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# 4-(4-Carboxybenzyl)-1-methylpiperazin-1-ium picrate

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Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.040; $wR$ factor = 0.104; data-to-parameter ratio = 11.7.

The title compound, $C_{13}H_{19}N_2O_2^+\cdot C_6H_2N_3O_7^-$, is a salt obtained by cocrystallization of 4-[(4-methylpiperazin-1-yl)methyl]benzoic acid and picric acid. The cations adopt an 'L-shaped' conformation and are linked into chains along [010] by O—H···N hydrogen bonds. The NH group of each piperazinium ring forms a hydrogen bond to the phenolate O atom of a picrate anion, and the picrate anions form face-to-face contacts with an interplanar separation of 3.023 (1) Å.

## Related literature

For general background, see: Druker *et al.* (2001). For related structures, see: Swamy *et al.* (2007); Bindya *et al.* (2007); Sarojini *et al.* (2007); Wang & Jia (2008).

## Experimental

### Crystal data

$C_{13}H_{19}N_2O_2^+\cdot C_6H_2N_3O_7^-$
$M_r$ = 463.41
Triclinic, $P\overline{1}$
$a$ = 7.3020 (12) Å
$b$ = 9.5993 (16) Å
$c$ = 15.131 (3) Å
$\alpha$ = 86.448 (2)°
$\beta$ = 79.145 (2)°
$\gamma$ = 79.950 (2)°
$V$ = 1025.2 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.12 mm$^{-1}$
$T$ = 296 K
0.30 × 0.20 × 0.20 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min}$ = 0.965, $T_{max}$ = 0.976
5373 measured reflections
3565 independent reflections
2745 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.104
$S$ = 1.06
3565 reflections
305 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O8—H8···N4$^{i}$ | 0.82 | 1.79 | 2.6006 (19) | 172 |
| N5—H5$A$···O1$^{ii}$ | 0.89 (2) | 1.89 (2) | 2.734 (2) | 156.9 (18) |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

QNMHA thanks R. L. Fine Chem, Bangalore, for a gift sample of 4-[(4-methylpiperazin-1-yl)methyl]benzoic acid. HSY thanks the University of Mysore for research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2341).

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# supporting information

*Acta Cryst.* (2009). E**65**, o518 [doi:10.1107/S1600536809004474]

## 4-(4-Carboxybenzyl)-1-methylpiperazin-1-ium picrate

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### S1. Comment

4-[(4-Methylpiperazin-1-yl)methyl]benzoic acid is an intermediate in the synthesis of Imatinib, a drug used to treat certain types of cancer. Its mesylate salt is currently marketed by Novartis as Gleevec (Druker *et al.*, 2001). Picric acid forms salts or charge-transfer complexes with many organic compounds. Crystal structures of picrate complexes with organic compounds of pharmaceutical importance *viz.*, desipraminium picrate (Swamy *et al.*, 2007) and amitriptylinium picrate (Bindya *et al.*, 2007) have been reported. A three-dimensional network in piperazine-1,4-diium-picrate-piperazine (1/2/1) is reported recently (Wang & Jia, 2008).

### S2. Experimental

The title compound was prepared by taking equimolar quantities of picric acid (0.92 g, 2 mmol) and 4-[(4-methyl-piperazin-1-yl)methyl]benzoic acid (0.47 g, 2 mmol) and dissolving them in water. The solution was stirred well at room temperature and slow evaporation of the solution resulted in the formation of the yellow coloured salt (yield 95%). Crystals suitable for single-crystal X-ray diffraction were grown from dimethyl formamide solvent.

### S3. Refinement

H atoms bound to C atoms were placed at calculated positions and refined using a riding model, with C—H = 0.93–0.97 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(C) for methyl H atoms. The H atom of the OH group was also placed geometrically and allowed to ride with $U_{iso}$(H) = 1.5$U_{eq}$(O). The H atom of the NH group was located in a difference Fourier map and refined isotropically without restraint.

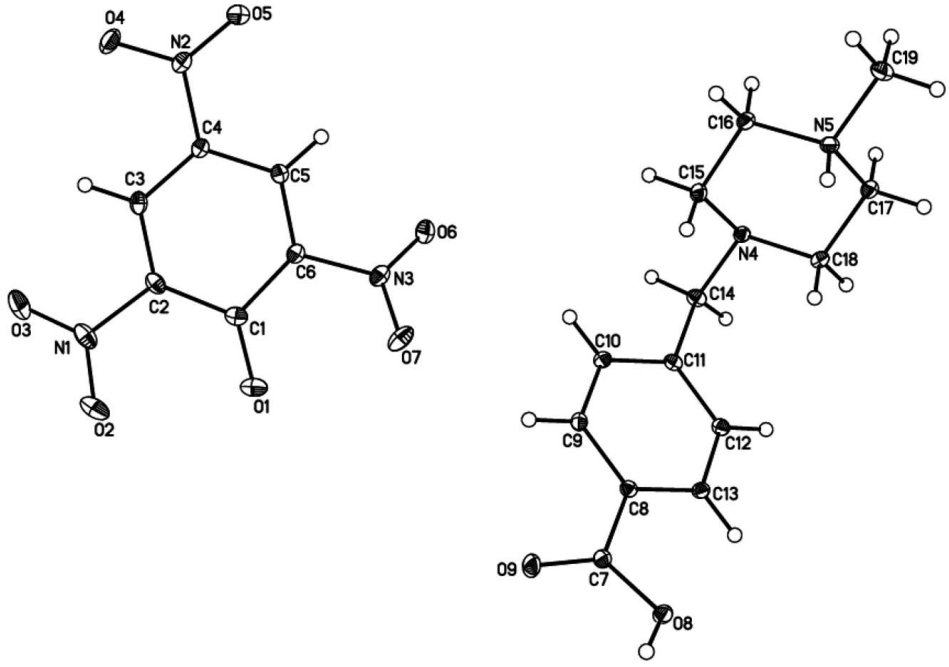


**Figure 1**

Molecular structure with displacement ellipsoids drawn at the 30% probability level for non-H atoms.

### 4-(4-Carboxybenzyl)-1-methylpiperazin-1-ium picrate

*Crystal data*

$C_{13}H_{19}N_2O_2^+ \cdot C_6H_2N_3O_7^-$
$M_r = 463.41$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.3020$ (12) Å
$b = 9.5993$ (16) Å
$c = 15.131$ (3) Å
$\alpha = 86.448$ (2)°
$\beta = 79.145$ (2)°
$\gamma = 79.950$ (2)°
$V = 1025.2$ (3) Å$^3$
$Z = 2$
$F(000) = 484$
$D_x = 1.501$ Mg m$^{-3}$
Melting point = 510–504 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1962 reflections
$\theta = 2.5$–26.9°
$\mu = 0.12$ mm$^{-1}$
$T = 296$ K
Block, colourless
0.30 × 0.20 × 0.20 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.965$, $T_{max} = 0.976$
5373 measured reflections
3565 independent reflections
2745 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -8 \rightarrow 6$
$k = -11 \rightarrow 9$
$l = -18 \rightarrow 18$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.06$
3565 reflections
305 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
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.2218P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.023 (2)

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.5333 (3) | 1.0778 (2) | 0.14228 (14) | 0.0426 (5) |
| C2 | 0.6431 (3) | 1.0691 (2) | 0.05175 (13) | 0.0438 (5) |
| C3 | 0.7751 (3) | 0.9547 (2) | 0.02127 (13) | 0.0430 (5) |
| H3 | 0.8395 | 0.9546 | −0.0379 | 0.052* |
| C4 | 0.8126 (3) | 0.8398 (2) | 0.07793 (12) | 0.0379 (4) |
| C5 | 0.7175 (2) | 0.83776 (19) | 0.16598 (12) | 0.0359 (4) |
| H5 | 0.7422 | 0.7595 | 0.2039 | 0.043* |
| C6 | 0.5870 (3) | 0.9521 (2) | 0.19627 (12) | 0.0372 (4) |
| C7 | 0.1636 (3) | 1.33630 (19) | 0.60024 (12) | 0.0366 (4) |
| C8 | 0.1280 (2) | 1.18702 (18) | 0.60753 (11) | 0.0320 (4) |
| C9 | 0.2178 (3) | 1.09572 (19) | 0.53938 (12) | 0.0380 (4) |
| H9 | 0.2943 | 1.1292 | 0.4892 | 0.046* |
| C10 | 0.1949 (3) | 0.95535 (19) | 0.54527 (12) | 0.0391 (4) |
| H10 | 0.2557 | 0.8954 | 0.4989 | 0.047* |
| C11 | 0.0818 (2) | 0.90303 (18) | 0.61993 (12) | 0.0349 (4) |
| C12 | −0.0108 (2) | 0.99528 (18) | 0.68722 (12) | 0.0361 (4) |
| H12 | −0.0897 | 0.9622 | 0.7367 | 0.043* |
| C13 | 0.0123 (2) | 1.13606 (18) | 0.68187 (12) | 0.0348 (4) |
| H13 | −0.0494 | 1.1964 | 0.7279 | 0.042* |
| C14 | 0.0608 (3) | 0.74891 (19) | 0.62770 (13) | 0.0413 (5) |
| H14A | −0.0640 | 0.7413 | 0.6616 | 0.050* |
| H14B | 0.0677 | 0.7156 | 0.5677 | 0.050* |
| C15 | 0.3984 (3) | 0.6541 (2) | 0.62183 (12) | 0.0399 (5) |

| | | | | |
|---|---|---|---|---|
| H15A | 0.4281 | 0.7488 | 0.6208 | 0.048* |
| H15B | 0.4063 | 0.6282 | 0.5601 | 0.048* |
| C16 | 0.5410 (3) | 0.5522 (2) | 0.66450 (12) | 0.0415 (5) |
| H16A | 0.5196 | 0.4562 | 0.6598 | 0.050* |
| H16B | 0.6674 | 0.5591 | 0.6324 | 0.050* |
| C17 | 0.3292 (3) | 0.5816 (2) | 0.80965 (12) | 0.0402 (5) |
| H17A | 0.3189 | 0.6046 | 0.8721 | 0.048* |
| H17B | 0.2985 | 0.4875 | 0.8083 | 0.048* |
| C18 | 0.1914 (3) | 0.68674 (19) | 0.76667 (12) | 0.0375 (4) |
| H18A | 0.0639 | 0.6846 | 0.7991 | 0.045* |
| H18B | 0.2190 | 0.7813 | 0.7701 | 0.045* |
| C19 | 0.6653 (3) | 0.4834 (2) | 0.80485 (15) | 0.0598 (6) |
| H19A | 0.6595 | 0.5121 | 0.8651 | 0.090* |
| H19B | 0.7903 | 0.4841 | 0.7710 | 0.090* |
| H19C | 0.6355 | 0.3896 | 0.8065 | 0.090* |
| N1 | 0.6141 (3) | 1.1856 (2) | −0.01420 (15) | 0.0587 (5) |
| N2 | 0.9524 (2) | 0.71935 (19) | 0.04516 (11) | 0.0471 (4) |
| N3 | 0.4925 (2) | 0.9427 (2) | 0.28970 (11) | 0.0469 (4) |
| N4 | 0.2038 (2) | 0.65332 (14) | 0.67160 (9) | 0.0340 (4) |
| N5 | 0.5264 (2) | 0.58329 (17) | 0.76126 (10) | 0.0375 (4) |
| O1 | 0.4059 (2) | 1.17657 (15) | 0.17135 (11) | 0.0614 (4) |
| O2 | 0.5114 (3) | 1.2956 (2) | 0.00975 (14) | 0.0921 (6) |
| O3 | 0.6952 (3) | 1.16659 (19) | −0.09220 (12) | 0.0799 (6) |
| O4 | 1.0379 (2) | 0.72647 (18) | −0.03240 (10) | 0.0680 (5) |
| O5 | 0.9804 (2) | 0.61680 (16) | 0.09632 (11) | 0.0649 (5) |
| O6 | 0.4639 (2) | 0.82634 (18) | 0.32167 (10) | 0.0633 (4) |
| O7 | 0.4470 (2) | 1.05126 (19) | 0.33248 (10) | 0.0707 (5) |
| O8 | 0.1067 (2) | 1.40458 (13) | 0.67570 (8) | 0.0445 (4) |
| H8 | 0.1397 | 1.4825 | 0.6691 | 0.067* |
| O9 | 0.2400 (2) | 1.38891 (15) | 0.53152 (9) | 0.0605 (4) |
| H5A | 0.551 (3) | 0.669 (2) | 0.7674 (13) | 0.045 (6)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0386 (11) | 0.0359 (11) | 0.0586 (13) | −0.0106 (8) | −0.0166 (9) | −0.0054 (9) |
| C2 | 0.0462 (12) | 0.0407 (11) | 0.0508 (12) | −0.0163 (9) | −0.0195 (10) | 0.0092 (9) |
| C3 | 0.0449 (11) | 0.0537 (13) | 0.0350 (10) | −0.0208 (10) | −0.0079 (9) | 0.0021 (9) |
| C4 | 0.0359 (10) | 0.0421 (11) | 0.0355 (10) | −0.0087 (8) | −0.0032 (8) | −0.0036 (8) |
| C5 | 0.0377 (10) | 0.0382 (10) | 0.0345 (10) | −0.0097 (8) | −0.0102 (8) | −0.0007 (8) |
| C6 | 0.0368 (10) | 0.0426 (11) | 0.0348 (10) | −0.0100 (8) | −0.0079 (8) | −0.0059 (8) |
| C7 | 0.0393 (10) | 0.0345 (10) | 0.0353 (10) | −0.0079 (8) | −0.0036 (8) | −0.0002 (8) |
| C8 | 0.0339 (9) | 0.0298 (9) | 0.0334 (9) | −0.0060 (7) | −0.0086 (8) | −0.0001 (7) |
| C9 | 0.0457 (11) | 0.0366 (10) | 0.0307 (9) | −0.0071 (8) | −0.0045 (8) | 0.0000 (8) |
| C10 | 0.0491 (11) | 0.0327 (10) | 0.0349 (10) | −0.0028 (8) | −0.0081 (9) | −0.0067 (8) |
| C11 | 0.0360 (10) | 0.0296 (10) | 0.0423 (10) | −0.0070 (7) | −0.0141 (8) | 0.0004 (8) |
| C12 | 0.0311 (10) | 0.0339 (10) | 0.0415 (10) | −0.0064 (7) | −0.0026 (8) | 0.0042 (8) |
| C13 | 0.0327 (9) | 0.0311 (10) | 0.0378 (10) | −0.0029 (7) | −0.0008 (8) | −0.0027 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C14 | 0.0461 (11) | 0.0317 (10) | 0.0503 (11) | −0.0104 (8) | −0.0157 (9) | −0.0015 (8) |
| C15 | 0.0448 (11) | 0.0371 (10) | 0.0347 (10) | −0.0087 (8) | 0.0013 (8) | 0.0020 (8) |
| C16 | 0.0423 (11) | 0.0371 (11) | 0.0385 (10) | −0.0016 (8) | 0.0047 (8) | −0.0018 (8) |
| C17 | 0.0392 (10) | 0.0418 (11) | 0.0348 (10) | −0.0040 (8) | 0.0030 (8) | −0.0016 (8) |
| C18 | 0.0349 (10) | 0.0371 (10) | 0.0380 (10) | −0.0026 (8) | −0.0013 (8) | −0.0070 (8) |
| C19 | 0.0513 (13) | 0.0579 (14) | 0.0596 (14) | 0.0144 (11) | −0.0087 (11) | 0.0092 (11) |
| N1 | 0.0678 (13) | 0.0507 (12) | 0.0688 (14) | −0.0265 (10) | −0.0316 (11) | 0.0184 (10) |
| N2 | 0.0420 (10) | 0.0529 (11) | 0.0439 (10) | −0.0091 (8) | 0.0012 (8) | −0.0076 (8) |
| N3 | 0.0368 (9) | 0.0614 (12) | 0.0420 (9) | −0.0061 (8) | −0.0046 (7) | −0.0111 (9) |
| N4 | 0.0385 (8) | 0.0289 (8) | 0.0338 (8) | −0.0064 (6) | −0.0031 (6) | −0.0028 (6) |
| N5 | 0.0363 (9) | 0.0317 (9) | 0.0407 (9) | −0.0006 (7) | −0.0023 (7) | −0.0001 (7) |
| O1 | 0.0513 (9) | 0.0413 (9) | 0.0904 (12) | −0.0006 (7) | −0.0138 (8) | −0.0095 (8) |
| O2 | 0.1085 (16) | 0.0526 (11) | 0.1104 (16) | 0.0045 (11) | −0.0328 (12) | 0.0230 (11) |
| O3 | 0.1177 (16) | 0.0729 (12) | 0.0587 (11) | −0.0338 (11) | −0.0321 (11) | 0.0242 (9) |
| O4 | 0.0656 (10) | 0.0825 (12) | 0.0461 (9) | −0.0069 (9) | 0.0138 (8) | −0.0138 (8) |
| O5 | 0.0638 (10) | 0.0524 (10) | 0.0677 (10) | 0.0059 (8) | −0.0006 (8) | 0.0038 (8) |
| O6 | 0.0623 (10) | 0.0701 (11) | 0.0503 (9) | −0.0117 (8) | 0.0055 (7) | 0.0075 (8) |
| O7 | 0.0693 (11) | 0.0822 (12) | 0.0591 (10) | −0.0126 (9) | 0.0035 (8) | −0.0371 (9) |
| O8 | 0.0599 (9) | 0.0308 (7) | 0.0409 (7) | −0.0161 (6) | 0.0051 (6) | −0.0049 (6) |
| O9 | 0.0948 (12) | 0.0441 (9) | 0.0388 (8) | −0.0271 (8) | 0.0105 (8) | 0.0014 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.244 (2) | C14—H14B | 0.970 |
| C1—C2 | 1.450 (3) | C15—N4 | 1.479 (2) |
| C1—C6 | 1.453 (3) | C15—C16 | 1.509 (3) |
| C2—C3 | 1.369 (3) | C15—H15A | 0.970 |
| C2—N1 | 1.466 (3) | C15—H15B | 0.970 |
| C3—C4 | 1.375 (3) | C16—N5 | 1.493 (2) |
| C3—H3 | 0.930 | C16—H16A | 0.970 |
| C4—C5 | 1.382 (2) | C16—H16B | 0.970 |
| C4—N2 | 1.447 (2) | C17—N5 | 1.490 (2) |
| C5—C6 | 1.362 (2) | C17—C18 | 1.505 (2) |
| C5—H5 | 0.930 | C17—H17A | 0.970 |
| C6—N3 | 1.456 (2) | C17—H17B | 0.970 |
| C7—O9 | 1.209 (2) | C18—N4 | 1.476 (2) |
| C7—O8 | 1.313 (2) | C18—H18A | 0.970 |
| C7—C8 | 1.494 (2) | C18—H18B | 0.970 |
| C8—C9 | 1.385 (2) | C19—N5 | 1.489 (2) |
| C8—C13 | 1.391 (2) | C19—H19A | 0.960 |
| C9—C10 | 1.382 (3) | C19—H19B | 0.960 |
| C9—H9 | 0.930 | C19—H19C | 0.960 |
| C10—C11 | 1.390 (3) | N1—O2 | 1.215 (3) |
| C10—H10 | 0.930 | N1—O3 | 1.226 (3) |
| C11—C12 | 1.386 (2) | N2—O4 | 1.225 (2) |
| C11—C14 | 1.509 (2) | N2—O5 | 1.227 (2) |
| C12—C13 | 1.386 (2) | N3—O7 | 1.223 (2) |
| C12—H12 | 0.930 | N3—O6 | 1.226 (2) |

| | | | |
|---|---|---|---|
| C13—H13 | 0.930 | N5—H5A | 0.89 (2) |
| C14—N4 | 1.491 (2) | O8—H8 | 0.820 |
| C14—H14A | 0.970 | | |

| | | | |
|---|---|---|---|
| O1—C1—C2 | 125.88 (19) | C16—C15—H15A | 109.3 |
| O1—C1—C6 | 122.99 (19) | N4—C15—H15B | 109.3 |
| C2—C1—C6 | 111.10 (16) | C16—C15—H15B | 109.3 |
| C3—C2—C1 | 123.83 (18) | H15A—C15—H15B | 108.0 |
| C3—C2—N1 | 115.70 (19) | N5—C16—C15 | 111.14 (14) |
| C1—C2—N1 | 120.46 (19) | N5—C16—H16A | 109.4 |
| C2—C3—C4 | 120.19 (18) | C15—C16—H16A | 109.4 |
| C2—C3—H3 | 119.9 | N5—C16—H16B | 109.4 |
| C4—C3—H3 | 119.9 | C15—C16—H16B | 109.4 |
| C3—C4—C5 | 120.72 (17) | H16A—C16—H16B | 108.0 |
| C3—C4—N2 | 119.81 (17) | N5—C17—C18 | 110.62 (15) |
| C5—C4—N2 | 119.47 (17) | N5—C17—H17A | 109.5 |
| C6—C5—C4 | 118.97 (17) | C18—C17—H17A | 109.5 |
| C6—C5—H5 | 120.5 | N5—C17—H17B | 109.5 |
| C4—C5—H5 | 120.5 | C18—C17—H17B | 109.5 |
| C5—C6—C1 | 125.15 (17) | H17A—C17—H17B | 108.1 |
| C5—C6—N3 | 115.99 (17) | N4—C18—C17 | 110.48 (14) |
| C1—C6—N3 | 118.84 (16) | N4—C18—H18A | 109.6 |
| O9—C7—O8 | 123.05 (17) | C17—C18—H18A | 109.6 |
| O9—C7—C8 | 123.12 (16) | N4—C18—H18B | 109.6 |
| O8—C7—C8 | 113.82 (15) | C17—C18—H18B | 109.6 |
| C9—C8—C13 | 119.15 (16) | H18A—C18—H18B | 108.1 |
| C9—C8—C7 | 118.80 (16) | N5—C19—H19A | 109.5 |
| C13—C8—C7 | 122.01 (15) | N5—C19—H19B | 109.5 |
| C10—C9—C8 | 120.65 (17) | H19A—C19—H19B | 109.5 |
| C10—C9—H9 | 119.7 | N5—C19—H19C | 109.5 |
| C8—C9—H9 | 119.7 | H19A—C19—H19C | 109.5 |
| C9—C10—C11 | 120.59 (16) | H19B—C19—H19C | 109.5 |
| C9—C10—H10 | 119.7 | O2—N1—O3 | 122.7 (2) |
| C11—C10—H10 | 119.7 | O2—N1—C2 | 119.6 (2) |
| C12—C11—C10 | 118.64 (16) | O3—N1—C2 | 117.7 (2) |
| C12—C11—C14 | 120.67 (16) | O4—N2—O5 | 123.64 (17) |
| C10—C11—C14 | 120.69 (16) | O4—N2—C4 | 117.71 (17) |
| C13—C12—C11 | 121.00 (17) | O5—N2—C4 | 118.64 (16) |
| C13—C12—H12 | 119.5 | O7—N3—O6 | 123.34 (18) |
| C11—C12—H12 | 119.5 | O7—N3—C6 | 118.32 (18) |
| C12—C13—C8 | 119.95 (16) | O6—N3—C6 | 118.34 (17) |
| C12—C13—H13 | 120.0 | C18—N4—C15 | 110.02 (14) |
| C8—C13—H13 | 120.0 | C18—N4—C14 | 112.50 (13) |
| N4—C14—C11 | 115.44 (15) | C15—N4—C14 | 111.92 (14) |
| N4—C14—H14A | 108.4 | C17—N5—C19 | 111.33 (15) |
| C11—C14—H14A | 108.4 | C17—N5—C16 | 109.59 (15) |
| N4—C14—H14B | 108.4 | C19—N5—C16 | 112.03 (15) |
| C11—C14—H14B | 108.4 | C17—N5—H5A | 106.5 (13) |

| | | | |
|---|---|---|---|
| H14A—C14—H14B | 107.5 | C19—N5—H5A | 105.9 (13) |
| N4—C15—C16 | 111.45 (14) | C16—N5—H5A | 111.3 (13) |
| N4—C15—H15A | 109.3 | C7—O8—H8 | 109.5 |
| | | | |
| O1—C1—C2—C3 | −176.28 (19) | C9—C8—C13—C12 | 0.4 (3) |
| C6—C1—C2—C3 | 2.0 (3) | C7—C8—C13—C12 | −177.54 (16) |
| O1—C1—C2—N1 | 2.5 (3) | C12—C11—C14—N4 | −90.9 (2) |
| C6—C1—C2—N1 | −179.22 (16) | C10—C11—C14—N4 | 88.9 (2) |
| C1—C2—C3—C4 | −1.1 (3) | N4—C15—C16—N5 | −55.9 (2) |
| N1—C2—C3—C4 | −179.94 (17) | N5—C17—C18—N4 | 59.5 (2) |
| C2—C3—C4—C5 | 0.3 (3) | C3—C2—N1—O2 | −173.7 (2) |
| C2—C3—C4—N2 | −179.94 (17) | C1—C2—N1—O2 | 7.4 (3) |
| C3—C4—C5—C6 | −0.7 (3) | C3—C2—N1—O3 | 6.7 (3) |
| N2—C4—C5—C6 | 179.59 (16) | C1—C2—N1—O3 | −172.20 (18) |
| C4—C5—C6—C1 | 1.9 (3) | C3—C4—N2—O4 | 2.3 (3) |
| C4—C5—C6—N3 | −179.92 (16) | C5—C4—N2—O4 | −177.91 (17) |
| O1—C1—C6—C5 | 175.93 (18) | C3—C4—N2—O5 | −178.37 (18) |
| C2—C1—C6—C5 | −2.4 (3) | C5—C4—N2—O5 | 1.4 (3) |
| O1—C1—C6—N3 | −2.2 (3) | C5—C6—N3—O7 | 146.71 (18) |
| C2—C1—C6—N3 | 179.41 (16) | C1—C6—N3—O7 | −35.0 (2) |
| O9—C7—C8—C9 | 13.3 (3) | C5—C6—N3—O6 | −32.8 (2) |
| O8—C7—C8—C9 | −165.86 (16) | C1—C6—N3—O6 | 145.57 (18) |
| O9—C7—C8—C13 | −168.83 (19) | C17—C18—N4—C15 | −58.31 (19) |
| O8—C7—C8—C13 | 12.1 (2) | C17—C18—N4—C14 | 176.17 (15) |
| C13—C8—C9—C10 | −0.7 (3) | C16—C15—N4—C18 | 56.68 (19) |
| C7—C8—C9—C10 | 177.30 (16) | C16—C15—N4—C14 | −177.48 (15) |
| C8—C9—C10—C11 | −0.3 (3) | C11—C14—N4—C18 | 64.0 (2) |
| C9—C10—C11—C12 | 1.5 (3) | C11—C14—N4—C15 | −60.5 (2) |
| C9—C10—C11—C14 | −178.33 (16) | C18—C17—N5—C19 | 178.02 (17) |
| C10—C11—C12—C13 | −1.8 (3) | C18—C17—N5—C16 | −57.47 (19) |
| C14—C11—C12—C13 | 178.01 (16) | C15—C16—N5—C17 | 55.6 (2) |
| C11—C12—C13—C8 | 0.9 (3) | C15—C16—N5—C19 | 179.69 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O8—H8···N4$^{i}$ | 0.82 | 1.79 | 2.6006 (19) | 172 |
| N5—H5*A*···O1$^{ii}$ | 0.89 (2) | 1.89 (2) | 2.734 (2) | 156.9 (18) |

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