# organic compounds

# (±)-3-Carboxy-2-(imidazol-3-ium-1-yl)-propanoate

**Sarah A. Reeb, Marlesa C. Shields and Kraig A. Wheeler\***

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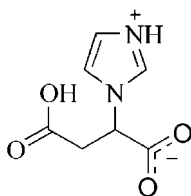
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The title compound, $C_7H_8N_2O_4$, crystallizes as a zwitterion, with molecules organized into molecular sheets *via* carboxyl–carboxylate and $N^+$—H···carboxylate contacts. These sheets are constructed from translationally related molecules that further link to neighboring motifs *via* $\pi$-stacking [centroid–centroid distance 3.504 (3) Å] and weak C—H···O contacts.

## Related literature

For related compounds, see: Centnerzwer (1899); Pasteur (1853); Wheeler *et al.* (2008). For a description of the Cambridge Structural Database, see: Allen (2002).

## Experimental

### Crystal data

| | |
|---|---|
| $C_7H_8N_2O_4$ | $V = 779.21$ (12) Å$^3$ |
| $M_r = 184.15$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 7.6328$ (7) Å | $\mu = 0.13$ mm$^{-1}$ |
| $b = 7.4701$ (7) Å | $T = 296$ K |
| $c = 13.7616$ (12) Å | $0.38 \times 0.28 \times 0.18$ mm |
| $\beta = 96.752$ (1)° | |

### Data collection

| | |
|---|---|
| Bruker *P4* CCD diffractometer | 4668 measured reflections |
| Absorption correction: multi-scan | 1540 independent reflections |
| (*SADABS*; Bruker, 2008) | 1254 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.952$, $T_{max} = 0.977$ | $R_{int} = 0.021$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of |
| $wR(F^2) = 0.115$ | independent and constrained |
| $S = 1.06$ | refinement |
| 1540 reflections | $\Delta\rho_{max} = 0.24$ e Å$^{-3}$ |
| 126 parameters | $\Delta\rho_{min} = -0.26$ e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H1···O2$^i$ | 0.95 (3) | 1.62 (3) | 2.5440 (18) | 163 (3) |
| N2—H3···O1$^{ii}$ | 0.89 (3) | 1.85 (3) | 2.732 (2) | 170 (2) |
| C7—H7···O1$^{iii}$ | 0.93 | 2.42 | 3.333 (2) | 168 |
| C5—H5···O4$^{iv}$ | 0.93 | 2.57 | 3.260 (3) | 131 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2685).

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2, SADABS, SAINT* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Centnerzwer, M. Z. (1899). *Z. Phys. Chem.* **29**, 715–725.
Pasteur, L. (1853). *Ann. Chim. Phys.* **38**, 437–483.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wheeler, K. A., Grove, R. C., Davis, R. E. & Kassel, W. S. (2008). *Angew. Chem. Int. Ed.* **47**, 78–81.

# supporting information

## (±)-3-Carboxy-2-(imidazol-3-ium-1-yl)propanoate

**Sarah A. Reeb, Marlesa C. Shields and Kraig A. Wheeler**

### S1. Comment

Our recent reinvestigation of Pasteur's 1853 quasiracemates (Pasteur, 1853; Wheeler *et al.*, 2008) has motivated us to explore other examples of these unusual materials of historical and supramolecular importance. In 1899, Centnerzwer reported that mixtures of (+)-chlorosuccinic acid and (-)-bromosuccinic acid formed a binary compound that also exhibited quasiracemic behavior (Centnerzwer, 1899). Our initial attempts to grow crystals of this quasiracemic phase were unsuccessful. This result was somewhat anticipated given that Centnerzwer's melting point phase diagrams showed the crystal stabilities of the homochiral phases more stable than the quasiracemate. We then turned our attention to investigating the effects of co-crystalline additives to crystal growth of this quasiracemate and the corresponding racemic and homochiral compounds. During the course of these co-crystal screening investigations, we observed the formation of crystals of the title compound from slow evaporation of a methanol:$CH_2Cl_2$ (1:1) solution of (±)-2-chlorosuccinic acid and imidazole.

The title compound, (I), formed from the substitution reaction of imidazole and 2-chlorosuccinic acid, crystallizes in space group $P2_1/c$ as the imidazolium carboxylate zwitterion (Fig. 1). Inspection of the molecular structure reveals a resonance stabilized imidazolium ring with (N1—C7) - (N2—C7) = +0.038 Å. A search of the Cambridge Structural Database (CSD, Version 5.30 with August 2008 and February 2009 updates; Allen, 2002) for other *N*-alkylimidazolium fragments uncovered 44 organic structures. This collection shows similar bonding patterns to (I) with a concentration of Δ(N—C) values near 0.00, +0.01, and +0.03 Å.

The crystal structure of (I) is organized by a complex blend of strong and weak intermolecular contacts (Table 1). Neighboring molecules are linked by carboxyl···carboxylate interactions to give a catemeric motif that propagates along the a-axis (Fig. 2). This motif is extended by N2$^+$—*H*···carboxylate contacts to produce a molecular sheet in the *ab* plane. The participation of the imidazolium N$^+$—H group in hydrogen bonding is also a common feature in the 44 structures retrieved from the CSD. Each of these structures show N$^+$—H···A contacts with a diverse set of acceptors [A = oxygen(52), nitrogen(3), halogen(15), or $\pi$(2); 72 contacts]. Interestingly, each molecular sheet in (I) consists of translationally related molecules with imidazolium groups exposed on one side of the motif and carboxyl O4 atoms on the other side. The crystal structure of (I) is characterized by the stacking of these molecular sheets with adjacent motifs related by inversion symmetry and linked by either interdigitated imadazolium···imidazolium stacks [3.504 (3) Å] or weak C5—H5···O4 interactions (Fig. 3).

### S2. Experimental

Single crystals of the title compound were prepared by slow evaporation at room temperature of a methanol:$CH_2Cl_2$ (1:1) solution of (±)-2-chlorosuccinic acid and imidazole (1:1).

## S3. Refinement

H atoms (for OH and NH) were located in difference Fourier synthesis and refined isotropically. The remaining H atoms were positioned geometrically with C—H = 0.93, 0.98 and 0.97 Å, for aromatic, methine and metnylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.
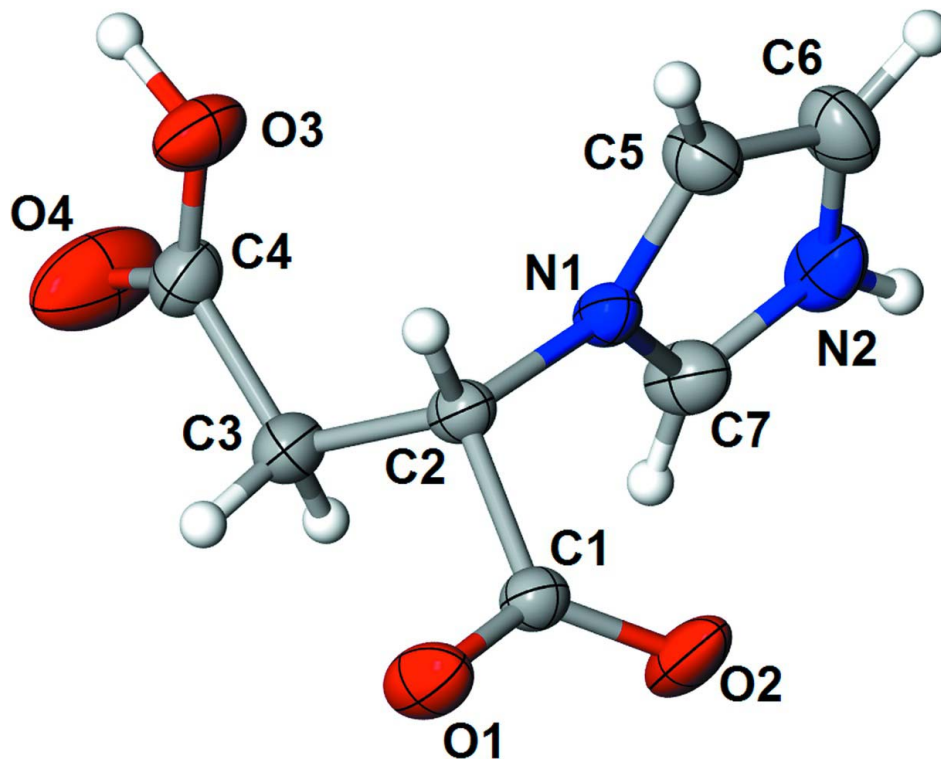


**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
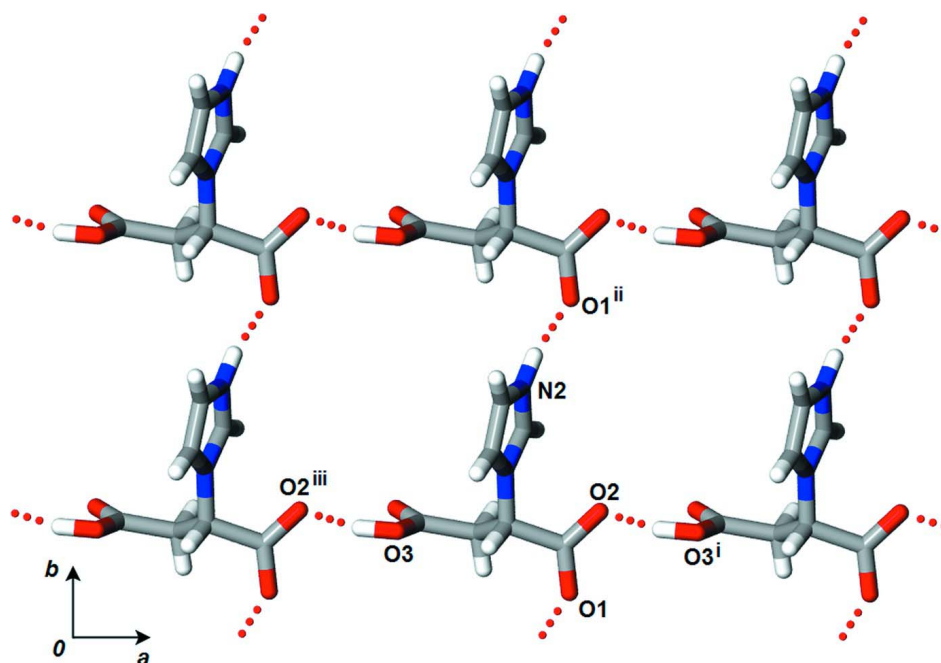
**Figure 2**

A partial packing diagram of the title compound, showing molecular sheets constructed from carboxyl···carboxylate and N—H···O contacts [symmetry codes: (i) $1 + x, y, z$, (ii) $x, 1 + y, z$; (iii) $x - 1, y, z$].
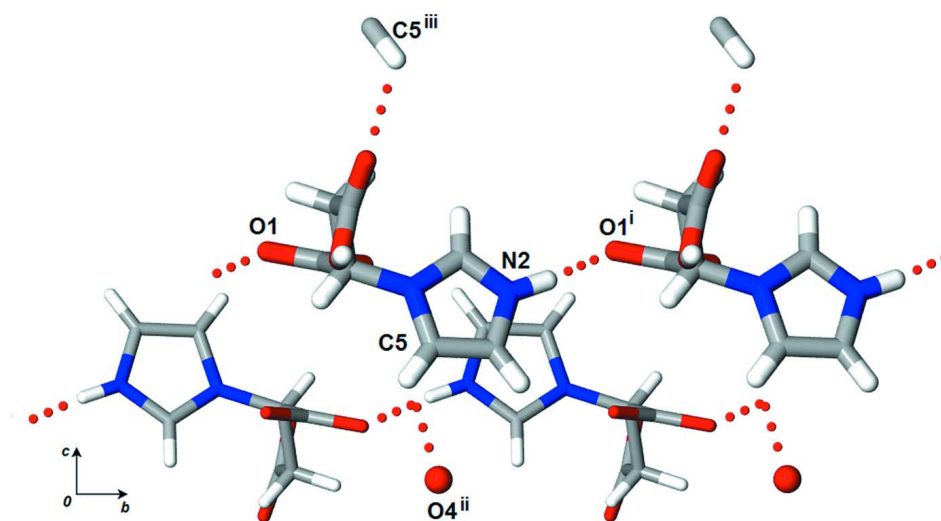


**Figure 3**

Projection showing alignment of molecular sheets with imidazolium $\pi$ stacking and C—H···O interactions [symmetry codes: i) $x, y - 1, z$, (ii) $x, 3/2 - y, 1/2 + z$; (iii) $x - 3, 3/2 - y, z - 1/2$].

**Figure 4**

The tautomeric forms of the title compound.

## (±)-3-Carboxy-2-(imidazol-3-ium-1-yl)propanoate

*Crystal data*

$C_7H_8N_2O_4$
$M_r = 184.15$
Monoclinic, $P2_1/c$
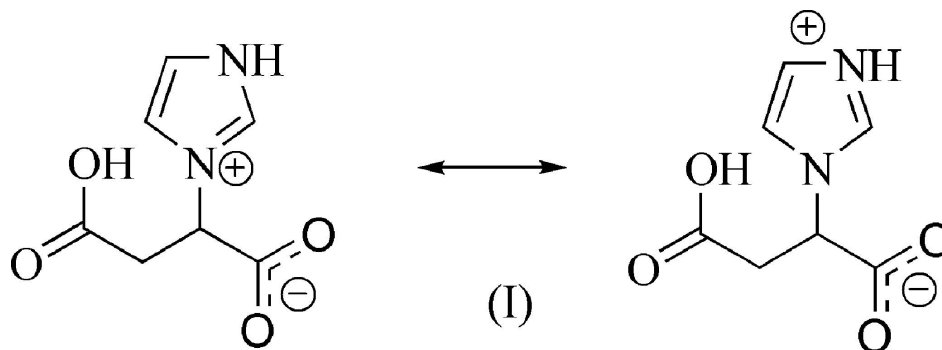Hall symbol: -P 2ybc
$a = 7.6328\ (7)$ Å
$b = 7.4701\ (7)$ Å
$c = 13.7616\ (12)$ Å
$\beta = 96.752\ (1)°$
$V = 779.21\ (12)$ Å$^3$
$Z = 4$

$F(000) = 384$
$D_x = 1.570$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1902 reflections
$\theta = 6.0–54.6°$
$\mu = 0.13$ mm$^{-1}$
$T = 296$ K
Transparent prism, colourless
$0.38 \times 0.28 \times 0.18$ mm

*Data collection*

Bruker P4 CCD
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
  (*SADABS*; Bruker, 2008)
$T_{min} = 0.952$, $T_{max} = 0.977$

4668 measured reflections
1540 independent reflections
1254 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.7°$
$h = -9\rightarrow9$
$k = -9\rightarrow8$
$l = -16\rightarrow16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.06$
1540 reflections
126 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 atoms treated by a mixture of independent
  and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.3288P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.26$ e Å$^{-3}$

*Special details*

**Experimental**. The instrument used for data collection was a Bruker P4 with a APEXII CCD detector upgrade.

**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$^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1 | 1.00100 (17) | 1.13604 (17) | 0.63749 (11) | 0.0446 (4) |
| O2 | 1.09600 (17) | 0.86066 (19) | 0.61600 (13) | 0.0558 (5) |
| O3 | 0.42339 (18) | 0.9309 (2) | 0.62306 (10) | 0.0475 (4) |
| O4 | 0.4539 (2) | 0.8529 (3) | 0.77836 (13) | 0.0813 (7) |
| N1 | 0.77182 (17) | 0.72061 (19) | 0.57875 (10) | 0.0293 (3) |
| N2 | 0.8241 (2) | 0.4386 (2) | 0.57164 (14) | 0.0448 (4) |
| C1 | 0.9788 (2) | 0.9740 (2) | 0.62128 (12) | 0.0296 (4) |
| C2 | 0.7853 (2) | 0.9081 (2) | 0.61136 (12) | 0.0290 (4) |
| H2 | 0.7163 | 0.9819 | 0.5619 | 0.035* |
| C3 | 0.7111 (2) | 0.9343 (3) | 0.70828 (13) | 0.0367 (4) |
| H3A | 0.7738 | 0.8551 | 0.7563 | 0.044* |
| H3B | 0.7355 | 1.0561 | 0.7301 | 0.044* |
| C4 | 0.5163 (2) | 0.9005 (3) | 0.70683 (14) | 0.0378 (4) |
| C5 | 0.7043 (2) | 0.6631 (3) | 0.48706 (14) | 0.0391 (5) |
| H5 | 0.6466 | 0.7330 | 0.4373 | 0.047* |
| C6 | 0.7375 (3) | 0.4871 (3) | 0.48305 (16) | 0.0474 (5) |
| H6 | 0.7071 | 0.4121 | 0.4298 | 0.057* |
| C7 | 0.8438 (2) | 0.5806 (2) | 0.62777 (15) | 0.0400 (5) |
| H7 | 0.8993 | 0.5830 | 0.6917 | 0.048* |
| H1 | 0.301 (5) | 0.920 (4) | 0.630 (2) | 0.098 (10)* |
| H3 | 0.870 (3) | 0.333 (4) | 0.5910 (17) | 0.061 (7)* |

*Atomic displacement parameters (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0352 (7) | 0.0277 (7) | 0.0694 (10) | −0.0049 (5) | −0.0004 (6) | −0.0018 (6) |
| O2 | 0.0231 (7) | 0.0362 (8) | 0.1069 (13) | 0.0015 (6) | 0.0032 (7) | −0.0128 (8) |
| O3 | 0.0277 (7) | 0.0630 (10) | 0.0517 (9) | −0.0032 (6) | 0.0042 (6) | 0.0051 (7) |
| O4 | 0.0476 (10) | 0.1370 (19) | 0.0607 (11) | −0.0101 (11) | 0.0125 (8) | 0.0310 (11) |
| N1 | 0.0244 (7) | 0.0263 (8) | 0.0370 (8) | −0.0015 (5) | 0.0021 (6) | −0.0016 (6) |
| N2 | 0.0378 (9) | 0.0255 (9) | 0.0715 (12) | 0.0012 (7) | 0.0078 (8) | 0.0026 (8) |
| C1 | 0.0255 (8) | 0.0299 (9) | 0.0330 (9) | −0.0015 (7) | 0.0021 (6) | −0.0006 (7) |
| C2 | 0.0249 (8) | 0.0259 (9) | 0.0356 (9) | 0.0001 (6) | 0.0006 (6) | −0.0008 (7) |
| C3 | 0.0290 (9) | 0.0422 (11) | 0.0387 (10) | 0.0019 (8) | 0.0028 (7) | −0.0039 (8) |
| C4 | 0.0308 (9) | 0.0384 (10) | 0.0449 (11) | 0.0021 (7) | 0.0078 (8) | 0.0001 (8) |

| C5 | 0.0409 (10) | 0.0372 (11) | 0.0383 (10) | −0.0025 (8) | 0.0007 (8) | −0.0041 (8) |
| C6 | 0.0541 (13) | 0.0360 (11) | 0.0527 (13) | −0.0051 (9) | 0.0079 (10) | −0.0120 (9) |
| C7 | 0.0374 (10) | 0.0317 (10) | 0.0492 (11) | −0.0007 (8) | −0.0023 (8) | 0.0039 (8) |

*Geometric parameters (Å, º)*

| O1—C1 | 1.239 (2) | C1—C2 | 1.548 (2) |
|---|---|---|---|
| O2—C1 | 1.240 (2) | C2—C3 | 1.522 (2) |
| O3—C4 | 1.300 (2) | C2—H2 | 0.9800 |
| O3—H1 | 0.95 (3) | C3—C4 | 1.506 (3) |
| O4—C4 | 1.197 (2) | C3—H3A | 0.9700 |
| N1—C7 | 1.328 (2) | C3—H3B | 0.9700 |
| N1—C5 | 1.374 (2) | C5—C6 | 1.341 (3) |
| N1—C2 | 1.471 (2) | C5—H5 | 0.9300 |
| N2—C7 | 1.310 (3) | C6—H6 | 0.9300 |
| N2—C6 | 1.366 (3) | C7—H7 | 0.9300 |
| N2—H3 | 0.89 (3) | | |
| | | | |
| C4—O3—H1 | 110 (2) | C4—C3—H3A | 108.3 |
| C7—N1—C5 | 107.96 (15) | C2—C3—H3A | 108.3 |
| C7—N1—C2 | 125.82 (15) | C4—C3—H3B | 108.3 |
| C5—N1—C2 | 125.65 (15) | C2—C3—H3B | 108.3 |
| C7—N2—C6 | 108.73 (17) | H3A—C3—H3B | 107.4 |
| C7—N2—H3 | 121.9 (16) | O4—C4—O3 | 123.55 (18) |
| C6—N2—H3 | 129.2 (16) | O4—C4—C3 | 121.78 (18) |
| O1—C1—O2 | 126.38 (16) | O3—C4—C3 | 114.66 (16) |
| O1—C1—C2 | 115.82 (15) | C6—C5—N1 | 106.96 (18) |
| O2—C1—C2 | 117.74 (15) | C6—C5—H5 | 126.5 |
| N1—C2—C3 | 111.71 (14) | N1—C5—H5 | 126.5 |
| N1—C2—C1 | 111.19 (13) | C5—C6—N2 | 107.30 (18) |
| C3—C2—C1 | 109.36 (13) | C5—C6—H6 | 126.3 |
| N1—C2—H2 | 108.2 | N2—C6—H6 | 126.3 |
| C3—C2—H2 | 108.2 | N2—C7—N1 | 109.04 (17) |
| C1—C2—H2 | 108.2 | N2—C7—H7 | 125.5 |
| C4—C3—C2 | 115.82 (15) | N1—C7—H7 | 125.5 |
| | | | |
| C7—N1—C2—C3 | −59.2 (2) | C2—C3—C4—O4 | 152.5 (2) |
| C5—N1—C2—C3 | 130.59 (17) | C2—C3—C4—O3 | −28.9 (2) |
| C7—N1—C2—C1 | 63.3 (2) | C7—N1—C5—C6 | 0.1 (2) |
| C5—N1—C2—C1 | −106.93 (18) | C2—N1—C5—C6 | 171.80 (16) |
| O1—C1—C2—N1 | 172.03 (15) | N1—C5—C6—N2 | 0.1 (2) |
| O2—C1—C2—N1 | −10.5 (2) | C7—N2—C6—C5 | −0.3 (2) |
| O1—C1—C2—C3 | −64.1 (2) | C6—N2—C7—N1 | 0.3 (2) |
| O2—C1—C2—C3 | 113.28 (18) | C5—N1—C7—N2 | −0.3 (2) |
| N1—C2—C3—C4 | −64.66 (19) | C2—N1—C7—N2 | −171.95 (16) |
| C1—C2—C3—C4 | 171.82 (15) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H1···O2[i] | 0.95 (3) | 1.62 (3) | 2.5440 (18) | 163 (3) |
| N2—H3···O1[ii] | 0.89 (3) | 1.85 (3) | 2.732 (2) | 170 (2) |
| C7—H7···O1[iii] | 0.93 | 2.42 | 3.333 (2) | 168 |
| C5—H5···O4[iv] | 0.93 | 2.57 | 3.260 (3) | 131 |

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