angles in that molecule are reasonably similar to those reported here. As shown in Fig. 1, the asymmetric unit consists of only one H_2L molecule. Interestingly, though crystallizing from alkaline solution, the H_2L retains the intact carboxylic acid groups in the crystal structure. The flexible benzimidazolyl arm is apt to rotate axially. As a result, the benzimidazolyl ring and central benzene rings are inclined at a dihedral angle of 68.17 °.

In the crystal structure O3–H5..O4 hydrogen bonds, Table 1, link adjacent molecules into inversion dimers. O1—H4···N1 contacts connect these dimers into zig-zag chains in the 010 plane, Fig. 2.

S2. Experimental

A reaction mixture comprising manganese chloride tetrahydrate (23.3 mg, 0.1 mmol), 5-((1*H*-benzo[*d*]imidazol-1-yl)methyl)isophthalic acid (29.6 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) in 10 ml H_2O was sealed in a 16 ml Teflon-lined stainless steel container and heated to 453 K for 3 days. After cooling to the room temperature, colorless block like crystals of the title compound were obtained.

S3. Refinement

Hydrogen atoms of the OH groups were found in difference Fourier maps and their coordinates were allowed to ride on those of the O atoms with $U_{iso}(H) = 1.2U_{eq}(O)$. Other hydrogen atoms were included in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

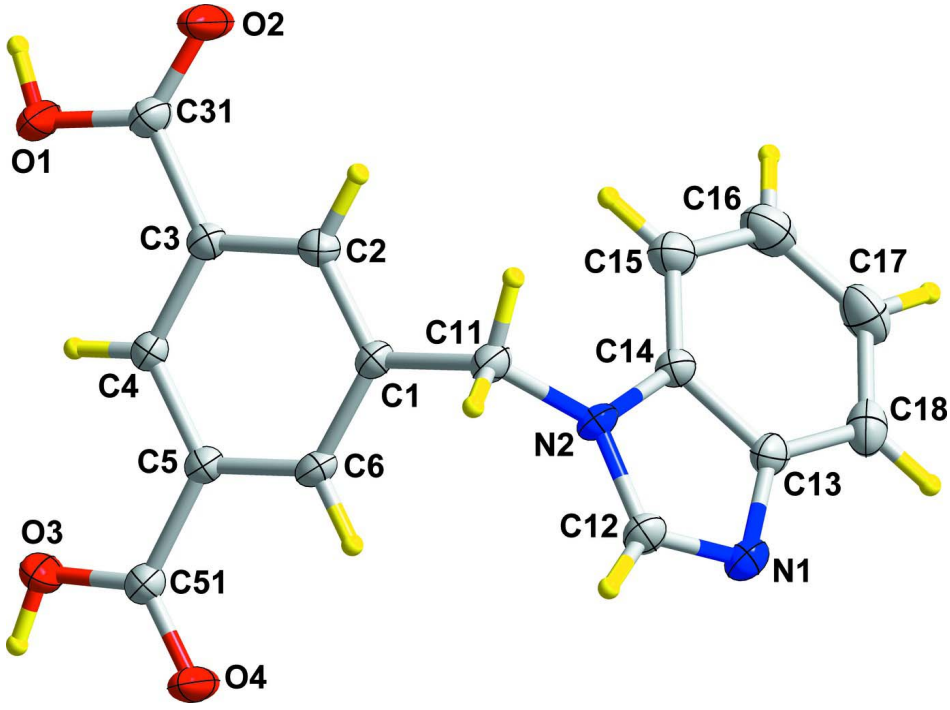

Figure 1

The crystal structure of the title compound showing 30% probability displacement ellipsoids.

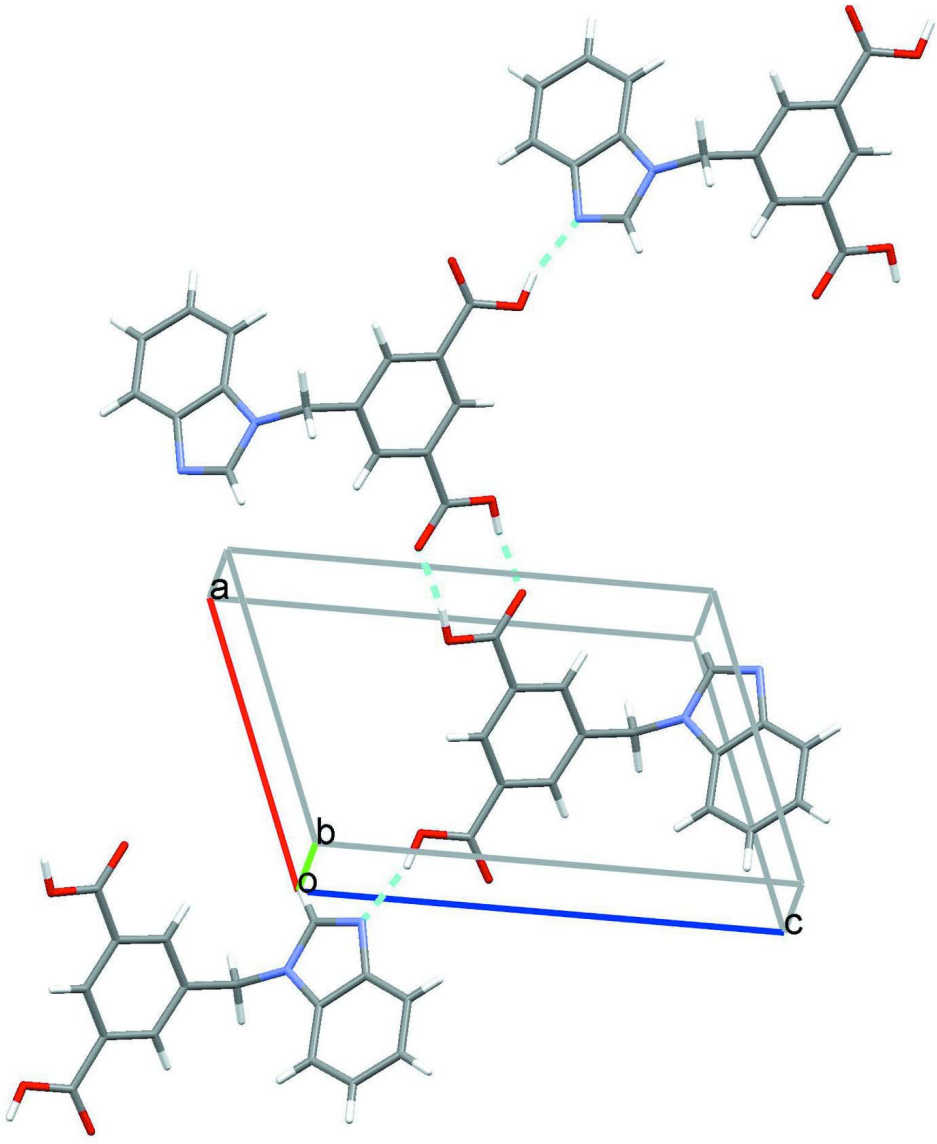

Figure 2

Crystal packing of the title compound.

5-[(1*H*-benzimidazol-1-yl)methyl]benzene-1,3-dicarboxylic acid

Crystal data

$C_{16}H_{12}N_2O_4$
$M_r = 296.28$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.401$ (5) Å
$b = 16.589$ (5) Å
$c = 11.762$ (4) Å
$\beta = 111.53$ (3)°
$V = 1343.3$ (11) Å^3
$Z = 4$
$F(000) = 616$
$D_x = 1.465$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 479 reflections
$\theta = 2.2$–18.5°
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Block, colorless
0.20 × 0.10 × 0.10 mm

Data collection

Bruker Smart APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.979, T_{max} = 0.989
6722 measured reflections
2358 independent reflections
1239 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 25.0°, θ_{min} = 2.2°
$h = -8 \rightarrow 6$
$k = -19 \rightarrow 19$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.152
S = 0.96
2358 reflections
200 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
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0052 (15)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.4929 (4)	0.81173 (19)	0.6457 (3)	0.0337 (8)
C2	0.3157 (4)	0.81097 (19)	0.5499 (3)	0.0359 (8)
H1	0.2128	0.7828	0.5586	0.043*
C3	0.2869 (4)	0.85118 (19)	0.4407 (3)	0.0334 (8)
C4	0.4398 (4)	0.89389 (18)	0.4285 (3)	0.0322 (8)
H2	0.4224	0.9211	0.3561	0.039*
C5	0.6190 (4)	0.89614 (19)	0.5242 (3)	0.0335 (8)
C6	0.6444 (4)	0.85508 (19)	0.6319 (3)	0.0369 (8)
H3	0.7645	0.8566	0.6957	0.044*
C11	0.5228 (4)	0.7621 (2)	0.7587 (2)	0.0393 (9)
H7	0.4032	0.7336	0.7480	0.047*
H6	0.6222	0.7220	0.7666	0.047*
C12	0.7566 (4)	0.8106 (2)	0.9604 (3)	0.0419 (9)
H8	0.8643	0.7849	0.9542	0.050*
C13	0.5734 (5)	0.87902 (19)	1.0306 (3)	0.0391 (9)

C14	0.4574 (4)	0.85280 (19)	0.9137 (3)	0.0359 (8)
C15	0.2615 (5)	0.8708 (2)	0.8615 (3)	0.0526 (10)
H9	0.1855	0.8535	0.7833	0.063*
C16	0.1854 (6)	0.9155 (2)	0.9315 (4)	0.0641 (11)
H10	0.0545	0.9293	0.8993	0.077*
C17	0.2977 (6)	0.9410 (2)	1.0494 (4)	0.0616 (11)
H11	0.2394	0.9698	1.0945	0.074*
C18	0.4931 (5)	0.9243 (2)	1.1002 (3)	0.0529 (10)
H12	0.5688	0.9424	1.1780	0.063*
C31	0.0929 (5)	0.8454 (2)	0.3395 (3)	0.0421 (9)
C51	0.7854 (5)	0.9411 (2)	0.5135 (3)	0.0393 (8)
N1	0.7629 (4)	0.85258 (17)	1.0568 (2)	0.0451 (8)
N2	0.5798 (3)	0.80875 (16)	0.8720 (2)	0.0363 (7)
O1	0.0865 (3)	0.87513 (17)	0.23681 (19)	0.0661 (8)
H4	−0.0285	0.8693	0.1880	0.079*
O2	−0.0442 (3)	0.81489 (18)	0.3545 (2)	0.0756 (9)
O3	0.7501 (3)	0.97884 (14)	0.41101 (19)	0.0493 (7)
H5	0.8528	1.0018	0.4151	0.059*
O4	0.9450 (3)	0.94199 (15)	0.5985 (2)	0.0584 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0290 (18)	0.043 (2)	0.0258 (17)	−0.0006 (16)	0.0059 (15)	0.0014 (15)
C2	0.0313 (18)	0.041 (2)	0.0351 (18)	−0.0055 (15)	0.0113 (15)	−0.0018 (16)
C3	0.0288 (18)	0.040 (2)	0.0296 (17)	0.0005 (15)	0.0088 (14)	0.0001 (16)
C4	0.0318 (18)	0.037 (2)	0.0259 (16)	−0.0018 (15)	0.0086 (15)	−0.0012 (15)
C5	0.0295 (18)	0.040 (2)	0.0282 (17)	−0.0039 (15)	0.0077 (15)	−0.0017 (15)
C6	0.0283 (19)	0.047 (2)	0.0283 (17)	−0.0037 (16)	0.0022 (15)	−0.0040 (16)
C11	0.0355 (19)	0.046 (2)	0.0304 (17)	−0.0040 (16)	0.0052 (15)	0.0010 (17)
C12	0.033 (2)	0.054 (2)	0.0341 (19)	0.0039 (17)	0.0064 (16)	0.0062 (18)
C13	0.037 (2)	0.047 (2)	0.0307 (18)	−0.0021 (17)	0.0093 (16)	0.0076 (17)
C14	0.0298 (19)	0.044 (2)	0.0327 (18)	−0.0008 (16)	0.0096 (15)	0.0020 (16)
C15	0.040 (2)	0.067 (3)	0.049 (2)	−0.0017 (19)	0.0143 (19)	0.007 (2)
C16	0.048 (2)	0.076 (3)	0.074 (3)	0.008 (2)	0.029 (2)	0.012 (2)
C17	0.063 (3)	0.065 (3)	0.071 (3)	0.014 (2)	0.042 (2)	0.008 (2)
C18	0.070 (3)	0.054 (3)	0.039 (2)	−0.003 (2)	0.026 (2)	−0.0002 (18)
C31	0.033 (2)	0.052 (2)	0.034 (2)	−0.0013 (17)	0.0048 (17)	0.0042 (18)
C51	0.035 (2)	0.050 (2)	0.0307 (18)	−0.0049 (17)	0.0092 (17)	−0.0014 (17)
N1	0.0376 (17)	0.059 (2)	0.0304 (15)	0.0002 (14)	0.0031 (13)	0.0004 (15)
N2	0.0275 (15)	0.0483 (18)	0.0257 (14)	−0.0005 (13)	0.0011 (12)	0.0013 (13)
O1	0.0401 (15)	0.115 (2)	0.0312 (13)	−0.0222 (14)	−0.0014 (12)	0.0127 (15)
O2	0.0357 (15)	0.123 (3)	0.0534 (16)	−0.0303 (15)	−0.0005 (13)	0.0262 (16)
O3	0.0402 (14)	0.0641 (17)	0.0421 (14)	−0.0163 (12)	0.0134 (11)	0.0060 (13)
O4	0.0310 (14)	0.088 (2)	0.0449 (14)	−0.0173 (13)	0.0008 (12)	0.0130 (14)

Geometric parameters (Å, º)

C1—C2	1.380 (4)	C13—N1	1.392 (4)
C1—C6	1.390 (4)	C13—C18	1.394 (4)
C1—C11	1.510 (4)	C13—C14	1.397 (4)
C2—C3	1.393 (4)	C14—C15	1.384 (4)
C2—H1	0.9300	C14—N2	1.386 (4)
C3—C4	1.386 (4)	C15—C16	1.374 (5)
C3—C31	1.494 (4)	C15—H9	0.9300
C4—C5	1.390 (4)	C16—C17	1.395 (5)
C4—H2	0.9300	C16—H10	0.9300
C5—C6	1.389 (4)	C17—C18	1.375 (5)
C5—C51	1.484 (4)	C17—H11	0.9300
C6—H3	0.9300	C18—H12	0.9300
C11—N2	1.463 (4)	C31—O2	1.203 (4)
C11—H7	0.9700	C31—O1	1.289 (4)
C11—H6	0.9700	C51—O4	1.236 (3)
C12—N1	1.317 (4)	C51—O3	1.297 (3)
C12—N2	1.340 (4)	O1—H4	0.8397
C12—H8	0.9300	O3—H5	0.8356
C2—C1—C6	118.4 (3)	C18—C13—C14	120.4 (3)
C2—C1—C11	120.1 (3)	C15—C14—N2	132.1 (3)
C6—C1—C11	121.4 (3)	C15—C14—C13	122.3 (3)
C1—C2—C3	121.7 (3)	N2—C14—C13	105.5 (3)
C1—C2—H1	119.1	C16—C15—C14	116.3 (3)
C3—C2—H1	119.1	C16—C15—H9	121.8
C4—C3—C2	119.1 (3)	C14—C15—H9	121.8
C4—C3—C31	122.2 (3)	C15—C16—C17	122.3 (4)
C2—C3—C31	118.8 (3)	C15—C16—H10	118.9
C3—C4—C5	120.2 (3)	C17—C16—H10	118.9
C3—C4—H2	119.9	C18—C17—C16	121.2 (4)
C5—C4—H2	119.9	C18—C17—H11	119.4
C6—C5—C4	119.6 (3)	C16—C17—H11	119.4
C6—C5—C51	119.1 (3)	C17—C18—C13	117.4 (3)
C4—C5—C51	121.3 (3)	C17—C18—H12	121.3
C5—C6—C1	121.0 (3)	C13—C18—H12	121.3
C5—C6—H3	119.5	O2—C31—O1	123.7 (3)
C1—C6—H3	119.5	O2—C31—C3	121.7 (3)
N2—C11—C1	114.4 (3)	O1—C31—C3	114.6 (3)
N2—C11—H7	108.7	O4—C51—O3	123.6 (3)
C1—C11—H7	108.7	O4—C51—C5	120.9 (3)
N2—C11—H6	108.7	O3—C51—C5	115.6 (3)
C1—C11—H6	108.7	C12—N1—C13	105.2 (3)
H7—C11—H6	107.6	C12—N2—C14	107.0 (3)
N1—C12—N2	113.4 (3)	C12—N2—C11	126.3 (3)
N1—C12—H8	123.3	C14—N2—C11	126.4 (3)
N2—C12—H8	123.3	C31—O1—H4	106.1

N1—C13—C18	130.7 (3)	C51—O3—H5	107.3
N1—C13—C14	109.0 (3)		
C6—C1—C2—C3	1.0 (5)	C16—C17—C18—C13	−1.7 (5)
C11—C1—C2—C3	−175.2 (3)	N1—C13—C18—C17	−179.7 (3)
C1—C2—C3—C4	−0.8 (5)	C14—C13—C18—C17	0.4 (5)
C1—C2—C3—C31	178.0 (3)	C4—C3—C31—O2	−172.8 (3)
C2—C3—C4—C5	0.1 (5)	C2—C3—C31—O2	8.5 (5)
C31—C3—C4—C5	−178.6 (3)	C4—C3—C31—O1	7.6 (5)
C3—C4—C5—C6	0.3 (4)	C2—C3—C31—O1	−171.1 (3)
C3—C4—C5—C51	179.7 (3)	C6—C5—C51—O4	0.3 (5)
C4—C5—C6—C1	−0.1 (5)	C4—C5—C51—O4	−179.2 (3)
C51—C5—C6—C1	−179.6 (3)	C6—C5—C51—O3	−179.1 (3)
C2—C1—C6—C5	−0.5 (5)	C4—C5—C51—O3	1.5 (4)
C11—C1—C6—C5	175.6 (3)	N2—C12—N1—C13	1.3 (4)
C2—C1—C11—N2	−121.4 (3)	C18—C13—N1—C12	178.4 (3)
C6—C1—C11—N2	62.6 (4)	C14—C13—N1—C12	−1.7 (4)
N1—C13—C14—C15	−179.2 (3)	N1—C12—N2—C14	−0.5 (4)
C18—C13—C14—C15	0.7 (5)	N1—C12—N2—C11	−174.7 (3)
N1—C13—C14—N2	1.4 (3)	C15—C14—N2—C12	−179.9 (3)
C18—C13—C14—N2	−178.7 (3)	C13—C14—N2—C12	−0.6 (3)
N2—C14—C15—C16	178.6 (3)	C15—C14—N2—C11	−5.7 (5)
C13—C14—C15—C16	−0.6 (5)	C13—C14—N2—C11	173.6 (3)
C14—C15—C16—C17	−0.7 (5)	C1—C11—N2—C12	−106.8 (3)
C15—C16—C17—C18	1.9 (6)	C1—C11—N2—C14	80.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H5···O4^{i}	0.84	1.82	2.649 (3)	171
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Symmetry codes: (i) −*x*+2, −*y*+2, −*z*+1; (ii) *x*−1, *y*, *z*−1.