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# A co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.046
*wR* factor = 0.135
Data-to-parameter ratio = 11.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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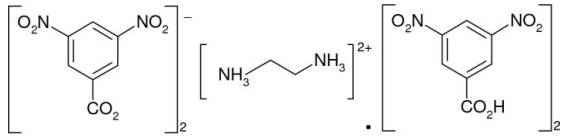
The co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid, namely ethylenediaminium–3,5-dinitrobenzoate–3,5-dinitrobenzoic acid (1/2/2), $C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O_6^{-}\cdot 2C_7H_4N_2O_6$, has as the asymmetric unit one 3,5-dinitrobenzoic acid molecule, one 3,5-dinitrobenzoate ion and one-half of the ethylenediammonium ion, as this cation lies on an inversion centre. Each ethylenediammonium ion is hydrogen bonded to four benzoate ions and two benzoic acid molecules.

## Comment

During experiments to measure the solubility of the monoclinic form of ethylenediammonium bis(3,5-dinitrobenzoate), cocrystals, (I), of this salt with 3,5-dinitrobenzoic acid were obtained.



(I)

To measure the solubility of ethylenediammonium bis(3,5-dinitrobenzoate) as a function of pH at 323 K, a suspension of the salt in water was prepared and allowed to equilibrate (Jones *et al.*, 2005). In one experiment, the pH was found to be unusually low for a slurry of this salt and the experiment was stopped, but the sample continued to be held at 323 K. The cocrystals grew as pale-yellow prisms and were recovered on filtration of the slurry. Formation of these cocrystals was not observed in other solubility measurements at higher pH. Protonated 3,5-dinitrobenzoic acid is only expected to be present below pH 5 at 323 K (de Levie *et al.*, 1999).

In the crystal structure, both a protonated and a deprotonated 3,5-dinitrobenzoic acid molecule are present in the asymmetric unit. The ethylenediammonium ion lies on an inversion centre so that only one-half of the ion is in the asymmetric unit. Fig. 1 shows the structure and atom labelling.

Each ethylenediammonium ion is hydrogen bonded to four benzoate ions and two benzoic acid molecules (Fig. 2). The crystal structure contains hydrogen-bonded chains of ethylenediammonium and benzoate ions along the *a* axis in the motif $C_2^2(6)$ (Fig. 3), hydrogen-bonded dimers of benzoate ions with benzoic acid molecules with an O—H···O hydrogen bond through atom H7 in the motif $D_1^1(2)$, and dimers of ethylenediammonium ions hydrogen bonded to the carbonyl group of a benzoic acid molecule in the motif $D_1^1(2)$. The benzoate ions in this structure all lie in one plane and the benzoic acid molecules all lie in another orientation.

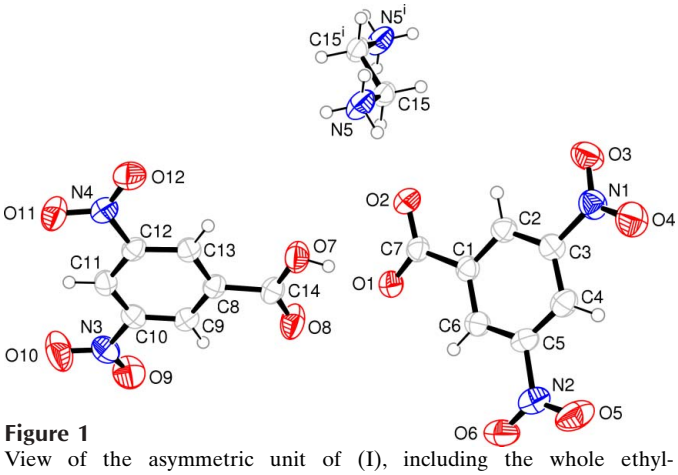



**Figure 1**
View of the asymmetric unit of (I), including the whole ethylenediaminium ion, which is on an inversion centre. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, -z$.]

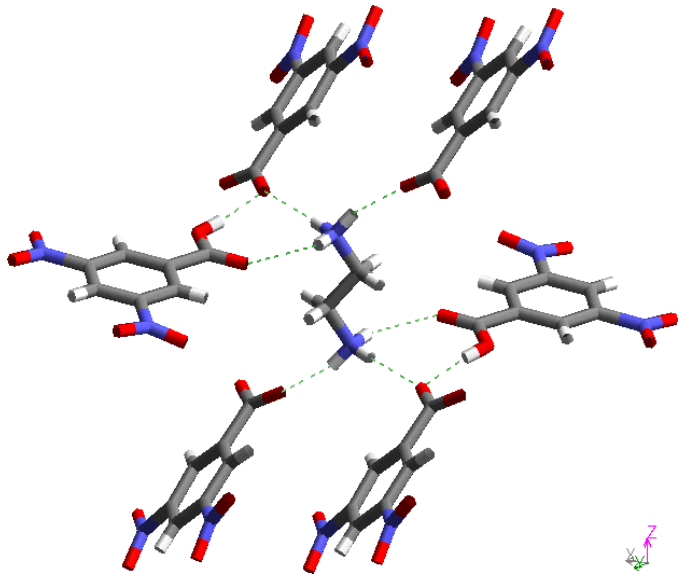


**Figure 2**
Hydrogen bonding (dashed lines) between the ethylenediaminium and 3,5-dinitrobenzoate ions and the 3,5-dinitrobenzoic acid molecules.

## Experimental

Monoclinic ethylenediaminium bis(3,5-dinitrobenzoate) was prepared by precipitation from a mixture of solutions of ethylenediamine (0.0145 mol) and 3,5-dinitrobenzoic acid (0.029 mol; supplied by Sigma–Aldrich, 99%) in ethanol (50 ml). An excess of monoclinic ethylenediammonium bis(3,5-dinitrobenzoate) (0.0145 mol) was suspended in water (40 ml) at 323 K with stirring. The solution pH was recorded as 3.79. After 20 h, stirring was stopped and the suspension was held at 323 K for 5 d. The suspension was filtered and pale-yellow prisms were observed in the powder of the monoclinic ethylenediammonium bis(3,5-dinitrobenzoate).

*Crystal data*

$C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O6^{-}\cdot\cdot 2C_7H_4N_2O_6$
$M_r = 908.6$
Triclinic, $P\overline{1}$
$a = 7.0452\ (3)$ Å
$b = 11.2345\ (4)$ Å
$c = 11.7627\ (5)$ Å
$\alpha = 91.838\ (2)^\circ$
$\beta = 96.230\ (2)^\circ$
$\gamma = 98.710\ (1)^\circ$
$V = 913.72\ (6)$ Å$^3$
$Z = 1$
$D_x = 1.651$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5294 reflections
$\theta = 1.0$–$25.0^\circ$
$\mu = 0.15$ mm$^{-1}$
$T = 293\ (2)$ K
Prism, pale yellow
0.3 × 0.2 × 0.1 mm

*Data collection*

Nonius KappaCCD diffractometer
Thick-slice $\varphi$ and $\omega$ scans to fill asymmetric unit
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.916$, $T_{max} = 0.986$
8852 measured reflections
3241 independent reflections
2256 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 25.2^\circ$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.136$
$S = 1.01$
3241 reflections
294 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{min} = -0.21$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.016 (4)

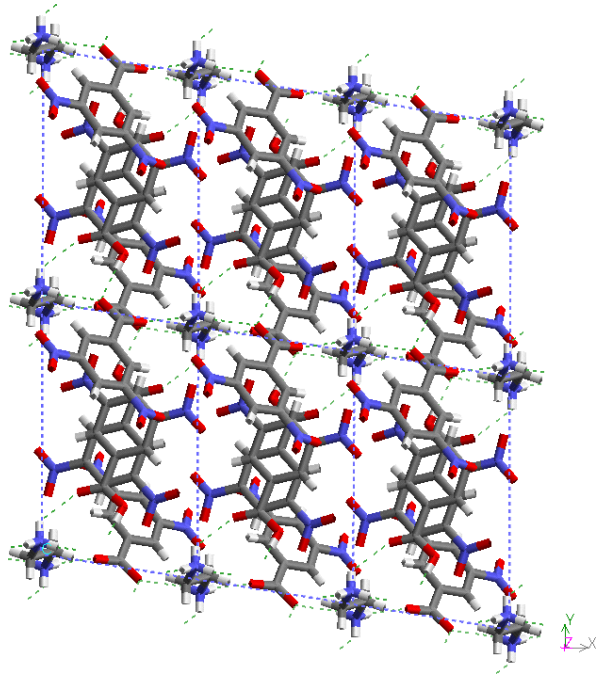


**Figure 3**
Unit cell contents, viewed along the $c$ axis, showing hydrogen-bonded chains (dashed lines) along the $a$ axis.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O7—H7···O1 | 0.83 (1) | 1.68 (1) | 2.507 (2) | 173 (4) |
| N5—H5$A$···O2 | 0.89 | 1.88 | 2.732 (3) | 161 |
| N5—H5$B$···O8$^{ii}$ | 0.89 | 2.17 | 2.820 (3) | 129 |
| N5—H5$C$···O1$^{ii}$ | 0.89 | 2.02 | 2.899 (3) | 170 |

Symmetry code: (ii) $x+1, y, z$.

All H atoms attached to C and N atoms were fixed using a riding model, with C—H distances 0.93 Å ($C_{Ar}H$) and 0.97 Å ($CH_2$), and N—H distances 0.89 Å. The $U_{iso}(H)$ values were set equal to $1.2U_{eq}$ of the carrier atom for these H atoms. The hydroxy H atom was located in a Fourier difference map and the coordinates were refined with the O—H bond distance restrained to 0.82 (1) Å.

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

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# supporting information

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## A co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid

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**ethylenediaminium–3,5-dinitrobenzoate–3,5-dinitrobenzoic acid (1/2/2), $C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O_6^-\cdot 2C_7H_4N_2O_6$**

*Crystal data*

$0.5C_2H_{10}N_2^{2+}\cdot C_7H_3N_2O_6^-\cdot C_7H_4N_2O_6$
$M_r$ = 454.3
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 7.0452 (3) Å
$b$ = 11.2345 (4) Å
$c$ = 11.7627 (5) Å
$\alpha$ = 91.838 (2)°
$\beta$ = 96.230 (2)°
$\gamma$ = 98.710 (1)°
$V$ = 913.72 (6) Å$^3$
$Z$ = 2
$F$(000) = 466
$D_x$ = 1.651 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 5294 reflections
$\theta$ = 1.0–25.0°
$\mu$ = 0.15 mm$^{-1}$
$T$ = 293 K
Prism, pale yellow
0.3 × 0.2 × 0.1 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: Enraf–Nonius FR590
Graphite monochromator
$\varphi$ or $\omega$ scans?
Absorption correction: multi-scan (Blessing, 1995)
$T_{min}$ = 0.916, $T_{max}$ = 0.986
8852 measured reflections
3241 independent reflections
2256 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.046
$\theta_{max}$ = 25.2°, $\theta_{min}$ = 2.5°
$h$ = −8→8
$k$ = −13→13
$l$ = −14→12

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.136
$S$ = 1.01
3241 reflections
294 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$
Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.016 (4)

*Special details*

**Experimental**. Solution pH was measured using an Accumet Basic AB15 pH meter with an Accumet glass calomel pH electrode and an ATC probe to compensate for temperature changes.

**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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.3739 (2) | 0.04198 (13) | 0.75723 (14) | 0.0508 (4) |
| O2 | 0.6632 (3) | −0.01493 (13) | 0.76044 (15) | 0.0553 (5) |
| O3 | 0.7755 (3) | −0.38263 (14) | 0.94862 (14) | 0.0596 (5) |
| O4 | 0.6306 (3) | −0.42815 (15) | 1.09778 (14) | 0.0648 (5) |
| O5 | 0.0621 (3) | −0.26099 (18) | 1.15926 (16) | 0.0718 (6) |
| O6 | −0.0276 (3) | −0.12294 (18) | 1.05344 (18) | 0.0724 (6) |
| O7 | 0.5246 (3) | 0.24130 (15) | 0.69250 (16) | 0.0590 (5) |
| O8 | 0.2299 (3) | 0.26663 (15) | 0.62078 (17) | 0.0680 (5) |
| O9 | 0.1253 (3) | 0.66997 (17) | 0.50938 (18) | 0.0741 (6) |
| O10 | 0.3350 (3) | 0.82267 (16) | 0.5700 (2) | 0.0889 (7) |
| O11 | 0.9653 (3) | 0.76827 (14) | 0.73491 (15) | 0.0618 (5) |
| O12 | 1.0348 (3) | 0.58912 (16) | 0.75615 (16) | 0.0638 (5) |
| N1 | 0.6524 (3) | −0.37047 (16) | 1.01241 (16) | 0.0475 (5) |
| N2 | 0.0813 (3) | −0.19415 (18) | 1.07990 (18) | 0.0520 (5) |
| N3 | 0.2801 (3) | 0.71433 (18) | 0.55839 (17) | 0.0537 (5) |
| N4 | 0.9221 (3) | 0.65764 (17) | 0.72899 (16) | 0.0455 (5) |
| N5 | 0.9846 (3) | 0.05043 (17) | 0.65242 (17) | 0.0571 (6) |
| H5A | 0.8995 | 0.0265 | 0.7009 | 0.069* |
| H5B | 0.9863 | 0.1285 | 0.6413 | 0.069* |
| H5C | 1.1016 | 0.0382 | 0.6816 | 0.069* |
| C1 | 0.4465 (3) | −0.11491 (17) | 0.87777 (17) | 0.0371 (5) |
| C2 | 0.5689 (3) | −0.19825 (17) | 0.90467 (17) | 0.0394 (5) |
| H2 | 0.681 | −0.1975 | 0.8694 | 0.047* |
| C3 | 0.5229 (3) | −0.28228 (18) | 0.98423 (17) | 0.0403 (5) |
| C4 | 0.3618 (3) | −0.28528 (19) | 1.04054 (18) | 0.0433 (6) |
| H4 | 0.332 | −0.3427 | 1.0937 | 0.052* |
| C5 | 0.2463 (3) | −0.19926 (18) | 1.01452 (17) | 0.0400 (5) |
| C6 | 0.2833 (3) | −0.11494 (18) | 0.93258 (18) | 0.0395 (5) |
| H6 | 0.1998 | −0.0598 | 0.9151 | 0.047* |
| C7 | 0.5006 (3) | −0.02253 (17) | 0.79096 (18) | 0.0403 (5) |
| C8 | 0.4724 (3) | 0.43735 (17) | 0.65036 (16) | 0.0368 (5) |
| C9 | 0.3459 (3) | 0.51274 (18) | 0.60851 (17) | 0.0391 (5) |
| H9 | 0.2179 | 0.482 | 0.5824 | 0.047* |

| | | | | |
|---|---|---|---|---|
| C10 | 0.4134 (3) | 0.63433 (18) | 0.60626 (17) | 0.0404 (5) |
| C11 | 0.5990 (3) | 0.68435 (18) | 0.64562 (17) | 0.0400 (5) |
| H11 | 0.6405 | 0.7669 | 0.6452 | 0.048* |
| C12 | 0.7218 (3) | 0.60689 (18) | 0.68589 (17) | 0.0375 (5) |
| C13 | 0.6631 (3) | 0.48361 (18) | 0.68852 (17) | 0.0382 (5) |
| H13 | 0.7496 | 0.4332 | 0.7152 | 0.046* |
| C14 | 0.3964 (4) | 0.30531 (19) | 0.65396 (18) | 0.0432 (6) |
| C15 | 0.9287 (3) | −0.01948 (18) | 0.54167 (18) | 0.0421 (5) |
| H15A | 0.8006 | −0.007 | 0.5102 | 0.051* |
| H15B | 0.9249 | −0.1048 | 0.5538 | 0.051* |
| H7 | 0.469 (5) | 0.1743 (18) | 0.709 (3) | 0.123 (14)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0486 (11) | 0.0417 (8) | 0.0650 (10) | 0.0101 (8) | 0.0127 (8) | 0.0141 (7) |
| O2 | 0.0492 (11) | 0.0509 (9) | 0.0700 (11) | 0.0061 (8) | 0.0237 (9) | 0.0159 (8) |
| O3 | 0.0678 (13) | 0.0629 (11) | 0.0573 (11) | 0.0291 (9) | 0.0207 (10) | 0.0089 (8) |
| O4 | 0.0793 (14) | 0.0686 (11) | 0.0535 (11) | 0.0243 (10) | 0.0148 (9) | 0.0255 (8) |
| O5 | 0.0613 (13) | 0.0999 (14) | 0.0587 (12) | 0.0094 (10) | 0.0249 (10) | 0.0247 (10) |
| O6 | 0.0568 (13) | 0.0806 (13) | 0.0898 (15) | 0.0248 (10) | 0.0301 (11) | 0.0154 (10) |
| O7 | 0.0558 (12) | 0.0416 (9) | 0.0771 (12) | 0.0025 (8) | 0.0011 (9) | 0.0145 (8) |
| O8 | 0.0566 (13) | 0.0474 (9) | 0.0902 (14) | −0.0091 (9) | −0.0146 (10) | 0.0145 (8) |
| O9 | 0.0581 (13) | 0.0767 (13) | 0.0840 (14) | 0.0186 (10) | −0.0189 (11) | 0.0052 (10) |
| O10 | 0.0967 (18) | 0.0460 (12) | 0.1208 (19) | 0.0235 (11) | −0.0197 (14) | 0.0052 (10) |
| O11 | 0.0587 (12) | 0.0467 (10) | 0.0724 (12) | −0.0097 (8) | −0.0015 (9) | 0.0027 (8) |
| O12 | 0.0422 (11) | 0.0674 (11) | 0.0818 (13) | 0.0111 (9) | 0.0032 (9) | 0.0066 (9) |
| N1 | 0.0557 (14) | 0.0459 (11) | 0.0427 (11) | 0.0130 (9) | 0.0059 (10) | 0.0060 (8) |
| N2 | 0.0418 (13) | 0.0608 (13) | 0.0524 (13) | 0.0015 (10) | 0.0105 (10) | 0.0023 (10) |
| N3 | 0.0579 (15) | 0.0534 (13) | 0.0521 (12) | 0.0192 (11) | 0.0023 (11) | 0.0025 (9) |
| N4 | 0.0413 (12) | 0.0497 (12) | 0.0449 (11) | 0.0020 (10) | 0.0083 (9) | 0.0036 (8) |
| N5 | 0.0560 (14) | 0.0594 (12) | 0.0518 (12) | −0.0124 (10) | 0.0190 (10) | −0.0014 (9) |
| C1 | 0.0410 (13) | 0.0337 (10) | 0.0355 (11) | 0.0020 (9) | 0.0051 (9) | −0.0013 (8) |
| C2 | 0.0416 (14) | 0.0407 (11) | 0.0364 (12) | 0.0055 (10) | 0.0084 (10) | −0.0011 (9) |
| C3 | 0.0445 (14) | 0.0409 (11) | 0.0361 (12) | 0.0086 (10) | 0.0046 (10) | 0.0020 (9) |
| C4 | 0.0466 (15) | 0.0454 (12) | 0.0368 (12) | 0.0013 (10) | 0.0072 (10) | 0.0036 (9) |
| C5 | 0.0350 (13) | 0.0474 (12) | 0.0369 (12) | 0.0012 (10) | 0.0093 (10) | −0.0024 (9) |
| C6 | 0.0379 (13) | 0.0394 (11) | 0.0407 (12) | 0.0051 (9) | 0.0040 (10) | −0.0014 (8) |
| C7 | 0.0431 (15) | 0.0329 (11) | 0.0438 (13) | −0.0003 (10) | 0.0092 (11) | −0.0014 (9) |
| C8 | 0.0415 (14) | 0.0384 (11) | 0.0298 (11) | 0.0020 (9) | 0.0066 (9) | 0.0032 (8) |
| C9 | 0.0379 (13) | 0.0452 (12) | 0.0328 (11) | 0.0020 (10) | 0.0041 (9) | −0.0004 (8) |
| C10 | 0.0472 (14) | 0.0430 (12) | 0.0327 (11) | 0.0117 (10) | 0.0055 (10) | 0.0020 (8) |
| C11 | 0.0482 (15) | 0.0356 (11) | 0.0361 (12) | 0.0048 (10) | 0.0069 (10) | 0.0015 (8) |
| C12 | 0.0387 (13) | 0.0415 (11) | 0.0316 (11) | 0.0011 (9) | 0.0077 (9) | 0.0020 (8) |
| C13 | 0.0444 (14) | 0.0393 (11) | 0.0320 (11) | 0.0069 (10) | 0.0075 (10) | 0.0039 (8) |
| C14 | 0.0467 (16) | 0.0424 (12) | 0.0385 (12) | 0.0002 (11) | 0.0041 (11) | 0.0059 (9) |
| C15 | 0.0437 (14) | 0.0389 (11) | 0.0434 (12) | 0.0004 (10) | 0.0103 (10) | 0.0060 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.271 (3) | C1—C2 | 1.388 (3) |
| O2—C7 | 1.229 (3) | C1—C7 | 1.516 (3) |
| O3—N1 | 1.226 (2) | C2—C3 | 1.379 (3) |
| O4—N1 | 1.224 (2) | C2—H2 | 0.93 |
| O5—N2 | 1.223 (3) | C3—C4 | 1.371 (3) |
| O6—N2 | 1.215 (3) | C4—C5 | 1.376 (3) |
| O7—C14 | 1.292 (3) | C4—H4 | 0.93 |
| O7—H7 | 0.833 (10) | C5—C6 | 1.390 (3) |
| O8—C14 | 1.205 (3) | C6—H6 | 0.93 |
| O9—N3 | 1.204 (3) | C8—C9 | 1.384 (3) |
| O10—N3 | 1.219 (3) | C8—C13 | 1.386 (3) |
| O11—N4 | 1.232 (2) | C8—C14 | 1.502 (3) |
| O12—N4 | 1.213 (2) | C9—C10 | 1.379 (3) |
| N1—C3 | 1.468 (3) | C9—H9 | 0.93 |
| N2—C5 | 1.469 (3) | C10—C11 | 1.367 (3) |
| N3—C10 | 1.477 (3) | C11—C12 | 1.377 (3) |
| N4—C12 | 1.468 (3) | C11—H11 | 0.93 |
| N5—C15 | 1.483 (3) | C12—C13 | 1.386 (3) |
| N5—H5A | 0.89 | C13—H13 | 0.93 |
| N5—H5B | 0.89 | C15—C15$^{i}$ | 1.506 (4) |
| N5—H5C | 0.89 | C15—H15A | 0.97 |
| C1—C6 | 1.377 (3) | C15—H15B | 0.97 |
| | | | |
| C14—O7—H7 | 109 (3) | C1—C6—C5 | 118.5 (2) |
| O4—N1—O3 | 123.8 (2) | C1—C6—H6 | 120.7 |
| O4—N1—C3 | 118.1 (2) | C5—C6—H6 | 120.7 |
| O3—N1—C3 | 118.10 (18) | O2—C7—O1 | 125.5 (2) |
| O6—N2—O5 | 123.3 (2) | O2—C7—C1 | 117.6 (2) |
| O6—N2—C5 | 118.5 (2) | O1—C7—C1 | 116.8 (2) |
| O5—N2—C5 | 118.1 (2) | C9—C8—C13 | 120.38 (19) |
| O9—N3—O10 | 123.6 (2) | C9—C8—C14 | 118.1 (2) |
| O9—N3—C10 | 118.95 (19) | C13—C8—C14 | 121.48 (19) |
| O10—N3—C10 | 117.5 (2) | C10—C9—C8 | 118.6 (2) |
| O12—N4—O11 | 124.0 (2) | C10—C9—H9 | 120.7 |
| O12—N4—C12 | 118.64 (18) | C8—C9—H9 | 120.7 |
| O11—N4—C12 | 117.41 (19) | C11—C10—C9 | 123.0 (2) |
| C15—N5—H5A | 109.5 | C11—C10—N3 | 118.33 (19) |
| C15—N5—H5B | 109.5 | C9—C10—N3 | 118.7 (2) |
| H5A—N5—H5B | 109.5 | C10—C11—C12 | 116.98 (19) |
| C15—N5—H5C | 109.5 | C10—C11—H11 | 121.5 |
| H5A—N5—H5C | 109.5 | C12—C11—H11 | 121.5 |
| H5B—N5—H5C | 109.5 | C11—C12—C13 | 122.6 (2) |
| C6—C1—C2 | 119.86 (19) | C11—C12—N4 | 118.40 (18) |
| C6—C1—C7 | 121.5 (2) | C13—C12—N4 | 119.0 (2) |
| C2—C1—C7 | 118.6 (2) | C8—C13—C12 | 118.3 (2) |
| C3—C2—C1 | 119.4 (2) | C8—C13—H13 | 120.8 |

| | | | |
|---|---|---|---|
| C3—C2—H2 | 120.3 | C12—C13—H13 | 120.8 |
| C1—C2—H2 | 120.3 | O8—C14—O7 | 125.3 (2) |
| C4—C3—C2 | 122.5 (2) | O8—C14—C8 | 120.6 (2) |
| C4—C3—N1 | 118.23 (19) | O7—C14—C8 | 114.1 (2) |
| C2—C3—N1 | 119.3 (2) | N5—C15—C15$^{i}$ | 110.4 (2) |
| C3—C4—C5 | 116.8 (2) | N5—C15—H15A | 109.6 |
| C3—C4—H4 | 121.6 | C15$^{i}$—C15—H15A | 109.6 |
| C5—C4—H4 | 121.6 | N5—C15—H15B | 109.6 |
| C4—C5—C6 | 122.9 (2) | C15$^{i}$—C15—H15B | 109.6 |
| C4—C5—N2 | 118.01 (19) | H15A—C15—H15B | 108.1 |
| C6—C5—N2 | 119.0 (2) | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O7—H7···O1 | 0.83 (1) | 1.68 (1) | 2.507 (2) | 173 (4) |
| N5—H5*A*···O2 | 0.89 | 1.88 | 2.732 (3) | 161 |
| N5—H5*B*···O8$^{ii}$ | 0.89 | 2.17 | 2.820 (3) | 129 |
| N5—H5*C*···O1$^{ii}$ | 0.89 | 2.02 | 2.899 (3) | 170 |

Symmetry code: (ii) $x+1, y, z$.