Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Diisopropyl{2-[2-(2-oxopyrrolidin-1-yl)-acetamido]ethyl}ammonium hydrogen sulfate

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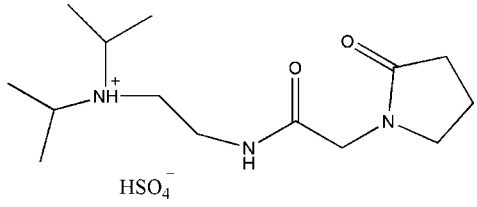
Received 12 May 2008; accepted 21 May 2008

Key indicators: single-crystal X-ray study; $T$ = 170 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.047; $wR$ factor = 0.133; data-to-parameter ratio = 14.6.

The structure of the title compound, $C_{14}H_{28}N_3O_2^+\cdot HSO_4^-$, a nootropic drug (pramiracetam) investigated for cognition-enhancing properties, is closely similar to that of the previously determined acetonitrile solvate, both structures being characterized by the presence of ribbons of hydrogen-bonded ions. The pyrrolidine ring adopts an envelope conformation.

## Related literature

For related literature, see: Claus *et al.* (1991); Gouliaev & Senning (1994); Mondadori *et al.* (1991); Pugsley *et al.* (1983). For a related structure, see: Bandoli *et al.* (1987).




## Experimental

### Crystal data

$C_{14}H_{28}N_3O_2^+\cdot HSO_4^-$
$M_r$ = 367.46
Triclinic, $P\overline{1}$
$a$ = 6.7834 (3) Å
$b$ = 11.1755 (4) Å
$c$ = 12.9012 (6) Å
$\alpha$ = 72.165 (4)°
$\beta$ = 89.394 (4)°
$\gamma$ = 89.509 (3)°
$V$ = 930.95 (7) Å$^3$
$Z$ = 2
Cu $K\alpha$ radiation
$\mu$ = 1.85 mm$^{-1}$
$T$ = 170 (2) K
0.50 × 0.25 × 0.10 mm

### Data collection

Oxford Diffraction Xcalibur PX Ultra CCD diffractometer
Absorption correction: multi-scan (*ABSPACK* in *CrysAlisPro RED*; Oxford Diffraction, 2006)
$T_{min}$ = 0.762, $T_{max}$ = 1.000 (expected range = 0.634–0.831)
7656 measured reflections
3356 independent reflections
3253 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.132
$S$ = 1.06
3356 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.57 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2···O3 | 0.86 (3) | 2.10 (3) | 2.948 (2) | 172 (2) |
| N3—H3···O4$^{i}$ | 0.97 (3) | 1.79 (3) | 2.764 (2) | 175 (2) |
| O6—H6···O1$^{ii}$ | 0.90 (4) | 1.68 (4) | 2.559 (2) | 167 (3) |
| C12—H12···O2$^{iii}$ | 1.00 | 2.40 | 3.362 (3) | 162 |
| C13—H131···O4$^{iv}$ | 0.98 | 2.59 | 3.559 (2) | 171 |
| C14—H143···O5 | 0.98 | 2.56 | 3.530 (2) | 172 |

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

Data collection: *CrysAlisPro CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlisPro CCD*; data reduction: *CrysAlisPro RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors acknowledge financial support from the Italian Ministero dell'Istruzione, dell'Universitá e della Ricerca.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2084).

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# supporting information

*Acta Cryst.* (2008). E**64**, o1160 [doi:10.1107/S1600536808015341]

# Diisopropyl{2-[2-(2-oxopyrrolidin-1-yl)acetamido]ethyl}ammonium hydrogen sulfate

**Massimo Bambagiotti-Alberti, Gianluca Bartolucci, Bruno Bruni, Silvia A. Coran and Massimo Di Vaira**

## S1. Comment

Pramiracetam is a nootropic drug (Gouliaev & Senning, 1994) whose neurochemical properties have been investigated (Pugsley *et al.*, 1983) also in view of possible applications as a memory aid (Mondadori *et al.*, 1991) and for symptomatic treatment of Alzheimer's desease (Claus *et al.*, 1991).

The contents of the asymmetric unit of the title compound (I) are shown in Fig 1. The atomic labelling is consistent with that previously adopted for the $CH_3CN$ solvate (Bandoli *et al.*, 1987) with which (I) is isomorphous and substantially isostructural, although the present conventional choice of labels for the axes does not match that of the previous report. There is a 3.8% reduction in the cell volume going from the solvated form to the present one, due to contraction of the two longest cell axes. The packing (Fig. 2) is controlled by a network of hydrogen bonds. The $HSO_4^-$ anion behaves as a hydrogen bond donor towards a carbonylic oxygen and acts as acceptor of two hydrogen bonds from the aminic and ammonium N atoms (details of hydrogen-bonding geometry have been provided in Table 1). In this way two centrosymmetric and adjacent loops, consisting of 14 and 18 non-hydrogen atoms, respectively, are formed. Each loop has contributions from parts of two anions and two cations and each of these ions contributes to two contiguous loops which share the N2—H2···O3—S strand. Such arrangement, combined with the operation of the c translation, generates ribbons in the structure (these were parallel to the a direction in the previously reported structure of the solvated form, due to the different labelling of cell axes). In the case of the $CH_3CN$ solvate the solvent molecules occupy large voids among the ribbons and are not involved in the network of hydrogen bonds. The largest difference in the conformation of the cation between the two structures is found for the C1—N1—C5—C6 torsion angle, whose value of -94.6 (2)° for (I) is significantly smaller than that, of -105.4(1.2)°, found for the structure of the solvate. The structure of (I) is stabilized by non-classical intermolecular and intramolecular hydrogen bonds of the type C—H···O (Table 1).

## S2. Experimental

Samples of pramiracetam were kindly provided by SIMS (SIMS srl, Reggello Firenze, Italy). Crystals of (I), suitable for X-ray diffraction analysis, were obtained by slow evaporation from 1:3 2-propanol:acetone solutions.

## S3. Refinement

A small fraction of data is missing from completeness because the structure appeared to be monoclinic at the time of data collection. It was impossible to collect a new set of data due to extreme difficulty to obtain suitable material for diffraction. Also, since crystals did not diffract strongly, it was deemed that collecting data at $\theta$ higher than 72° would not yield significant improvement. H atoms bound to carbon atoms were in geometrically generated positions, riding; the coordinates of those bound to N and O atoms were refined freely. The constraint $U(H) = 1.2U_{eq}(C,N)$ was applied [$U(H)$

= 1.5$U_{eq}$(C) for methyl group H atoms]. Bond distances involving refined hydrogen atoms: N2—H2 0.86 (3) Å, N3—H3 0.97 (3) Å, O6—H6 0.90 (4) Å. The only residual electron density of any numerical, but not chemical significance is in close proximity of the O and S atoms of the counterion. The existence of voids (57.0 Å$^3$) in the structure is likely due to the stability of the hydrogen-bonds framework, as the solvents used for crystallization could not fit into the available spacing.

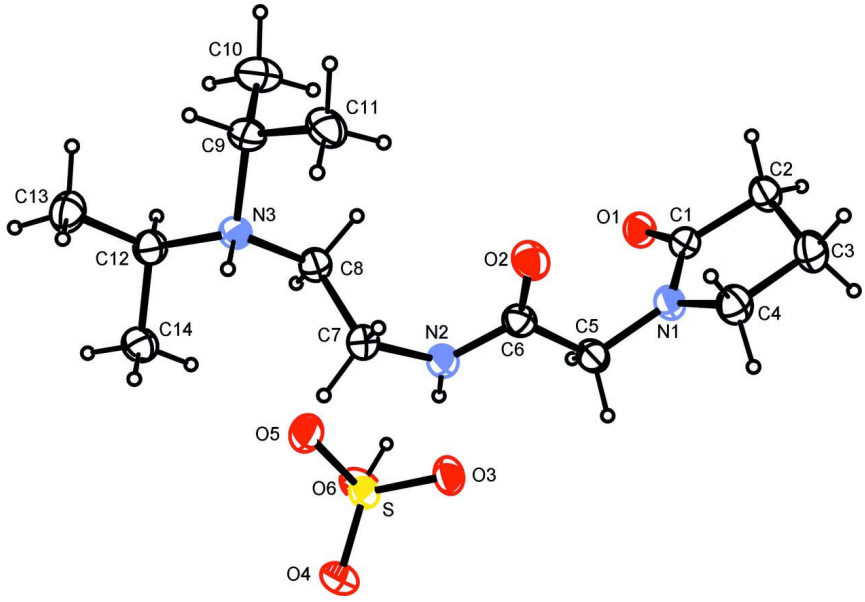


**Figure 1**

A view of the content of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

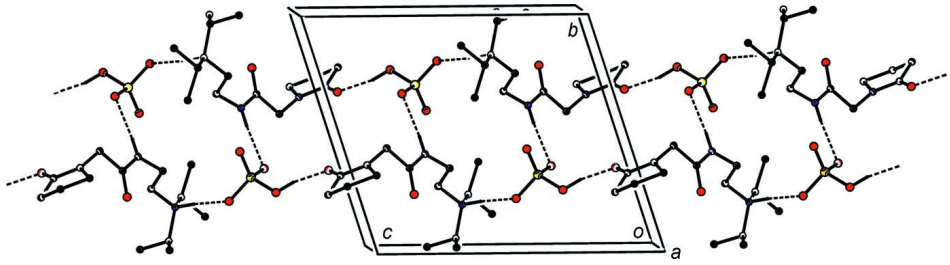


**Figure 2**

A view of the crystal packing in the structure of (I), showing the presence of ribbons formed by hydrogen–bonded ions. Hydrogen bonds are denoted by dashed lines. Only hydrogen atoms involved in the formation of hydrogen bonds are shown.

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*Crystal data*

$C_{14}H_{28}N_3O_2^+ \cdot HSO_4^-$
$M_r$ = 367.46
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 6.7834 (3) Å
$b$ = 11.1755 (4) Å
$c$ = 12.9012 (6) Å
$\alpha$ = 72.165 (4)°
$\beta$ = 89.394 (4)°
$\gamma$ = 89.509 (3)°

$V$ = 930.95 (7) Å$^3$
$Z$ = 2
$F$(000) = 396
$D_x$ = 1.311 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54180 Å
Cell parameters from 6722 reflections

$\theta$ = 4.6–72.4°
$\mu$ = 1.85 mm$^{-1}$
$T$ = 170 K
Prism, pale yellow
0.50 × 0.25 × 0.10 mm

*Data collection*

Oxford Diffraction Xcalibur PX Ultra CCD diffractometer
Radiation source: fine-focus sealed tube
Oxford Diffraction Enhance ULTRA assembly monochromator
Detector resolution: 8.1241 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (ABSPACK in *CrysAlis PRO* RED; Oxford Diffraction, 2006)

$T_{min}$ = 0.762, $T_{max}$ = 1.000
7656 measured reflections
3356 independent reflections
3253 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018
$\theta_{max}$ = 72.7°, $\theta_{min}$ = 4.6°
$h$ = −8→8
$k$ = −13→13
$l$ = −15→15

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.132
$S$ = 1.06
3356 reflections
230 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
$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 0.7081P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.57 e Å$^{-3}$

*Special details*

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S | 0.38398 (7) | 0.68601 (4) | 0.65914 (4) | 0.02428 (17) |
| O3 | 0.5651 (2) | 0.65687 (14) | 0.72078 (13) | 0.0327 (4) |
| O4 | 0.4059 (2) | 0.78663 (14) | 0.55696 (12) | 0.0308 (3) |
| O5 | 0.2944 (2) | 0.57503 (15) | 0.64603 (14) | 0.0386 (4) |
| O6 | 0.2374 (3) | 0.74531 (16) | 0.72349 (14) | 0.0384 (4) |
| H6 | 0.234 (5) | 0.703 (3) | 0.795 (3) | 0.058* |
| N1 | 1.0351 (2) | 0.37637 (16) | 0.93852 (14) | 0.0254 (4) |
| C1 | 0.9684 (3) | 0.33125 (18) | 1.04001 (16) | 0.0243 (4) |

| | | | | |
|---|---|---|---|---|
| O1 | 0.7977 (2) | 0.34687 (14) | 1.06959 (12) | 0.0289 (3) |
| C2 | 1.1312 (3) | 0.2564 (2) | 1.11073 (17) | 0.0287 (4) |
| H21 | 1.1096 | 0.1649 | 1.1271 | 0.034* |
| H22 | 1.1402 | 0.2768 | 1.1800 | 0.034* |
| C3 | 1.3171 (3) | 0.2979 (2) | 1.04077 (18) | 0.0328 (5) |
| H31 | 1.3827 | 0.3679 | 1.0584 | 0.039* |
| H32 | 1.4116 | 0.2272 | 1.0515 | 0.039* |
| C4 | 1.2393 (3) | 0.3403 (2) | 0.92434 (18) | 0.0310 (5) |
| H41 | 1.3151 | 0.4126 | 0.8779 | 0.037* |
| H42 | 1.2451 | 0.2710 | 0.8916 | 0.037* |
| C5 | 0.9126 (3) | 0.44164 (18) | 0.84733 (17) | 0.0267 (4) |
| H51 | 0.9903 | 0.5092 | 0.7960 | 0.032* |
| H52 | 0.8002 | 0.4815 | 0.8740 | 0.032* |
| C6 | 0.8339 (3) | 0.35436 (18) | 0.78717 (16) | 0.0254 (4) |
| O2 | 0.8971 (2) | 0.24667 (13) | 0.80310 (13) | 0.0322 (4) |
| N2 | 0.6967 (3) | 0.40757 (16) | 0.71317 (14) | 0.0268 (4) |
| H2 | 0.649 (4) | 0.479 (3) | 0.711 (2) | 0.032* |
| C7 | 0.6169 (3) | 0.34383 (19) | 0.64051 (17) | 0.0268 (4) |
| H71 | 0.7204 | 0.2906 | 0.6220 | 0.032* |
| H72 | 0.5733 | 0.4067 | 0.5722 | 0.032* |
| C8 | 0.4429 (3) | 0.26239 (18) | 0.69493 (16) | 0.0254 (4) |
| H81 | 0.4831 | 0.2079 | 0.7678 | 0.031* |
| H82 | 0.3340 | 0.3173 | 0.7052 | 0.031* |
| N3 | 0.3696 (2) | 0.18130 (15) | 0.62949 (14) | 0.0236 (4) |
| H3 | 0.449 (4) | 0.197 (2) | 0.564 (2) | 0.028* |
| C9 | 0.3977 (3) | 0.04104 (18) | 0.69036 (18) | 0.0289 (4) |
| H9 | 0.3453 | −0.0071 | 0.6429 | 0.035* |
| C10 | 0.2806 (4) | 0.0020 (2) | 0.7957 (2) | 0.0398 (5) |
| H101 | 0.1418 | 0.0254 | 0.7806 | 0.060* |
| H102 | 0.3327 | 0.0445 | 0.8456 | 0.060* |
| H103 | 0.2914 | −0.0892 | 0.8291 | 0.060* |
| C11 | 0.6165 (3) | 0.0111 (2) | 0.70570 (19) | 0.0342 (5) |
| H111 | 0.6351 | −0.0801 | 0.7359 | 0.051* |
| H112 | 0.6708 | 0.0525 | 0.7559 | 0.051* |
| H113 | 0.6847 | 0.0415 | 0.6352 | 0.051* |
| C12 | 0.1589 (3) | 0.21577 (18) | 0.58962 (17) | 0.0264 (4) |
| H12 | 0.0700 | 0.2061 | 0.6540 | 0.032* |
| C13 | 0.0884 (3) | 0.1305 (2) | 0.5264 (2) | 0.0341 (5) |
| H131 | −0.0412 | 0.1593 | 0.4953 | 0.051* |
| H132 | 0.0780 | 0.0443 | 0.5754 | 0.051* |
| H133 | 0.1825 | 0.1328 | 0.4677 | 0.051* |
| C14 | 0.1534 (3) | 0.35207 (19) | 0.51788 (18) | 0.0297 (4) |
| H141 | 0.0187 | 0.3748 | 0.4923 | 0.045* |
| H142 | 0.2418 | 0.3626 | 0.4552 | 0.045* |
| H143 | 0.1963 | 0.4067 | 0.5599 | 0.045* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S | 0.0230 (3) | 0.0252 (3) | 0.0239 (3) | 0.00295 (18) | −0.0020 (2) | −0.00645 (19) |
| O3 | 0.0279 (8) | 0.0345 (8) | 0.0357 (8) | 0.0053 (6) | −0.0098 (7) | −0.0106 (6) |
| O4 | 0.0319 (7) | 0.0303 (7) | 0.0256 (8) | 0.0063 (6) | 0.0024 (6) | −0.0022 (6) |
| O5 | 0.0385 (9) | 0.0306 (8) | 0.0474 (10) | −0.0018 (6) | −0.0117 (7) | −0.0125 (7) |
| O6 | 0.0424 (9) | 0.0405 (9) | 0.0283 (8) | 0.0153 (7) | 0.0044 (7) | −0.0053 (7) |
| N1 | 0.0230 (8) | 0.0282 (8) | 0.0241 (9) | 0.0020 (6) | −0.0028 (7) | −0.0067 (7) |
| C1 | 0.0241 (9) | 0.0234 (9) | 0.0252 (10) | −0.0011 (7) | −0.0019 (8) | −0.0072 (7) |
| O1 | 0.0231 (7) | 0.0332 (8) | 0.0289 (8) | 0.0015 (6) | 0.0000 (6) | −0.0076 (6) |
| C2 | 0.0264 (10) | 0.0312 (10) | 0.0266 (10) | 0.0037 (8) | −0.0050 (8) | −0.0062 (8) |
| C3 | 0.0243 (10) | 0.0404 (12) | 0.0331 (12) | 0.0042 (8) | −0.0041 (9) | −0.0104 (9) |
| C4 | 0.0248 (10) | 0.0379 (11) | 0.0294 (11) | 0.0019 (8) | 0.0013 (9) | −0.0091 (9) |
| C5 | 0.0295 (10) | 0.0252 (9) | 0.0244 (10) | 0.0024 (8) | −0.0043 (8) | −0.0063 (8) |
| C6 | 0.0258 (9) | 0.0259 (9) | 0.0232 (10) | 0.0002 (7) | 0.0007 (8) | −0.0057 (8) |
| O2 | 0.0353 (8) | 0.0266 (7) | 0.0358 (8) | 0.0074 (6) | −0.0075 (7) | −0.0111 (6) |
| N2 | 0.0289 (9) | 0.0230 (8) | 0.0284 (9) | 0.0009 (7) | −0.0062 (7) | −0.0073 (7) |
| C7 | 0.0274 (10) | 0.0274 (10) | 0.0254 (10) | −0.0018 (8) | −0.0034 (8) | −0.0076 (8) |
| C8 | 0.0256 (9) | 0.0260 (9) | 0.0246 (10) | 0.0001 (7) | −0.0019 (8) | −0.0076 (8) |
| N3 | 0.0220 (8) | 0.0221 (8) | 0.0256 (9) | 0.0010 (6) | −0.0015 (7) | −0.0057 (6) |
| C9 | 0.0315 (11) | 0.0209 (9) | 0.0314 (11) | 0.0025 (8) | −0.0032 (9) | −0.0038 (8) |
| C10 | 0.0436 (13) | 0.0301 (11) | 0.0390 (13) | 0.0002 (9) | 0.0036 (11) | −0.0007 (9) |
| C11 | 0.0336 (11) | 0.0307 (11) | 0.0355 (12) | 0.0085 (9) | −0.0063 (9) | −0.0062 (9) |
| C12 | 0.0213 (9) | 0.0265 (10) | 0.0304 (11) | 0.0009 (7) | −0.0007 (8) | −0.0074 (8) |
| C13 | 0.0282 (10) | 0.0330 (11) | 0.0430 (13) | 0.0013 (8) | −0.0073 (9) | −0.0145 (10) |
| C14 | 0.0262 (10) | 0.0269 (10) | 0.0335 (11) | 0.0043 (8) | −0.0033 (9) | −0.0056 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S—O5 | 1.4422 (16) | C7—H71 | 0.9900 |
| S—O3 | 1.4504 (14) | C7—H72 | 0.9900 |
| S—O4 | 1.4543 (15) | C8—N3 | 1.505 (2) |
| S—O6 | 1.5574 (16) | C8—H81 | 0.9900 |
| O6—H6 | 0.90 (4) | C8—H82 | 0.9900 |
| N1—C1 | 1.327 (3) | N3—C12 | 1.530 (2) |
| N1—C5 | 1.446 (2) | N3—C9 | 1.534 (2) |
| N1—C4 | 1.465 (3) | N3—H3 | 0.97 (3) |
| C1—O1 | 1.243 (2) | C9—C10 | 1.512 (3) |
| C1—C2 | 1.514 (3) | C9—C11 | 1.521 (3) |
| C2—C3 | 1.533 (3) | C9—H9 | 1.0000 |
| C2—H21 | 0.9900 | C10—H101 | 0.9800 |
| C2—H22 | 0.9900 | C10—H102 | 0.9800 |
| C3—C4 | 1.528 (3) | C10—H103 | 0.9800 |
| C3—H31 | 0.9900 | C11—H111 | 0.9800 |
| C3—H32 | 0.9900 | C11—H112 | 0.9800 |
| C4—H41 | 0.9900 | C11—H113 | 0.9800 |
| C4—H42 | 0.9900 | C12—C13 | 1.514 (3) |

| | | | |
|---|---|---|---|
| C5—C6 | 1.523 (3) | C12—C14 | 1.521 (3) |
| C5—H51 | 0.9900 | C12—H12 | 1.0000 |
| C5—H52 | 0.9900 | C13—H131 | 0.9800 |
| C6—O2 | 1.231 (2) | C13—H132 | 0.9800 |
| C6—N2 | 1.339 (3) | C13—H133 | 0.9800 |
| N2—C7 | 1.451 (2) | C14—H141 | 0.9800 |
| N2—H2 | 0.86 (3) | C14—H142 | 0.9800 |
| C7—C8 | 1.525 (3) | C14—H143 | 0.9800 |
| | | | |
| O5—S—O3 | 111.94 (9) | N3—C8—C7 | 112.54 (16) |
| O5—S—O4 | 112.97 (10) | N3—C8—H81 | 109.1 |
| O3—S—O4 | 113.20 (9) | C7—C8—H81 | 109.1 |
| O5—S—O6 | 108.27 (10) | N3—C8—H82 | 109.1 |
| O3—S—O6 | 107.71 (9) | C7—C8—H82 | 109.1 |
| O4—S—O6 | 102.03 (9) | H81—C8—H82 | 107.8 |
| S—O6—H6 | 113 (2) | C8—N3—C12 | 112.04 (15) |
| C1—N1—C5 | 123.65 (17) | C8—N3—C9 | 111.57 (15) |
| C1—N1—C4 | 113.69 (16) | C12—N3—C9 | 113.44 (15) |
| C5—N1—C4 | 122.23 (17) | C8—N3—H3 | 108.8 (14) |
| O1—C1—N1 | 124.46 (18) | C12—N3—H3 | 104.9 (14) |
| O1—C1—C2 | 126.64 (18) | C9—N3—H3 | 105.5 (15) |
| N1—C1—C2 | 108.87 (17) | C10—C9—C11 | 113.40 (19) |
| C1—C2—C3 | 103.44 (17) | C10—C9—N3 | 111.46 (18) |
| C1—C2—H21 | 111.1 | C11—C9—N3 | 109.53 (16) |
| C3—C2—H21 | 111.1 | C10—C9—H9 | 107.4 |
| C1—C2—H22 | 111.1 | C11—C9—H9 | 107.4 |
| C3—C2—H22 | 111.1 | N3—C9—H9 | 107.4 |
| H21—C2—H22 | 109.0 | C9—C10—H101 | 109.5 |
| C4—C3—C2 | 103.68 (16) | C9—C10—H102 | 109.5 |
| C4—C3—H31 | 111.0 | H101—C10—H102 | 109.5 |
| C2—C3—H31 | 111.0 | C9—C10—H103 | 109.5 |
| C4—C3—H32 | 111.0 | H101—C10—H103 | 109.5 |
| C2—C3—H32 | 111.0 | H102—C10—H103 | 109.5 |
| H31—C3—H32 | 109.0 | C9—C11—H111 | 109.5 |
| N1—C4—C3 | 102.97 (17) | C9—C11—H112 | 109.5 |
| N1—C4—H41 | 111.2 | H111—C11—H112 | 109.5 |
| C3—C4—H41 | 111.2 | C9—C11—H113 | 109.5 |
| N1—C4—H42 | 111.2 | H111—C11—H113 | 109.5 |
| C3—C4—H42 | 111.2 | H112—C11—H113 | 109.5 |
| H41—C4—H42 | 109.1 | C13—C12—C14 | 110.05 (18) |
| N1—C5—C6 | 112.43 (16) | C13—C12—N3 | 110.61 (16) |
| N1—C5—H51 | 109.1 | C14—C12—N3 | 109.11 (16) |
| C6—C5—H51 | 109.1 | C13—C12—H12 | 109.0 |
| N1—C5—H52 | 109.1 | C14—C12—H12 | 109.0 |
| C6—C5—H52 | 109.1 | N3—C12—H12 | 109.0 |
| H51—C5—H52 | 107.9 | C12—C13—H131 | 109.5 |
| O2—C6—N2 | 123.75 (18) | C12—C13—H132 | 109.5 |
| O2—C6—C5 | 122.51 (18) | H131—C13—H132 | 109.5 |

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| N2—C6—C5 | 113.70 (17) | C12—C13—H133 | 109.5 |
| C6—N2—C7 | 122.02 (17) | H131—C13—H133 | 109.5 |
| C6—N2—H2 | 119.3 (17) | H132—C13—H133 | 109.5 |
| C7—N2—H2 | 118.6 (17) | C12—C14—H141 | 109.5 |
| N2—C7—C8 | 109.99 (17) | C12—C14—H142 | 109.5 |
| N2—C7—H71 | 109.7 | H141—C14—H142 | 109.5 |
| C8—C7—H71 | 109.7 | C12—C14—H143 | 109.5 |
| N2—C7—H72 | 109.7 | H141—C14—H143 | 109.5 |
| C8—C7—H72 | 109.7 | H142—C14—H143 | 109.5 |
| H71—C7—H72 | 108.2 | | |

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| C5—N1—C1—O1 | −5.0 (3) | O2—C6—N2—C7 | −3.3 (3) |
| C4—N1—C1—O1 | −177.65 (18) | C5—C6—N2—C7 | 174.22 (18) |
| C5—N1—C1—C2 | 173.48 (17) | C6—N2—C7—C8 | 87.1 (2) |
| C4—N1—C1—C2 | 0.8 (2) | N2—C7—C8—N3 | −172.82 (15) |
| O1—C1—C2—C3 | −165.6 (2) | C7—C8—N3—C12 | −115.80 (18) |
| N1—C1—C2—C3 | 16.0 (2) | C7—C8—N3—C9 | 115.77 (18) |
| C1—C2—C3—C4 | −25.4 (2) | C8—N3—C9—C10 | 62.2 (2) |
| C1—N1—C4—C3 | −17.3 (2) | C12—N3—C9—C10 | −65.5 (2) |
| C5—N1—C4—C3 | 169.93 (18) | C8—N3—C9—C11 | −64.1 (2) |
| C2—C3—C4—N1 | 25.7 (2) | C12—N3—C9—C11 | 168.21 (18) |
| C1—N1—C5—C6 | −94.6 (2) | C8—N3—C12—C13 | −178.70 (17) |
| C4—N1—C5—C6 | 77.4 (2) | C9—N3—C12—C13 | −51.3 (2) |
| N1—C5—C6—O2 | −12.1 (3) | C8—N3—C12—C14 | 60.1 (2) |
| N1—C5—C6—N2 | 170.35 (18) | C9—N3—C12—C14 | −172.46 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O3 | 0.86 (3) | 2.10 (3) | 2.948 (2) | 172 (2) |
| N3—H3···O4$^{i}$ | 0.97 (3) | 1.79 (3) | 2.764 (2) | 175 (2) |
| O6—H6···O1$^{ii}$ | 0.90 (4) | 1.68 (4) | 2.559 (2) | 167 (3) |
| C12—H12···O2$^{iii}$ | 1.00 | 2.40 | 3.362 (3) | 162 |
| C13—H131···O4$^{iv}$ | 0.98 | 2.59 | 3.559 (2) | 171 |
| C14—H143···O5 | 0.98 | 2.56 | 3.530 (2) | 172 |

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