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# Benzoic acid–3,4-bis[(pyridin-3-ylmethyl)amino]cyclobut-3-ene-1,2-dione (1/2)

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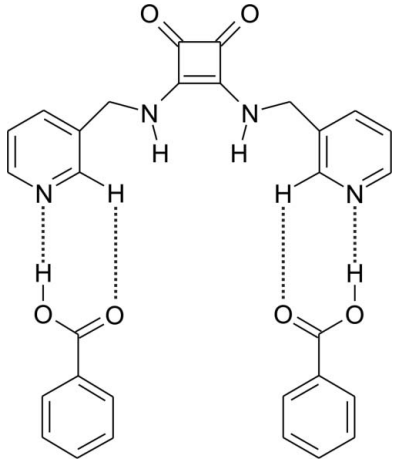
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.044; $wR$ factor = 0.116; data-to-parameter ratio = 16.7.

In the title co-crystal, $C_{16}H_{14}N_4O_2{\cdot}2C_7H_6O_2$, the 3,4-bis[(pyridin-3-ylmethyl)amino]cyclobut-3-ene-1,2-dione squaramide molecules assemble into chains along the $b$ axis *via* N—H···O hydrogen bonds. The benzoic acid molecules then hydrogen bond to the pyridine rings *via* O—H···N hydrogen bonds, supported by weaker C—H···O hydrogen bonds, forming extended ribbons. The asymmetric unit consists of a half squaramide molecule, sitting on a special position around a twofold axis, and one benzoic acid molecule on a general position.

## Related literature

For the synthesis of related squaramides and co-crystals, see: Liu *et al.* (2002).



## Experimental

### Crystal data

$C_{16}H_{14}N_4O_2{\cdot}2C_7H_6O_2$
$M_r$ = 538.55
Monoclinic, $C2/c$
$a$ = 24.617 (5) Å
$b$ = 6.0285 (12) Å
$c$ = 17.806 (4) Å
$\beta$ = 93.08 (3)°
$V$ = 2638.6 (9) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 173 K
0.49 × 0.16 × 0.14 mm

### Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 2004)
$T_{min}$ = 0.944, $T_{max}$ = 0.989
15016 measured reflections
3166 independent reflections
2110 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.076

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.116
$S$ = 0.99
3166 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{i}$ | 0.915 (16) | 1.889 (17) | 2.7697 (15) | 161.0 (13) |
| O2—H2···N2 | 1.07 (2) | 1.57 (2) | 2.6380 (15) | 178.0 (17) |
| C2—H2*A*···O3 | 0.95 | 2.68 | 3.3341 (18) | 127 |

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

This work was supported by the University of the Witwatersrand, which is thanked for providing the infrastructure required to do this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2039).

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# supporting information

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## Benzoic acid–3,4-bis[(pyridin-3-ylmethyl)amino]cyclobut-3-ene-1,2-dione (1/2)

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### S1. Comment

The title compound is a further example of co-crystals formed by squareamide molecules, in this case 3,4-bis[(pyridin-3-ylmethyl)amino]cyclobut-3-ene-1,2-dione, with carboxylic acid containing co-former molecules. Related co-crystals where the squaureamide molecule has the pyridine N atom in the 4 position are reported by Liu *et al.* (2002). The asymmetric unit consists of one half squareamide molecule, sitting around a twofold axis, and one complete benzoic acid molecule, on a general position (Fig. 1). The squareamide self-assembles into chains using the two N—H···O hydrogen bonds formed from the two amine N—-H groups to the diketones. The pyridine rings then act as hydrogen bond acceptors to the carboxylic acid functional group of the two benzoic acid molecules (Fig. 2).

### S2. Experimental

The title squareamide compound was synthesized according to literature procedures (Liu *et al.*, 2002) by double condensation of diethyl squarate with 1-(pyridin-3-yl)methanamine in ethanol by stirring for 12 h. The resulting solid was filtered and dried. The squareamide was then dissolved in a 1:2 stoichiometric ratio with benzoic acid in a 1/1 *v*/*v* mixture of methanol and water. Plate-like, colourless crystals were harvested after a few days by slow evaporation at ambient conditions.

### S3. Refinement

The C-bound H atoms were geometrically placed with C—H bond lengths of 0.95 Å (aromatic CH) and 0.99 Å (methylene $CH_2$) and were refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound and O-bound H atoms were located in the difference map and their coordinates and isotropic displacement parameters were refined freely.

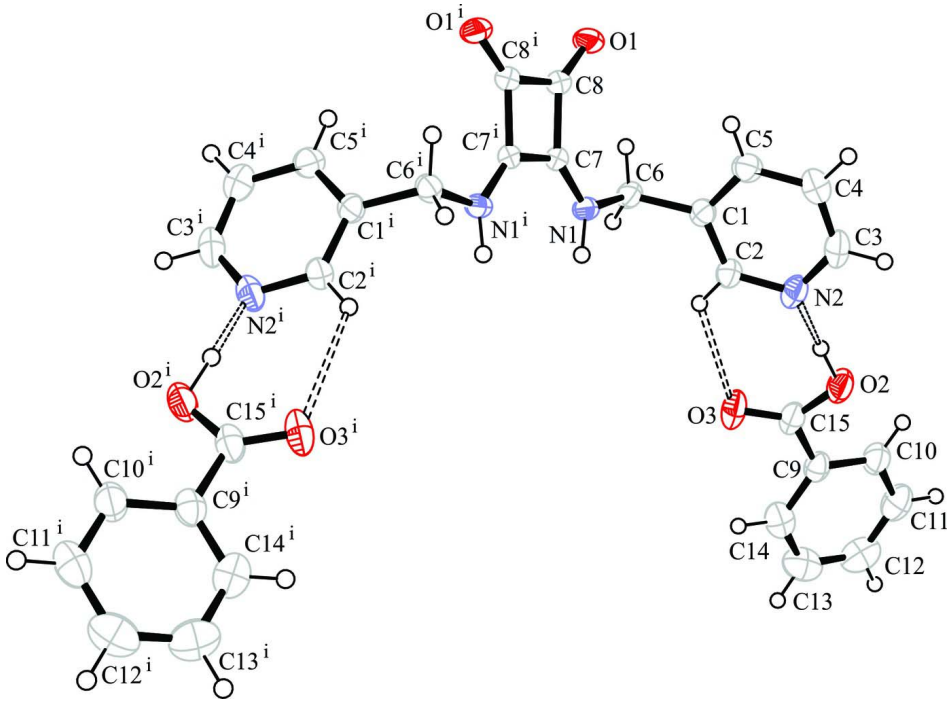


**Figure 1**

The asymmetric unit of (I) showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Atoms with superscript i are generated by the symmetry operation (-*x*, *y*, -*z* + 1/2).

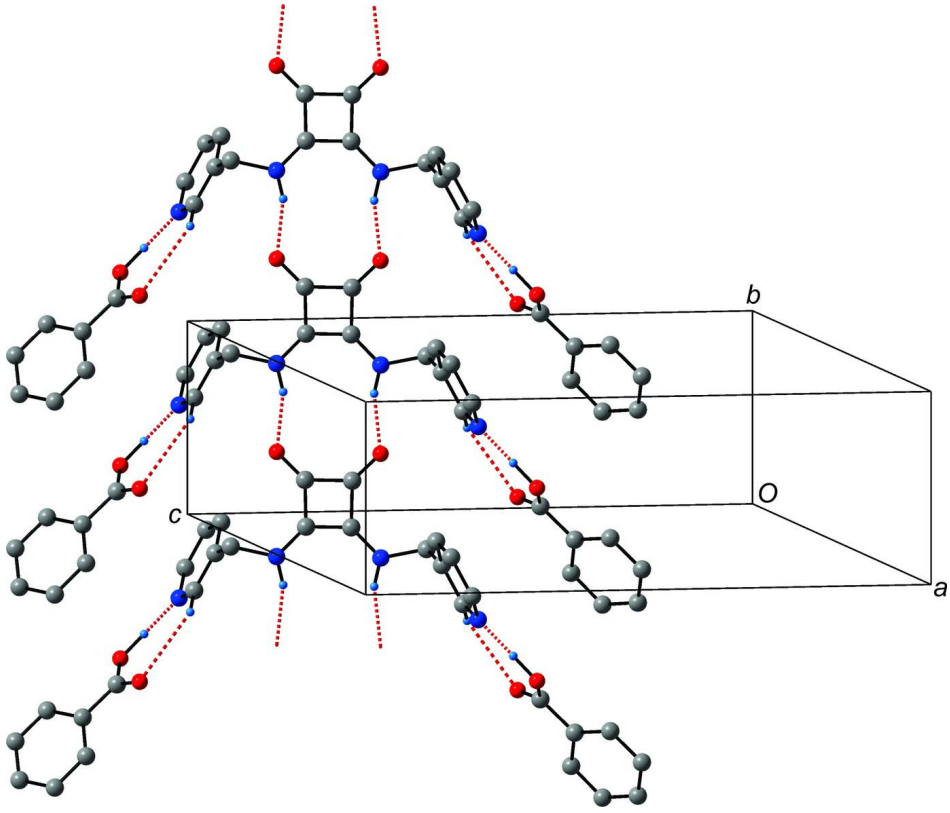


**Figure 2**

Hydrogen bonding diagram of the ribbons of (I). Intermolecular N—H···O and O—H···N hydrogen bonds are shown as dashed red lines.

### Benzoic acid–3,4-bis[(pyridin-3-ylmethyl)amino]cyclobut-3-ene-1,2-dione (1/2)

*Crystal data*

$C_{16}H_{14}N_4O_2·2C_7H_6O_2$
$M_r$ = 538.55
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a$ = 24.617 (5) Å
$b$ = 6.0285 (12) Å
$c$ = 17.806 (4) Å
$\beta$ = 93.08 (3)°
$V$ = 2638.6 (9) Å$^3$
$Z$ = 4
$F(000)$ = 1128
$D_x$ = 1.356 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 16004 reflections
$\theta$ = 0.2–28.3°
$\mu$ = 0.10 mm$^{-1}$
$T$ = 173 K
Plate, colourless
0.49 × 0.16 × 0.14 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
2.0° $\omega$ scans
Absorption correction: integration (*XPREP*; Bruker, 2004)
$T_{min}$ = 0.944, $T_{max}$ = 0.989
15016 measured reflections
3166 independent reflections
2110 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.076
$\theta_{max}$ = 28.0°, $\theta_{min}$ = 2.3°
$h$ = −32→26
$k$ = −7→7
$l$ = −23→21

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.116$
$S = 0.99$
3166 reflections
190 parameters
0 restraints

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + ]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.24$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0097 (11)

*Special details*

**Experimental**. Numerical integration absorption corrections based on indexed crystal faces were applied using the *XPREP* routine (Bruker, 2004).
**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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.09548 (5) | 0.7538 (2) | 0.57965 (7) | 0.0286 (3) |
| C2 | 0.10973 (5) | 0.5561 (2) | 0.54679 (7) | 0.0333 (3) |
| H2A | 0.0814 | 0.4569 | 0.5308 | 0.04* |
| C3 | 0.20066 (6) | 0.6353 (3) | 0.55968 (8) | 0.0417 (4) |
| H3 | 0.2373 | 0.5946 | 0.5526 | 0.05* |
| C4 | 0.19060 (6) | 0.8346 (3) | 0.59354 (8) | 0.0430 (4) |
| H4 | 0.2198 | 0.929 | 0.61 | 0.052* |
| C5 | 0.13726 (6) | 0.8956 (2) | 0.60321 (7) | 0.0366 (3) |
| H5 | 0.1293 | 1.0337 | 0.6259 | 0.044* |
| C6 | 0.03667 (5) | 0.8124 (2) | 0.58837 (7) | 0.0307 (3) |
| H6A | 0.0312 | 0.9723 | 0.5777 | 0.037* |
| H6B | 0.0136 | 0.7275 | 0.5513 | 0.037* |
| C7 | 0.00897 (5) | 0.91990 (19) | 0.71280 (7) | 0.0261 (3) |
| C8 | 0.01001 (5) | 1.16213 (19) | 0.71131 (7) | 0.0293 (3) |
| N1 | 0.02002 (4) | 0.76350 (17) | 0.66414 (6) | 0.0298 (3) |
| H1 | 0.0195 (6) | 0.616 (3) | 0.6757 (8) | 0.041 (4)* |
| N2 | 0.16108 (5) | 0.49629 (19) | 0.53623 (6) | 0.0384 (3) |
| O1 | 0.02247 (4) | 1.30418 (13) | 0.66529 (5) | 0.0373 (3) |
| C9 | 0.14385 (5) | −0.1060 (2) | 0.36020 (7) | 0.0350 (3) |
| C10 | 0.18500 (6) | −0.0836 (2) | 0.31016 (8) | 0.0423 (4) |
| H10 | 0.208 | 0.0431 | 0.3128 | 0.051* |
| C11 | 0.19255 (7) | −0.2448 (3) | 0.25655 (9) | 0.0513 (4) |
| H11 | 0.2201 | −0.2273 | 0.2217 | 0.062* |
| C12 | 0.16006 (8) | −0.4312 (3) | 0.25359 (9) | 0.0573 (5) |
| H12 | 0.1657 | −0.543 | 0.2172 | 0.069* |
| C13 | 0.11934 (8) | −0.4557 (3) | 0.30324 (10) | 0.0559 (5) |
| H13 | 0.0972 | −0.5848 | 0.3013 | 0.067* |

| | | | | |
|---|---|---|---|---|
| C14 | 0.11075 (6) | −0.2923 (3) | 0.35590 (8) | 0.0452 (4) |
| H14 | 0.0821 | −0.3078 | 0.3892 | 0.054* |
| C15 | 0.13450 (6) | 0.0665 (2) | 0.41783 (8) | 0.0374 (4) |
| O2 | 0.17883 (4) | 0.18069 (17) | 0.43789 (6) | 0.0443 (3) |
| H2 | 0.1708 (7) | 0.309 (3) | 0.4774 (11) | 0.080 (6)* |
| O3 | 0.09068 (4) | 0.09691 (18) | 0.44435 (6) | 0.0484 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0315 (7) | 0.0303 (7) | 0.0247 (6) | 0.0022 (5) | 0.0069 (5) | 0.0042 (5) |
| C2 | 0.0308 (7) | 0.0342 (7) | 0.0355 (7) | 0.0025 (6) | 0.0083 (6) | −0.0004 (5) |
| C3 | 0.0282 (8) | 0.0576 (9) | 0.0400 (8) | 0.0050 (7) | 0.0092 (6) | 0.0049 (7) |
| C4 | 0.0339 (8) | 0.0501 (9) | 0.0452 (8) | −0.0078 (7) | 0.0033 (6) | 0.0024 (7) |
| C5 | 0.0401 (8) | 0.0324 (7) | 0.0376 (8) | −0.0007 (6) | 0.0065 (6) | 0.0003 (6) |
| C6 | 0.0320 (7) | 0.0289 (7) | 0.0319 (7) | 0.0048 (5) | 0.0081 (5) | 0.0008 (5) |
| C7 | 0.0227 (6) | 0.0211 (6) | 0.0353 (7) | 0.0006 (5) | 0.0073 (5) | 0.0000 (5) |
| C8 | 0.0282 (7) | 0.0219 (6) | 0.0384 (7) | 0.0012 (5) | 0.0084 (5) | 0.0004 (5) |
| N1 | 0.0355 (6) | 0.0203 (6) | 0.0348 (6) | 0.0017 (5) | 0.0130 (5) | 0.0013 (4) |
| N2 | 0.0335 (7) | 0.0443 (7) | 0.0384 (7) | 0.0092 (5) | 0.0103 (5) | −0.0012 (5) |
| O1 | 0.0468 (6) | 0.0225 (5) | 0.0440 (5) | −0.0014 (4) | 0.0159 (4) | 0.0046 (4) |
| C9 | 0.0308 (7) | 0.0419 (8) | 0.0324 (7) | 0.0077 (6) | 0.0018 (6) | 0.0064 (6) |
| C10 | 0.0372 (8) | 0.0459 (8) | 0.0445 (9) | 0.0044 (6) | 0.0093 (7) | 0.0008 (6) |
| C11 | 0.0507 (10) | 0.0624 (11) | 0.0417 (9) | 0.0148 (8) | 0.0099 (7) | −0.0028 (8) |
| C12 | 0.0702 (12) | 0.0560 (11) | 0.0441 (9) | 0.0146 (9) | −0.0110 (9) | −0.0100 (7) |
| C13 | 0.0640 (12) | 0.0507 (10) | 0.0510 (10) | −0.0084 (8) | −0.0155 (9) | −0.0003 (8) |
| C14 | 0.0393 (9) | 0.0593 (10) | 0.0367 (8) | −0.0032 (7) | −0.0025 (6) | 0.0077 (7) |
| C15 | 0.0310 (8) | 0.0460 (9) | 0.0356 (8) | 0.0100 (6) | 0.0066 (6) | 0.0074 (6) |
| O2 | 0.0331 (6) | 0.0490 (6) | 0.0518 (6) | 0.0063 (5) | 0.0112 (5) | −0.0115 (5) |
| O3 | 0.0322 (6) | 0.0669 (7) | 0.0472 (6) | 0.0120 (5) | 0.0133 (5) | 0.0027 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.3816 (18) | C8—C8$^{i}$ | 1.488 (3) |
| C1—C5 | 1.3849 (19) | N1—H1 | 0.915 (16) |
| C1—C6 | 1.5061 (18) | C9—C14 | 1.387 (2) |
| C2—N2 | 1.3374 (17) | C9—C10 | 1.391 (2) |
| C2—H2A | 0.95 | C9—C15 | 1.487 (2) |
| C3—N2 | 1.3351 (19) | C10—C11 | 1.382 (2) |
| C3—C4 | 1.373 (2) | C10—H10 | 0.95 |
| C3—H3 | 0.95 | C11—C12 | 1.378 (2) |
| C4—C5 | 1.383 (2) | C11—H11 | 0.95 |
| C4—H4 | 0.95 | C12—C13 | 1.380 (3) |
| C5—H5 | 0.95 | C12—H12 | 0.95 |
| C6—N1 | 1.4612 (16) | C13—C14 | 1.384 (2) |
| C6—H6A | 0.99 | C13—H13 | 0.95 |
| C6—H6B | 0.99 | C14—H14 | 0.95 |
| C7—N1 | 1.3187 (16) | C15—O3 | 1.2146 (16) |

| | | | |
|---|---|---|---|
| C7—C7$^{i}$ | 1.419 (2) | C15—O2 | 1.3231 (17) |
| C7—C8 | 1.4607 (17) | O2—H2 | 1.07 (2) |
| C8—O1 | 1.2354 (15) | | |

| | | | |
|---|---|---|---|
| C2—C1—C5 | 117.35 (12) | C7—N1—C6 | 122.71 (11) |
| C2—C1—C6 | 120.89 (12) | C7—N1—H1 | 122.9 (9) |
| C5—C1—C6 | 121.76 (12) | C6—N1—H1 | 114.3 (9) |
| N2—C2—C1 | 123.74 (13) | C3—N2—C2 | 117.80 (12) |
| N2—C2—H2A | 118.1 | C14—C9—C10 | 119.28 (14) |
| C1—C2—H2A | 118.1 | C14—C9—C15 | 119.46 (13) |
| N2—C3—C4 | 122.74 (13) | C10—C9—C15 | 121.26 (13) |
| N2—C3—H3 | 118.6 | C11—C10—C9 | 120.24 (15) |
| C4—C3—H3 | 118.6 | C11—C10—H10 | 119.9 |
| C3—C4—C5 | 118.83 (14) | C9—C10—H10 | 119.9 |
| C3—C4—H4 | 120.6 | C12—C11—C10 | 120.03 (16) |
| C5—C4—H4 | 120.6 | C12—C11—H11 | 120 |
| C4—C5—C1 | 119.53 (13) | C10—C11—H11 | 120 |
| C4—C5—H5 | 120.2 | C11—C12—C13 | 120.19 (15) |
| C1—C5—H5 | 120.2 | C11—C12—H12 | 119.9 |
| N1—C6—C1 | 111.52 (10) | C13—C12—H12 | 119.9 |
| N1—C6—H6A | 109.3 | C12—C13—C14 | 120.03 (16) |
| C1—C6—H6A | 109.3 | C12—C13—H13 | 120 |
| N1—C6—H6B | 109.3 | C14—C13—H13 | 120 |
| C1—C6—H6B | 109.3 | C13—C14—C9 | 120.20 (16) |
| H6A—C6—H6B | 108 | C13—C14—H14 | 119.9 |
| N1—C7—C7$^{i}$ | 134.35 (7) | C9—C14—H14 | 119.9 |
| N1—C7—C8 | 134.30 (12) | O3—C15—O2 | 123.58 (13) |
| C7$^{i}$—C7—C8 | 91.35 (7) | O3—C15—C9 | 123.19 (14) |
| O1—C8—C7 | 135.25 (12) | O2—C15—C9 | 113.22 (12) |
| O1—C8—C8$^{i}$ | 136.11 (7) | C15—O2—H2 | 111.9 (10) |
| C7—C8—C8$^{i}$ | 88.64 (7) | | |

| | | | |
|---|---|---|---|
| C5—C1—C2—N2 | −0.52 (19) | C4—C3—N2—C2 | −0.2 (2) |
| C6—C1—C2—N2 | 178.76 (11) | C1—C2—N2—C3 | 0.8 (2) |
| N2—C3—C4—C5 | −0.7 (2) | C14—C9—C10—C11 | 0.3 (2) |
| C3—C4—C5—C1 | 0.9 (2) | C15—C9—C10—C11 | −179.30 (13) |
| C2—C1—C5—C4 | −0.35 (19) | C9—C10—C11—C12 | −1.5 (2) |
| C6—C1—C5—C4 | −179.62 (12) | C10—C11—C12—C13 | 1.1 (2) |
| C2—C1—C6—N1 | 98.57 (14) | C11—C12—C13—C14 | 0.5 (2) |
| C5—C1—C6—N1 | −82.19 (14) | C12—C13—C14—C9 | −1.6 (2) |
| N1—C7—C8—O1 | −1.8 (3) | C10—C9—C14—C13 | 1.2 (2) |
| C7$^{i}$—C7—C8—O1 | 178.55 (15) | C15—C9—C14—C13 | −179.17 (13) |
| N1—C7—C8—C8$^{i}$ | 178.45 (15) | C14—C9—C15—O3 | −25.7 (2) |
| C7$^{i}$—C7—C8—C8$^{i}$ | −1.20 (14) | C10—C9—C15—O3 | 153.96 (14) |
| C7$^{i}$—C7—N1—C6 | 178.04 (17) | C14—C9—C15—O2 | 153.46 (12) |

| | | | |
|---|---|---|---|
| C8—C7—N1—C6 | −1.5 (2) | C10—C9—C15—O2 | −26.92 (18) |
| C1—C6—N1—C7 | 110.22 (13) | | |

Symmetry code: (i) −*x*, *y*, −*z*+3/2.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1$^{ii}$ | 0.915 (16) | 1.889 (17) | 2.7697 (15) | 161.0 (13) |
| O2—H2···N2 | 1.07 (2) | 1.57 (2) | 2.6380 (15) | 178.0 (17) |
| C2—H2*A*···O3 | 0.95 | 2.68 | 3.3341 (18) | 127 |

Symmetry code: (ii) *x*, *y*−1, *z*.