# Revision of the crystal structure of 'bis(glycine) squaric acid'[1]

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The crystal structure of 'bis(glycine) squaric acid' [Tyagi et al. (2016). RSC Adv. **6**, 24565–24576], is revised. Re-refinement of the structure against the original X-ray intensity data after correct placement of the donor H atoms proves that the compound is in fact the previously reported diglycinium squarate [systematic name: bis(carboxymethanaminium) 3,4-dioxocyclobut-1-ene-1,2-diolate; Anioła et al. (2014). New J. Chem. **38**, 3556–3568]. The findings are consistent with the $pK_a$ rule.

**3D view**
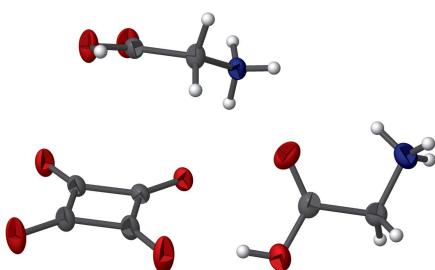


**Chemical scheme**
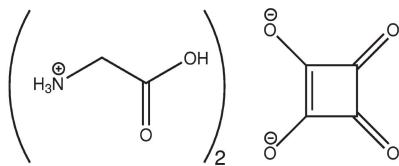


## Structure description

In a search of the Cambridge Structural Database (CSD Version 5.39 with February 2018 updates; Groom et al., 2016) for salts of squaric acid ($H_2C_4O_4$) and $\alpha$-amino acids, we stumbled upon CSD entries SIZKIX and SIZKIX01 (additional database identifier VABNUK). SIZKIX is diglycinium squarate, i.e. a 2:1 proton-transfer compound of glycine and squaric acid, and was reported by Anioła et al. (2014). SIZKIX01, however, is reportedly a 2:1 non-ionized acid–base complex of glycine and squaric acid (Tyagi et al., 2016). In the original publication (Tyagi et al., 2016), the compound was designated as ''bis glycine' squarate' whereas in the CSD, 'bis(glycine) squaric acid' was assigned as the common name. Since squaric acid is a remarkably strong diprotic acid (Gilli et al., 2001), the formation of a non-ionized acid–base complex rather than a salt with a glycinium cation would be very unusual. Considering that incorrect placement of H atoms is a common pitfall in crystal structure refinement (Spek, 2009; Bernal & Watkins, 2013; Schwalbe, 2018), this prompted us to scrutinize the structure and crystallographic data of SIZKIX01.

First of all, visual inspection of the original structural model for SIZKIX01 revealed that the hydrogen-bonding pattern is not sensible. Moreover, several checkCIF/ PLATON (Spek, 2009) alerts concerning a strange C—O—H geometry (level A alert),

# data reports

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1—H1A⋯O4 | 0.89 | 2.08 | 2.9148 (15) | 156 |
| N1—H1A⋯O11$^{i}$ | 0.89 | 2.57 | 3.0297 (16) | 113 |
| N1—H1B⋯O3$^{ii}$ | 0.89 | 2.11 | 2.8933 (15) | 146 |
| N1—H1C⋯O4$^{iii}$ | 0.89 | 1.98 | 2.7890 (15) | 151 |
| N2—H2A⋯O3$^{ii}$ | 0.89 | 2.33 | 3.1075 (19) | 146 |
| N2—H2A⋯O11$^{i}$ | 0.89 | 2.60 | 3.0591 (18) | 113 |
| N2—H2B⋯O3$^{i}$ | 0.89 | 1.93 | 2.8064 (17) | 167 |
| N2—H2C⋯O1$^{iv}$ | 0.89 | 2.48 | 3.1602 (18) | 134 |
| N2—H2C⋯O6$^{ii}$ | 0.89 | 2.13 | 2.8007 (16) | 132 |
| O6—H6⋯O2$^{v}$ | 0.82 | 1.64 | 2.4406 (16) | 167 |
| O9—H9⋯O1 | 0.82 | 1.75 | 2.5629 (15) | 169 |

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

short intra- and intermolecular $D-H\cdots H-D$ ($D$ = hydrogen-bond donor) contacts (level B alerts), positive and negative residual electron density at N and O atoms (level C alerts) and a C—O bond without an H atom attached longer than 1.3 Å, indicated incorrectly positioned hydrogen atoms.

It is instructive to inspect the $F_{obs}-F_{calc}$ difference electron-density map to identify incorrectly (and correctly) positioned H atoms. From Fig. 1 it is obvious that the positions of the N—H and O—H hydrogen atoms are incorrect, with the exception of that bonded to O6. After re-refinement of the crystal structure with correctly positioned donor H atoms against original diffraction data, $R1$ [$I > 2\sigma(I)$] dropped from 0.0589 to 0.0426. It should be noted that the $R$ factors reported in the article by Tyagi *et al.* (2016) do not agree with those in the corresponding deposited CIF (CCDC 1052856). The residual difference electron densities after re-refinement are 0.35 and $-0.28$ e Å$^{-3}$ (originally 0.63 and $-0.68$ e Å$^{-3}$). Fig. 2 depicts the revised and re-refined structural model for SIZKIX01. A detailed description of the crystal structure of diglycinium squarate can be found in the article by Anioła *et al.* (2014). It is worth noting that the carboxy group of one glycinium ion adopts a *syn* conformation, whereas the other exhibits an *anti*
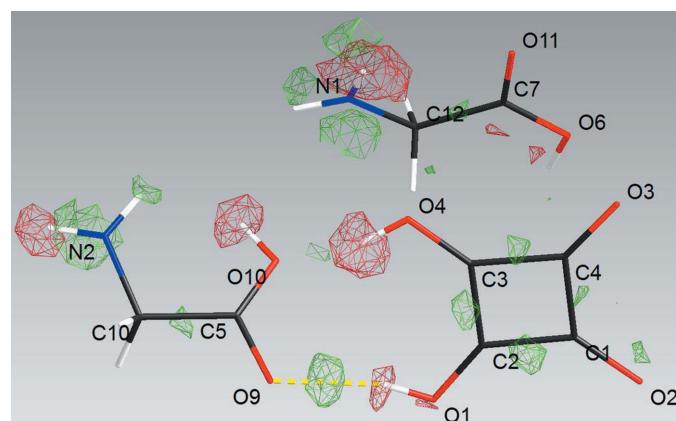
conformation. The crystal packing of diglycinium squarate is governed by H bonds of the N—H⋯O and O—H⋯O type (Table 1). For other squarate salts of $\alpha$-amino acids, see: Seidel & Zareva (2018), and references cited therein.

Considering that for $\Delta pK_a = pK_a[\text{protonated base}] - pK_a[\text{acid}] > 4$ ionized acid–base proton-transfer compounds were observed exclusively (Cruz-Cabeza, 2012), the formation of a non-ionized acid–base complex of glycine and squaric acid appears to be very unlikely. The $pK_a$ value of the amino group in glycine is 9.6 (Dawson *et al.*, 1986), and for squaric acid, $pK_{a1}$ values of $0.51\pm0.02$ and $0.55\pm0.15$ were obtained by conductometric determination (Gelb, 1971) and potentiometric titration (Schwartz & Howard, 1970), respectively, although based on earlier studies $pK_{a1}$ values in the range of 1.2–1.7 were reported (Gilli *et al.*, 2001).

In conclusion, the crystal structure of the compound previously described as 'bis(glycine) squaric acid' (CSD refcode: SIZKIX01) is revised. It has been demonstrated that the structure is in fact the known proton-transfer compound diglycinium squarate and, thus, identical with CSD entry SIZKIX. Consequently, the results of Hirshfeld surface analysis in the original report by Tyagi *et al.* (2016), using the incorrect structure model, must be questioned. It is to be hoped that this contribution helps to avoid such errors in crystal structure refinement in the future.

## Synthesis and crystallization

The crystallization of the compound was described by Tyagi *et al.* (2016).

## Refinement

The original data (CCDC 1052856) were retrieved in CIF format from the Cambridge Crystallographic Data Centre (CCDC) *via* http://www.ccdc.cam.ac.uk/structures. The reflection data (*HKL*) and the *SHELXL* instruction file (INS) were



**Figure 1**
$F_{obs}-F_{calc}$ difference electron density map 1.41 Å around visible atoms for SIZKIX01: 0.11 e$^{-}$ Å$^{-3}$ (green), $-0.11$ e$^{-}$ Å$^{-3}$ (red), $\sigma = 0.039$. Misplaced hydrogen atoms show up as negative density (red), and the correct positions appear as positive density (green).
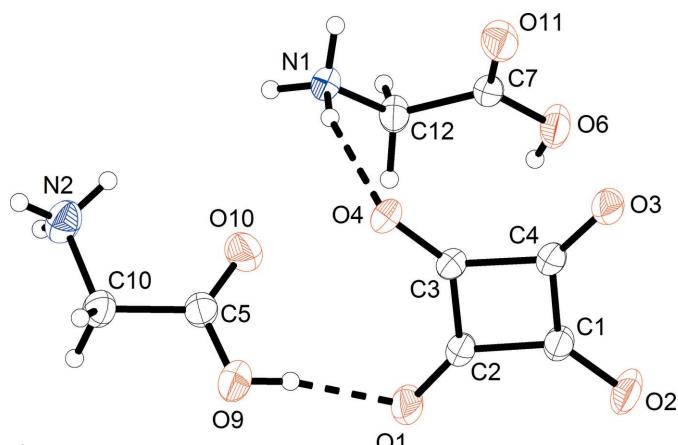


**Figure 2**
Revised and re-refined structural model for SIZKIX01, proving that the structure is indeed diglycinium squarate and thus identical with SIZKIX. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines.

**Table 2**
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_4O_4 \cdot 2C_2H_6NO_2$ |
| $M_r$ | 264.20 |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Temperature (K) | 293 |
| $a, b, c$ (Å) | 16.8050 (16), 8.3008 (8), 15.7976 (13) |
| $\beta$ (°) | 100.259 (9) |
| $V$ (Å$^3$) | 2168.5 (3) |
| $Z$ | 8 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.15 |
| Crystal size (mm) | $0.50 \times 0.50 \times 0.50$ |
| | |
| **Data collection** | |
| Diffractometer | Rigaku Oxford Diffraction Xcalibur, Sapphire3 |
| Absorption correction | Multi-scan (ABSPACK in *CrysAlis PRO*; Rigaku OD, 2014) |
| $T_{min}$, $T_{max}$ | 0.403, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 7067, 2570, 2277 |
| $R_{int}$ | 0.036 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.692 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.043, 0.113, 1.04 |
| No. of reflections | 2570 |
| No. of parameters | 168 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.35, −0.28 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2014), *SHELXT2018/3* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *shelXle* (Hübschle *et al.*, 2011), *DIAMOND* (Brandenburg, 2014), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

extracted from the CIF using the program *shredCIF*, which is distributed with *SHELXL* (Sheldrick, 2015b). A structure factor file (FCF) was generated with *SHELXL2018*/3 using the LIST 6 command, and the $F_{obs}- F_{calc}$ difference electron-density map was visualized as a three-dimensional mesh (Fig. 1), using *shelXle* (Hübschle *et al.*, 2011).

A re-refinement against the original intensity data was carried out with *SHELXL2018/3* (Sheldrick, 2015b). For the sake of consistency, the chosen asymmetric unit and atom labels, as shown in Fig. 1, were maintained. The positions of carbon-bound H atoms were calculated geometrically and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The C—H bond lengths were set at 0.97 Å. The initial torsion angles of the protonated amino groups and the carboxy O—H groups were determined *via* difference Fourier syntheses and subsequently refined while maintaining the tetrahedral angles, and with $U_{iso}(H) = 1.5 U_{eq}(N,O)$. The N—H bond lengths were set at 0.89 Å and the O—H bond lengths were set at 0.82 Å. Crystal data, data collection and structure refinement details are given in Table 2.

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# full crystallographic data

## Revision of the crystal structure of `bis(glycine) squaric acid′

**Rüdiger W. Seidel**

**Bis(carboxymethanaminium) 3,4-dioxocyclobut-1-ene-1,2-diolate**

*Crystal data*

| | |
|---|---|
| $C_4O_4 \cdot 2C_2H_6NO_2$ | $F(000) = 1104$ |
| $M_r = 264.20$ | $D_x = 1.619$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 16.8050\,(16)$ Å | Cell parameters from 2994 reflections |
| $b = 8.3008\,(8)$ Å | $\theta = 3.6–29.4°$ |
| $c = 15.7976\,(13)$ Å | $\mu = 0.15$ mm$^{-1}$ |
| $\beta = 100.259\,(9)°$ | $T = 293$ K |
| $V = 2168.5\,(3)$ Å$^3$ | Prism, colourless |
| $Z = 8$ | $0.50 \times 0.50 \times 0.50$ mm |

*Data collection*

| | |
|---|---|
| Rigaku Oxford Diffraction Xcalibur, Sapphire3 diffractometer | 7067 measured reflections |
| Radiation source: Enhance (Mo) X-ray Source | 2570 independent reflections |
| Detector resolution: 15.9853 pixels mm$^{-1}$ | 2277 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.036$ |
| Absorption correction: multi-scan (ABSPACK in CrysAlisPro; Rigaku OD, 2014) | $\theta_{max} = 29.5°$, $\theta_{min} = 3.6°$ |
| | $h = -21 \rightarrow 22$ |
| | $k = -10 \rightarrow 11$ |
| $T_{min} = 0.403$, $T_{max} = 1.000$ | $l = -21 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: mixed |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | $w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 1.323P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.113$ | |
| $S = 1.04$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 2570 reflections | $\Delta\rho_{max} = 0.35$ e Å$^{-3}$ |
| 168 parameters | $\Delta\rho_{min} = -0.28$ e Å$^{-3}$ |
| 0 restraints | Extinction correction: SHELXL-2018/3 (Sheldrick 2015b), |
| Primary atom site location: structure-invariant direct methods | Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.0281 (16) |

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

|      | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|------|-----|-----|-----|---------------------|
| C1   | 0.09201 (8)  | 0.84696 (17) | −0.03393 (8)  | 0.0264 (3) |
| C2   | 0.09470 (9)  | 0.75825 (17) | 0.04588 (8)   | 0.0277 (3) |
| C3   | 0.17481 (8)  | 0.82723 (16) | 0.07796 (8)   | 0.0232 (3) |
| C4   | 0.17066 (8)  | 0.91641 (17) | −0.00344 (8)  | 0.0245 (3) |
| C5   | 0.10057 (8)  | 0.62754 (18) | 0.28928 (9)   | 0.0274 (3) |
| C7   | 0.15012 (8)  | 1.19712 (16) | 0.15276 (8)   | 0.0244 (3) |
| C10  | 0.11860 (9)  | 0.53370 (17) | 0.37145 (8)   | 0.0295 (3) |
| H10A | 0.071281     | 0.472052     | 0.378862      | 0.035* |
| H10B | 0.162392     | 0.458753     | 0.368893      | 0.035* |
| C12  | 0.12634 (8)  | 1.10722 (18) | 0.22754 (8)   | 0.0269 (3) |
| H12A | 0.100022     | 1.180301     | 0.261757      | 0.032* |
| H12B | 0.088457     | 1.022138     | 0.206253      | 0.032* |
| N1   | 0.19877 (7)  | 1.03746 (14) | 0.28119 (7)   | 0.0270 (3) |
| H1A  | 0.218164     | 0.958976     | 0.252287      | 0.041* |
| H1B  | 0.185750     | 0.997609     | 0.329215      | 0.041* |
| H1C  | 0.236182     | 1.113628     | 0.294491      | 0.041* |
| N2   | 0.14146 (9)  | 0.64295 (17) | 0.44486 (8)   | 0.0361 (3) |
| H2A  | 0.154562     | 0.738718     | 0.426043      | 0.054* |
| H2B  | 0.183654     | 0.602342     | 0.480560      | 0.054* |
| H2C  | 0.100009     | 0.654023     | 0.472474      | 0.054* |
| O1   | 0.04871 (8)  | 0.66282 (16) | 0.07434 (7)   | 0.0471 (3) |
| O2   | 0.04301 (7)  | 0.85940 (16) | −0.10400 (6)  | 0.0408 (3) |
| O3   | 0.21416 (7)  | 1.01203 (14) | −0.03532 (6)  | 0.0353 (3) |
| O4   | 0.22470 (6)  | 0.81538 (12) | 0.14578 (6)   | 0.0297 (3) |
| O6   | 0.09122 (6)  | 1.24195 (15) | 0.09348 (6)   | 0.0366 (3) |
| H6   | 0.048364     | 1.209417     | 0.105110      | 0.055* |
| O9   | 0.09184 (8)  | 0.53179 (14) | 0.22230 (7)   | 0.0443 (3) |
| H9   | 0.080061     | 0.585235     | 0.178194      | 0.066* |
| O10  | 0.09541 (7)  | 0.77080 (13) | 0.28753 (7)   | 0.0392 (3) |
| O11  | 0.22034 (6)  | 1.22618 (15) | 0.15001 (7)   | 0.0370 (3) |

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

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| C1   | 0.0260 (6) | 0.0325 (7) | 0.0201 (6) | −0.0021 (6) | 0.0021 (5) | 0.0027 (5) |
| C2   | 0.0307 (7) | 0.0320 (7) | 0.0188 (6) | −0.0057 (6) | 0.0003 (5) | 0.0025 (5) |
| C3   | 0.0262 (6) | 0.0241 (6) | 0.0186 (6) | −0.0007 (5) | 0.0022 (5) | −0.0012 (4) |
| C4   | 0.0274 (6) | 0.0275 (7) | 0.0182 (6) | −0.0015 (5) | 0.0028 (5) | −0.0003 (5) |
| C5   | 0.0206 (6) | 0.0319 (7) | 0.0284 (6) | −0.0028 (6) | 0.0006 (5) | 0.0048 (5) |
| C7   | 0.0277 (6) | 0.0255 (6) | 0.0200 (6) | −0.0034 (5) | 0.0040 (5) | 0.0002 (5) |
| C10  | 0.0318 (7) | 0.0288 (7) | 0.0262 (7) | 0.0038 (6) | 0.0006 (5) | 0.0017 (5) |
| C12  | 0.0263 (6) | 0.0312 (7) | 0.0231 (6) | 0.0006 (6) | 0.0041 (5) | 0.0054 (5) |
| N1   | 0.0319 (6) | 0.0274 (6) | 0.0201 (5) | −0.0015 (5) | 0.0000 (4) | 0.0018 (4) |
| N2   | 0.0432 (7) | 0.0391 (7) | 0.0257 (6) | 0.0067 (6) | 0.0057 (5) | −0.0018 (5) |
| O1   | 0.0467 (7) | 0.0612 (8) | 0.0289 (6) | −0.0282 (6) | −0.0053 (5) | 0.0161 (5) |

| O2 | 0.0312 (5) | 0.0648 (8) | 0.0226 (5) | −0.0073 (5) | −0.0052 (4) | 0.0123 (5) |
| O3 | 0.0364 (6) | 0.0446 (6) | 0.0238 (5) | −0.0150 (5) | 0.0024 (4) | 0.0059 (4) |
| O4 | 0.0319 (5) | 0.0332 (5) | 0.0207 (4) | −0.0029 (4) | −0.0049 (4) | 0.0019 (4) |
| O6 | 0.0310 (5) | 0.0514 (7) | 0.0252 (5) | −0.0043 (5) | −0.0005 (4) | 0.0130 (4) |
| O9 | 0.0659 (8) | 0.0400 (6) | 0.0237 (5) | −0.0044 (6) | −0.0012 (5) | 0.0027 (4) |
| O10 | 0.0407 (6) | 0.0306 (6) | 0.0427 (6) | −0.0029 (5) | −0.0025 (5) | 0.0086 (5) |
| O11 | 0.0291 (5) | 0.0470 (7) | 0.0350 (6) | −0.0088 (5) | 0.0064 (4) | 0.0080 (5) |

*Geometric parameters (Å, °)*

| C1—O2 | 1.2608 (16) | C10—N2 | 1.4684 (18) |
| C1—C4 | 1.4437 (18) | C10—H10A | 0.9700 |
| C1—C2 | 1.4538 (18) | C10—H10B | 0.9700 |
| C2—O1 | 1.2453 (18) | C12—N1 | 1.4724 (16) |
| C2—C3 | 1.4676 (18) | C12—H12A | 0.9700 |
| C3—O4 | 1.2413 (15) | C12—H12B | 0.9700 |
| C3—C4 | 1.4746 (17) | N1—H1A | 0.8900 |
| C4—O3 | 1.2447 (17) | N1—H1B | 0.8900 |
| C5—O10 | 1.1923 (18) | N1—H1C | 0.8900 |
| C5—O9 | 1.3106 (18) | N2—H2A | 0.8900 |
| C5—C10 | 1.4979 (18) | N2—H2B | 0.8900 |
| C7—O11 | 1.2126 (17) | N2—H2C | 0.8900 |
| C7—O6 | 1.2904 (16) | O6—H6 | 0.8200 |
| C7—C12 | 1.5101 (18) | O9—H9 | 0.8200 |
| | | | |
| O2—C1—C4 | 132.55 (13) | C5—C10—H10B | 109.6 |
| O2—C1—C2 | 135.85 (13) | H10A—C10—H10B | 108.1 |
| C4—C1—C2 | 91.59 (10) | N1—C12—C7 | 109.74 (11) |
| O1—C2—C1 | 135.23 (13) | N1—C12—H12A | 109.7 |
| O1—C2—C3 | 135.53 (12) | C7—C12—H12A | 109.7 |
| C1—C2—C3 | 89.24 (11) | N1—C12—H12B | 109.7 |
| O4—C3—C2 | 134.77 (12) | C7—C12—H12B | 109.7 |
| O4—C3—C4 | 135.42 (13) | H12A—C12—H12B | 108.2 |
| C2—C3—C4 | 89.81 (10) | C12—N1—H1A | 109.5 |
| O3—C4—C1 | 133.50 (12) | C12—N1—H1B | 109.5 |
| O3—C4—C3 | 137.14 (12) | H1A—N1—H1B | 109.5 |
| C1—C4—C3 | 89.35 (10) | C12—N1—H1C | 109.5 |
| O10—C5—O9 | 126.08 (13) | H1A—N1—H1C | 109.5 |
| O10—C5—C10 | 122.79 (13) | H1B—N1—H1C | 109.5 |
| O9—C5—C10 | 111.13 (12) | C10—N2—H2A | 109.5 |
| O11—C7—O6 | 122.84 (12) | C10—N2—H2B | 109.5 |
| O11—C7—C12 | 121.40 (12) | H2A—N2—H2B | 109.5 |
| O6—C7—C12 | 115.75 (12) | C10—N2—H2C | 109.5 |
| N2—C10—C5 | 110.32 (12) | H2A—N2—H2C | 109.5 |
| N2—C10—H10A | 109.6 | H2B—N2—H2C | 109.5 |
| C5—C10—H10A | 109.6 | C7—O6—H6 | 109.5 |
| N2—C10—H10B | 109.6 | C5—O9—H9 | 109.5 |

| | | | |
|---|---|---|---|
| O2—C1—C2—O1 | −0.9 (3) | O2—C1—C4—C3 | −178.53 (17) |
| C4—C1—C2—O1 | −179.47 (19) | C2—C1—C4—C3 | 0.14 (11) |
| O2—C1—C2—C3 | 178.46 (18) | O4—C3—C4—O3 | 0.0 (3) |
| C4—C1—C2—C3 | −0.14 (11) | C2—C3—C4—O3 | 179.65 (18) |
| O1—C2—C3—O4 | −0.9 (3) | O4—C3—C4—C1 | −179.79 (16) |
| C1—C2—C3—O4 | 179.79 (16) | C2—C3—C4—C1 | −0.14 (11) |
| O1—C2—C3—C4 | 179.5 (2) | O10—C5—C10—N2 | −9.3 (2) |
| C1—C2—C3—C4 | 0.14 (11) | O9—C5—C10—N2 | 170.58 (12) |
| O2—C1—C4—O3 | 1.7 (3) | O11—C7—C12—N1 | −11.53 (19) |
| C2—C1—C4—O3 | −179.66 (17) | O6—C7—C12—N1 | 169.34 (12) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1*A*···O4 | 0.89 | 2.08 | 2.9148 (15) | 156 |
| N1—H1*A*···O11[i] | 0.89 | 2.57 | 3.0297 (16) | 113 |
| N1—H1*B*···O3[ii] | 0.89 | 2.11 | 2.8933 (15) | 146 |
| N1—H1*C*···O4[iii] | 0.89 | 1.98 | 2.7890 (15) | 151 |
| N2—H2*A*···O3[ii] | 0.89 | 2.33 | 3.1075 (19) | 146 |
| N2—H2*A*···O11[i] | 0.89 | 2.60 | 3.0591 (18) | 113 |
| N2—H2*B*···O3[i] | 0.89 | 1.93 | 2.8064 (17) | 167 |
| N2—H2*C*···O1[iv] | 0.89 | 2.48 | 3.1602 (18) | 134 |
| N2—H2*C*···O6[ii] | 0.89 | 2.13 | 2.8007 (16) | 132 |
| O6—H6···O2[v] | 0.82 | 1.64 | 2.4406 (16) | 167 |
| O9—H9···O1 | 0.82 | 1.75 | 2.5629 (15) | 169 |

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