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2-Methylpyridinium 2-carboxybenzoate–benzene-1,2-dicarboxylic acid (2/1)

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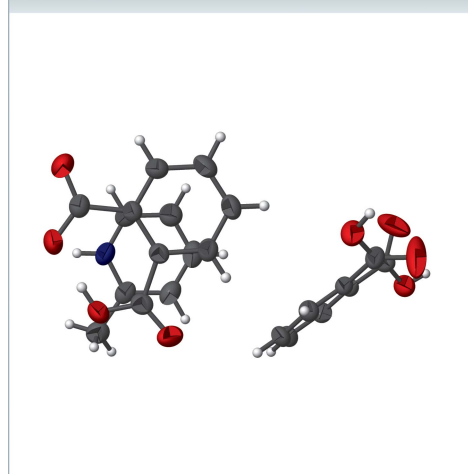
Keywords: crystal structure; molecular salt; hydrogen bonding.

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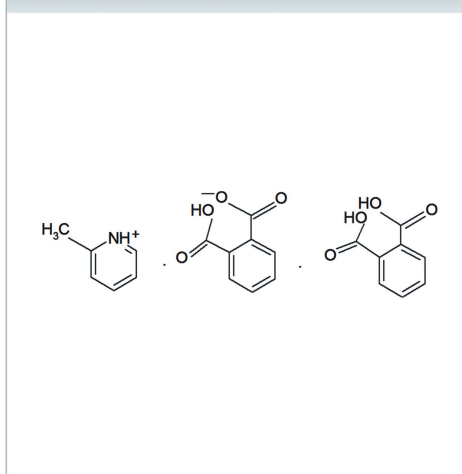
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $C_6H_8N^+ \cdot C_8H_5O_4^- \cdot 0.5C_8H_6O_4$, contains a 2-methylpyridinium cation, a 2-carboxybenzoate monoanion and half of the co-crystallized benzene-1,2-dicarboxylic acid molecule, which lies on a mirror plane. The N atom of the pyridine ring is protonated, while the anion of this salt is generated by deprotonation of the OH group of one of the carboxylic acid substituents of the benzene-1,2-dicarboxylic acid molecule. The pyridine ring of the cation is inclined to the benzene ring of the anion at an angle of $2.27(11)^\circ$. The benzene ring of the anion makes dihedral angles of $2.8(2)$ and $6.0(2)^\circ$ with the carboxylate and carboxyl substituents, respectively. An intramolecular O–H...O hydrogen bond in the anion closes an $S(7)$ ring. In the crystal, weak N–H...O, O–H...O and C–H...O hydrogen bonds lead to the formation of a three-dimensional network. Weak offset π – π contacts [centroid-to-centroid distance = $3.852(1) \text{ \AA}$] are also observed.

3D view



Chemical scheme



Structure description

Pyridine derivatives exhibit anti-inflammatory (Abdel-Alim *et al.*, 2005) and anticancer (Girgis *et al.* 2006) activities. We report herein the synthesis and the crystal structure of a co-crystal of the 2-methylpyridinium 2-carboxybenzoate salt and a benzene-1,2-dicarboxylic acid molecule (Fig. 1). The asymmetric unit contains a 2-methylpyridinium cation, a 2-carboxybenzoate anion and half of a benzene-1,2-dicarboxylic acid molecule, which lies on a mirror plane. The N atom of the pyridine ring is protonated while the OH group of one of the carboxylic acid substituents of a benzene-1,2-dicarboxylic acid molecule is deprotonated to form the monoanion.

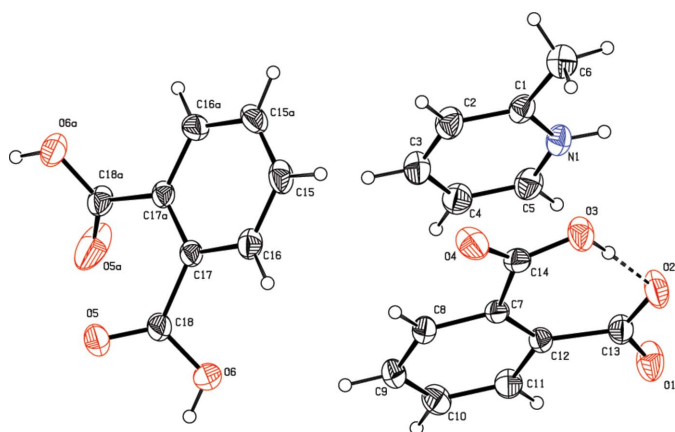


Figure 1
The structure of the title co-crystal, showing the atom labelling and 30% probability displacement ellipsoids. Atoms labelled with the suffix 'a' are generated by the symmetry operation $(-x + 1, y, -z + \frac{1}{2})$.

The N1/C1–C5 pyridinium ring and the C7–C12 benzene ring of the 2-carboxybenzoate monoanion are inclined at an angle of $2.27(11)^\circ$ to one another. The co-crystallized benzene-1,2-dicarboxylic acid molecule lies on a mirror plane. The C7–C12 benzene ring of the anion makes dihedral angles of $2.8(2)$ and $6.0(2)^\circ$ with the attached carboxylate (C13/O1/O2) and carboxyl (C14/O3/O4) groups, respectively.

An intramolecular O3–H2A···O2 hydrogen bond in the anion (Fig. 1) forms an $S(7)$ graph-set motif. The crystal structure features N–H···O, O–H···O and C–H···O hydrogen bonds (Fig. 2, Table 1), which generate a three-dimensional network. Weak offset π – π contacts are also observed in the crystal structure [$Cg2 \cdots Cg3^{iv} = 3.852(1)$, $Cg3 \cdots Cg2^v = 3.852(1)$ Å; symmetry codes: (iv) $\frac{1}{2} + x, -\frac{1}{2} + y, z$; (v) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; Cg2 and Cg3 are the centroids of the C7–C12 and N1/C1–C5, rings respectively].

Synthesis and crystallization

2-Picoline (0.93 g) and phthalic acid (1.66 g) dissolved in 20 ml of methanol were magnetically stirred for 3 hr in a round-bottomed flask. The solvent was allowed to evaporate slowly

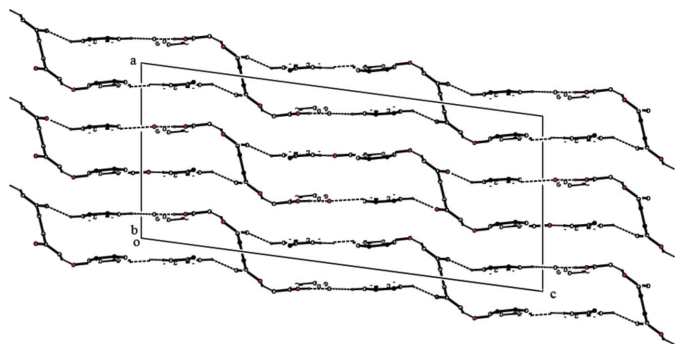


Figure 2
Crystal packing of the title compound viewed along the b axis. Hydrogen bonds are shown as dashed lines (see Table 1). C-bound H atoms have been omitted for clarity.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3–H2A···O2	0.84 (1)	1.52 (1)	2.365 (2)	178 (4)
N1–H1···O1 ⁱ	0.86	1.84	2.697 (2)	176
N1–H1···O2 ⁱ	0.86	2.59	3.194 (2)	128
O6–H6···O4 ⁱⁱ	0.83 (1)	1.84 (1)	2.640 (2)	162 (3)
C2–H2···O5 ⁱⁱⁱ	0.93	2.44	3.244 (3)	144
C5–H5···O2 ⁱ	0.93	2.60	3.207 (3)	124

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x, y - 1, z$; (iii) $-x + 1, y + 1, -z + \frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_8N^+ \cdot C_8H_5O_4^- \cdot 0.5C_8H_6O_4$
M_r	342.32
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	295
a, b, c (Å)	13.0967 (8), 8.1049 (4), 30.3013 (18)
β (°)	97.543 (3)
V (Å ³)	3188.6 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.24 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2004)
T_{min}, T_{max}	0.975, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25680, 3706, 1961
R_{int}	0.059
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.654
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.139, 1.00
No. of reflections	3706
No. of parameters	243
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.29, -0.25

Computer programs: APEX2 and SAINT (Bruker, 2004), SHELXS97 and SHELXL97 (Sheldrick, 2008) and PLATON (Spek, 2009).

at room temperature. Over 15 days, crystals suitable for X-ray diffraction were obtained.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160817 [doi:10.1107/S2414314616008178]

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P. Sivakumar, S. Sudhahar, B. Gunasekaran, S. Israel and G. Chakkaravarthi

2-Methylpyridinium 2-carboxybenzoate–benzene-1,2-dicarboxylic acid (2/1)

Crystal data

$C_6H_8N^+ \cdot C_8H_5O_4^- \cdot 0.5C_8H_6O_4$

$M_r = 342.32$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 13.0967$ (8) Å

$b = 8.1049$ (4) Å

$c = 30.3013$ (18) Å

$\beta = 97.543$ (3)°

$V = 3188.6$ (3) Å³

$Z = 8$

$F(000) = 1432$

$D_x = 1.426$ Mg m⁻³

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

Cell parameters from 2963 reflections

$\theta = 2.7$ – 22.6 °

$\mu = 0.11$ mm⁻¹

$T = 295$ K

Block, colourless

$0.24 \times 0.20 \times 0.18$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scan

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

$T_{\min} = 0.975$, $T_{\max} = 0.981$

25680 measured reflections

3706 independent reflections

1961 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\max} = 27.7$ °, $\theta_{\min} = 2.7$ °

$h = -17 \rightarrow 17$

$k = -10 \rightarrow 10$

$l = -39 \rightarrow 39$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.139$

$S = 1.00$

3706 reflections

243 parameters

6 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.7843P]$

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

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

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ 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. 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.41428 (15)	0.4797 (3)	0.11616 (7)	0.0442 (5)
C2	0.41880 (18)	0.3486 (3)	0.14524 (8)	0.0548 (6)
H2	0.4318	0.3671	0.1757	0.066*
C3	0.40426 (19)	0.1908 (3)	0.12937 (8)	0.0602 (7)
H3	0.4078	0.1025	0.1491	0.072*
C4	0.38447 (18)	0.1628 (3)	0.08442 (8)	0.0553 (6)
H4	0.3740	0.0563	0.0733	0.066*
C5	0.38050 (18)	0.2941 (3)	0.05662 (8)	0.0538 (6)
H5	0.3675	0.2778	0.0260	0.065*
C6	0.42957 (18)	0.6547 (3)	0.12976 (8)	0.0565 (6)
H6A	0.5018	0.6761	0.1375	0.085*
H6B	0.3943	0.6762	0.1550	0.085*
H6C	0.4025	0.7251	0.1055	0.085*
C7	0.66307 (14)	0.2220 (2)	0.10324 (6)	0.0354 (5)
C8	0.66764 (16)	0.0815 (2)	0.12987 (7)	0.0432 (5)
H8	0.6837	0.0933	0.1605	0.052*
C9	0.64932 (17)	-0.0741 (2)	0.11253 (8)	0.0489 (6)
H9	0.6533	-0.1657	0.1312	0.059*
C10	0.62521 (18)	-0.0921 (3)	0.06759 (8)	0.0533 (6)
H10	0.6108	-0.1961	0.0554	0.064*
C11	0.62217 (17)	0.0433 (2)	0.04044 (7)	0.0474 (5)
H11	0.6071	0.0285	0.0098	0.057*
C12	0.64073 (15)	0.2021 (2)	0.05690 (6)	0.0364 (5)
C13	0.63393 (17)	0.3339 (3)	0.02139 (7)	0.0465 (5)
C14	0.68093 (16)	0.3795 (2)	0.12974 (7)	0.0423 (5)
C15	0.54949 (19)	0.1071 (2)	0.24500 (8)	0.0543 (6)
C16	0.59899 (19)	-0.0401 (2)	0.23966 (7)	0.0471 (6)
C17	0.54999 (15)	-0.1893 (2)	0.24464 (6)	0.0394 (5)
C18	0.60728 (19)	-0.3451 (3)	0.23892 (7)	0.0500 (6)
N1	0.39510 (13)	0.4462 (2)	0.07275 (6)	0.0476 (5)
H1	0.3920	0.5270	0.0542	0.057*
O1	0.61695 (14)	0.29077 (18)	-0.01781 (5)	0.0679 (5)
O2	0.64605 (15)	0.48431 (18)	0.03183 (5)	0.0704 (5)
O3	0.67044 (15)	0.51902 (18)	0.11001 (6)	0.0637 (5)
O4	0.70341 (14)	0.37269 (17)	0.17001 (5)	0.0642 (5)
O5	0.6114 (2)	-0.4596 (2)	0.26340 (7)	0.1240 (10)
O6	0.65490 (14)	-0.34266 (19)	0.20419 (5)	0.0592 (5)
H6	0.679 (2)	-0.434 (2)	0.1988 (10)	0.099 (11)*
H15	0.5865 (15)	0.2030 (17)	0.2412 (7)	0.064 (7)*
H16	0.6671 (7)	-0.040 (2)	0.2337 (7)	0.044 (6)*

H2A 0.661 (3) 0.509 (4) 0.0821 (4) 0.109 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0380 (12)	0.0578 (13)	0.0367 (12)	-0.0011 (10)	0.0047 (9)	0.0053 (10)
C2	0.0593 (15)	0.0656 (16)	0.0387 (13)	0.0028 (12)	0.0031 (11)	0.0082 (11)
C3	0.0664 (16)	0.0583 (15)	0.0568 (16)	0.0037 (12)	0.0115 (13)	0.0155 (12)
C4	0.0596 (15)	0.0534 (14)	0.0535 (15)	-0.0029 (11)	0.0100 (12)	-0.0006 (11)
C5	0.0611 (15)	0.0591 (15)	0.0414 (13)	-0.0041 (12)	0.0072 (11)	-0.0009 (11)
C6	0.0592 (15)	0.0588 (14)	0.0498 (14)	-0.0067 (12)	0.0005 (12)	-0.0012 (11)
C7	0.0365 (11)	0.0327 (10)	0.0381 (11)	0.0001 (8)	0.0096 (9)	-0.0014 (8)
C8	0.0501 (13)	0.0413 (12)	0.0392 (12)	0.0003 (10)	0.0098 (10)	0.0050 (9)
C9	0.0600 (15)	0.0349 (11)	0.0531 (14)	-0.0008 (10)	0.0129 (12)	0.0069 (10)
C10	0.0663 (16)	0.0331 (11)	0.0609 (16)	-0.0060 (10)	0.0103 (12)	-0.0055 (10)
C11	0.0603 (15)	0.0417 (12)	0.0402 (12)	-0.0039 (10)	0.0066 (11)	-0.0054 (9)
C12	0.0397 (11)	0.0330 (10)	0.0370 (11)	-0.0007 (8)	0.0060 (9)	0.0015 (8)
C13	0.0544 (14)	0.0439 (13)	0.0414 (13)	-0.0008 (10)	0.0068 (10)	0.0053 (10)
C14	0.0454 (13)	0.0390 (12)	0.0442 (13)	0.0021 (9)	0.0128 (10)	-0.0036 (10)
C15	0.0856 (18)	0.0320 (11)	0.0456 (13)	-0.0115 (11)	0.0102 (13)	0.0003 (10)
C16	0.0615 (16)	0.0401 (12)	0.0409 (13)	-0.0085 (11)	0.0106 (11)	0.0011 (9)
C17	0.0573 (13)	0.0323 (10)	0.0292 (10)	0.0017 (9)	0.0085 (10)	0.0004 (8)
C18	0.0746 (16)	0.0412 (12)	0.0366 (12)	0.0079 (11)	0.0159 (11)	0.0045 (10)
N1	0.0504 (11)	0.0546 (12)	0.0373 (10)	-0.0022 (9)	0.0039 (8)	0.0084 (8)
O1	0.1035 (14)	0.0600 (10)	0.0367 (9)	-0.0097 (9)	-0.0034 (9)	0.0063 (8)
O2	0.1260 (16)	0.0365 (9)	0.0489 (10)	-0.0010 (9)	0.0125 (10)	0.0090 (7)
O3	0.1106 (15)	0.0334 (9)	0.0496 (11)	-0.0058 (8)	0.0203 (10)	-0.0023 (8)
O4	0.0962 (13)	0.0516 (9)	0.0418 (10)	0.0133 (9)	-0.0025 (9)	-0.0093 (7)
O5	0.230 (3)	0.0662 (12)	0.0978 (16)	0.0684 (15)	0.1034 (18)	0.0428 (11)
O6	0.0841 (12)	0.0502 (10)	0.0482 (10)	0.0138 (9)	0.0267 (9)	0.0016 (8)

Geometric parameters (Å, °)

C1—N1	1.334 (3)	C10—C11	1.369 (3)
C1—C2	1.377 (3)	C10—H10	0.9300
C1—C6	1.483 (3)	C11—C12	1.390 (3)
C2—C3	1.371 (3)	C11—H11	0.9300
C2—H2	0.9300	C12—C13	1.511 (3)
C3—C4	1.371 (3)	C13—O1	1.230 (2)
C3—H3	0.9300	C13—O2	1.264 (2)
C4—C5	1.354 (3)	C14—O4	1.218 (2)
C4—H4	0.9300	C14—O3	1.278 (2)
C5—N1	1.330 (3)	C15—C15 ⁱ	1.370 (5)
C5—H5	0.9300	C15—C16	1.378 (3)
C6—H6A	0.9600	C15—H15	0.931 (7)
C6—H6B	0.9600	C16—C17	1.387 (3)
C6—H6C	0.9600	C16—H16	0.933 (7)
C7—C8	1.392 (3)	C17—C17 ⁱ	1.390 (4)

C7—C12	1.406 (3)	C17—C18	1.490 (3)
C7—C14	1.510 (3)	C18—O5	1.185 (3)
C8—C9	1.375 (3)	C18—O6	1.292 (3)
C8—H8	0.9300	N1—H1	0.8600
C9—C10	1.365 (3)	O3—H2A	0.842 (10)
C9—H9	0.9300	O6—H6	0.830 (10)
N1—C1—C2	117.4 (2)	C9—C10—H10	120.0
N1—C1—C6	118.05 (19)	C11—C10—H10	120.0
C2—C1—C6	124.6 (2)	C10—C11—C12	122.4 (2)
C3—C2—C1	120.2 (2)	C10—C11—H11	118.8
C3—C2—H2	119.9	C12—C11—H11	118.8
C1—C2—H2	119.9	C11—C12—C7	117.93 (17)
C2—C3—C4	120.1 (2)	C11—C12—C13	114.09 (18)
C2—C3—H3	119.9	C7—C12—C13	127.98 (17)
C4—C3—H3	119.9	O1—C13—O2	121.09 (19)
C5—C4—C3	118.4 (2)	O1—C13—C12	118.23 (19)
C5—C4—H4	120.8	O2—C13—C12	120.68 (19)
C3—C4—H4	120.8	O4—C14—O3	120.38 (19)
N1—C5—C4	120.5 (2)	O4—C14—C7	119.62 (18)
N1—C5—H5	119.8	O3—C14—C7	119.98 (19)
C4—C5—H5	119.8	C15 ⁱ —C15—C16	119.98 (14)
C1—C6—H6A	109.5	C15 ⁱ —C15—H15	123.4 (14)
C1—C6—H6B	109.5	C16—C15—H15	116.6 (14)
H6A—C6—H6B	109.5	C15—C16—C17	120.7 (2)
C1—C6—H6C	109.5	C15—C16—H16	119.9 (12)
H6A—C6—H6C	109.5	C17—C16—H16	119.3 (12)
H6B—C6—H6C	109.5	C16—C17—C17 ⁱ	119.28 (13)
C8—C7—C12	118.19 (17)	C16—C17—C18	118.61 (19)
C8—C7—C14	113.06 (17)	C17 ⁱ —C17—C18	122.10 (12)
C12—C7—C14	128.73 (17)	O5—C18—O6	122.3 (2)
C9—C8—C7	122.46 (19)	O5—C18—C17	124.9 (2)
C9—C8—H8	118.8	O6—C18—C17	112.71 (17)
C7—C8—H8	118.8	C5—N1—C1	123.41 (19)
C10—C9—C8	119.0 (2)	C5—N1—H1	118.3
C10—C9—H9	120.5	C1—N1—H1	118.3
C8—C9—H9	120.5	C14—O3—H2A	112 (2)
C9—C10—C11	119.9 (2)	C18—O6—H6	112 (2)
N1—C1—C2—C3	0.2 (3)	C7—C12—C13—O1	177.4 (2)
C6—C1—C2—C3	-179.5 (2)	C11—C12—C13—O2	177.9 (2)
C1—C2—C3—C4	-0.4 (4)	C7—C12—C13—O2	-2.2 (3)
C2—C3—C4—C5	0.4 (4)	C8—C7—C14—O4	4.5 (3)
C3—C4—C5—N1	-0.3 (4)	C12—C7—C14—O4	-177.2 (2)
C12—C7—C8—C9	-1.2 (3)	C8—C7—C14—O3	-174.1 (2)
C14—C7—C8—C9	177.23 (19)	C12—C7—C14—O3	4.1 (3)
C7—C8—C9—C10	-0.3 (3)	C15 ⁱ —C15—C16—C17	-0.5 (4)
C8—C9—C10—C11	1.7 (3)	C15—C16—C17—C17 ⁱ	-0.3 (4)

C9—C10—C11—C12	-1.4 (3)	C15—C16—C17—C18	-179.4 (2)
C10—C11—C12—C7	-0.2 (3)	C16—C17—C18—O5	133.3 (3)
C10—C11—C12—C13	179.8 (2)	C17 ⁱ —C17—C18—O5	-45.8 (4)
C8—C7—C12—C11	1.4 (3)	C16—C17—C18—O6	-45.6 (3)
C14—C7—C12—C11	-176.75 (19)	C17 ⁱ —C17—C18—O6	135.3 (3)
C8—C7—C12—C13	-178.55 (19)	C4—C5—N1—C1	0.1 (3)
C14—C7—C12—C13	3.3 (3)	C2—C1—N1—C5	-0.1 (3)
C11—C12—C13—O1	-2.6 (3)	C6—C1—N1—C5	179.7 (2)

Symmetry code: (i) $-x+1, y, -z+1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H2A ⁱⁱⁱ —O2	0.84 (1)	1.52 (1)	2.365 (2)	178 (4)
N1—H1 ⁱⁱ —O1 ⁱⁱ	0.86	1.84	2.697 (2)	176
N1—H1 ⁱⁱ —O2 ⁱⁱ	0.86	2.59	3.194 (2)	128
O6—H6 ⁱⁱⁱ —O4 ⁱⁱⁱ	0.83 (1)	1.84 (1)	2.640 (2)	162 (3)
C2—H2 ^{iv} —O5 ^{iv}	0.93	2.44	3.244 (3)	144
C5—H5 ⁱⁱ —O2 ⁱⁱ	0.93	2.60	3.207 (3)	124

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