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

# 2-Methyl-1*H*-benzimidazol-3-ium hydrogen phthalate

**Feng Lin,[a] Shouwen Jin,[b]* Kai Tong,[a] Haidong He[a] and YuanQi Yu[a]**

[a]Faculty of Science ZheJiang A & F University, Lin'An 311300, People's Republic of China, and [b]Tianmu college of ZheJiang A & F University, Lin'An 311300, People's Republic of China
Correspondence e-mail: JINSW@yahoo.cn

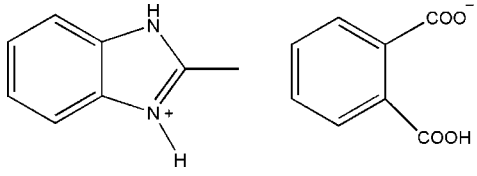
Received 25 August 2011; accepted 5 September 2011

Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.008 Å; $R$ factor = 0.082; $wR$ factor = 0.232; data-to-parameter ratio = 12.4.

The asymmetric unit of the title compound, $C_8H_9N_2^+\cdot C_8H_5O_4^-$, contains two independent ion pairs. In each 2-methyl-1*H*-benzimidazolium ion, an intramolecular O—H···O bond forms an $S(7)$ graph-set motif. In the crystal, the components are linked by N—H···O hydrogen bonds, forming chains along [210]. Further stabilization is provided by weak C—H···O hydrogen bonds.

## Related literature

For general background to hydrogen-bonding interactions, see: Lam & Mak (2000); Desiraju (2002); Liu *et al.* (2008); Biswas *et al.* (2009); Jin & Wang (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).




## Experimental

### Crystal data

$C_8H_9N_2^+\cdot C_8H_5O_4^-$
$M_r$ = 298.29
Triclinic, $P\overline{1}$
$a$ = 3.8545 (16) Å
$b$ = 17.689 (7) Å
$c$ = 20.752 (9) Å
$\alpha$ = 86.754 (8)°
$\beta$ = 86.585 (7)°
$\gamma$ = 84.169 (7)°
$V$ = 1403.3 (10) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 298 K
0.45 × 0.39 × 0.30 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min}$ = 0.955, $T_{max}$ = 0.970
7520 measured reflections
4923 independent reflections
1846 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.058

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.082
$wR(F^2)$ = 0.232
$S$ = 0.89
4923 reflections
397 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O4$^{i}$ | 0.86 | 1.81 | 2.649 (6) | 166 |
| N2—H2···O5$^{ii}$ | 0.86 | 1.91 | 2.750 (6) | 165 |
| N2—H2···O6$^{ii}$ | 0.86 | 2.58 | 3.226 (6) | 133 |
| N3—H3···O8$^{iii}$ | 0.86 | 1.79 | 2.631 (6) | 166 |
| N4—H4···O1$^{iv}$ | 0.86 | 1.83 | 2.680 (6) | 168 |
| N4—H4···O2$^{iv}$ | 0.86 | 2.58 | 3.232 (6) | 133 |
| O3—H3*A*···O2 | 0.82 | 1.55 | 2.372 (5) | 175 |
| O7—H7···O6 | 0.82 | 1.56 | 2.379 (5) | 179 |
| C7—H7*A*···O6$^{ii}$ | 0.93 | 2.53 | 3.244 (7) | 134 |

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge financial support by the Education Office Foundation of Zhejiang Province (project No. Y201017321) and the Innovation Project of Zhejiang A & F University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5327).

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2011). E**67**, o2592 [https://doi.org/10.1107/S1600536811036178]

## 2-Methyl-1*H*-benzimidazol-3-ium hydrogen phthalate

**Feng Lin, Shouwen Jin, Kai Tong, Haidong He and YuanQi Yu**

### S1. Comment

Intermolecular interactions are responsible for crystal packing and gaining an understanding of these interactions allows the comprehension of the collective properties and permits the design of new crystals with specific physical and chemical properties (Lam & Mak, 2000). Hydrogen bonding is one of the most important noncovalent interactions that determines and controls the assembly of molecules and ions (Desiraju, 2002, Liu *et al.*, 2008, Biswas *et al.*, 2009). As an extension of our study concentrating on hydrogen bonded assembly of organic acids and organic bases (Jin *et al.*, 2010), herein we report the crystal structure of the 1:1 salt of 2-methyl-1*H*-benzimidazolium hydrogen phthalate.

The asymmetric unit of the compound consists of two independent 2-methyl-1*H*-benzimidazolium and two independent hydrogen phthalate ions (Fig. 1). Intramolecular hydrogen bonds between the carbonyl groups and the hydroxy groups form S(7) graph motifs (Bernstein *et al.*, 1995). The cations and the anions are connected *via* the N—H···O hydrogen bonds to form one-dimensional chains along [210] (Fig. 2). Further stabilization of the chain is provided by weak intrachain C—H···O hydrogen bonds.

### S2. Experimental

A solution of 2-methyl-1*H*-benzimidazole (13.2 mg, 0.1 mmol) in 3 ml of MeOH was added to a MeOH solution (3 ml) containing phthalic acid acid (16.6 mg, 0.1 mmol) under continuous stirring. The solution was stirred for about 1 h at room temperature, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, colorless block-shaped crystals were isolated after slow evaporation of the solution in air at ambient temperature.

### S3. Refinement

All H atoms were placed in calculated positions with C—H = 0.93–0.96 Å, N—H = 0.86Å and O—H = 0.82Å and were included in the refinement with $U_{iso}$(H) = 1.2$U_{eq}$(C,*N*) or $U_{iso}$(H) = 1.2$U_{eq}$($C_{methyl}$,*O*).

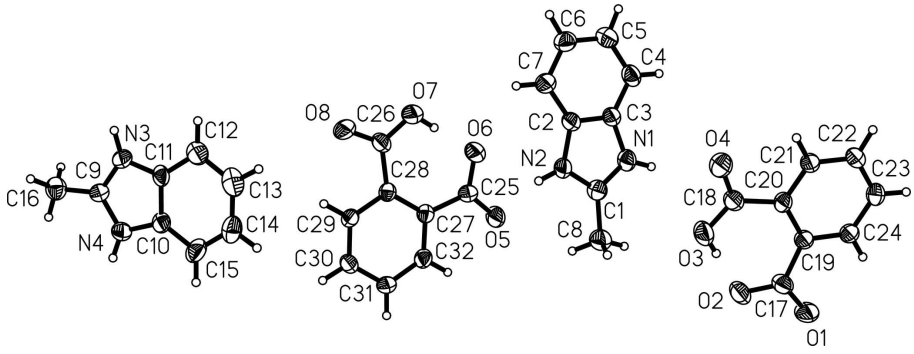


**Figure 1**

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

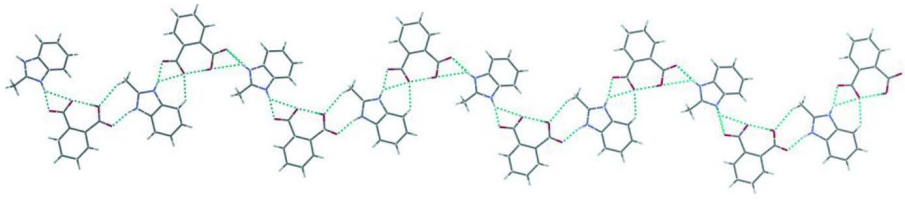

**Figure 2**

One dimensional chain running along [210] with hydrogen bonds shown as dashed lines.

### 2-Methyl-1*H*-benzimidazol-3-ium 2-carboxybenzoate

*Crystal data*

$C_8H_9N_2^+·C_8H_5O_4^-$
$M_r$ = 298.29
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 3.8545 (16) Å
$b$ = 17.689 (7) Å
$c$ = 20.752 (9) Å
$\alpha$ = 86.754 (8)°
$\beta$ = 86.585 (7)°
$\gamma$ = 84.169 (7)°
$V$ = 1403.3 (10) Å$^3$
$Z$ = 4
$F$(000) = 624
$D_x$ = 1.412 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 700 reflections
$\theta$ = 2.2–19.6°
$\mu$ = 0.10 mm$^{-1}$
$T$ = 298 K
Block, colorless
0.45 × 0.39 × 0.30 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min}$ = 0.955, $T_{max}$ = 0.970
7520 measured reflections
4923 independent reflections
1846 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.058
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.2°
$h$ = −4→4
$k$ = −20→19
$l$ = −21→24

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.232$
$S = 0.89$
4923 reflections
397 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å$^{-3}$
$\Delta\rho_{min} = -0.31$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.6243 (11) | 0.5633 (2) | 0.1657 (2) | 0.0614 (13) |
| H1 | 0.7074 | 0.6025 | 0.1465 | 0.074* |
| N2 | 0.3976 (11) | 0.4903 (2) | 0.2389 (2) | 0.0572 (12) |
| H2 | 0.3100 | 0.4741 | 0.2756 | 0.069* |
| N3 | 0.4721 (12) | −0.0649 (2) | 0.6631 (2) | 0.0661 (14) |
| H3 | 0.4929 | −0.1059 | 0.6423 | 0.079* |
| N4 | 0.4893 (12) | 0.0117 (3) | 0.7390 (2) | 0.0615 (13) |
| H4 | 0.5221 | 0.0285 | 0.7760 | 0.074* |
| O1 | 0.3597 (12) | 0.9545 (2) | 0.14225 (18) | 0.0842 (14) |
| O2 | 0.2701 (12) | 0.8461 (2) | 0.18961 (19) | 0.0886 (14) |
| O3 | 0.0573 (12) | 0.7292 (2) | 0.16867 (19) | 0.0829 (13) |
| H3A | 0.1415 | 0.7687 | 0.1753 | 0.124* |
| O4 | −0.1224 (12) | 0.6721 (2) | 0.0893 (2) | 0.0863 (14) |
| O5 | 1.0493 (11) | 0.4630 (2) | 0.35612 (17) | 0.0766 (13) |
| O6 | 0.9446 (12) | 0.3625 (2) | 0.30921 (19) | 0.0867 (14) |
| O7 | 0.7319 (12) | 0.2419 (2) | 0.33335 (19) | 0.0838 (13) |
| H7 | 0.8077 | 0.2833 | 0.3253 | 0.126* |
| O8 | 0.5216 (13) | 0.1768 (2) | 0.4153 (2) | 0.0917 (15) |
| C1 | 0.5080 (14) | 0.5583 (3) | 0.2263 (3) | 0.0572 (15) |
| C2 | 0.4456 (15) | 0.4496 (3) | 0.1839 (3) | 0.0561 (14) |
| C3 | 0.5921 (14) | 0.4953 (3) | 0.1373 (3) | 0.0529 (14) |
| C4 | 0.6727 (14) | 0.4745 (3) | 0.0752 (3) | 0.0643 (16) |
| H4A | 0.7639 | 0.5075 | 0.0436 | 0.077* |
| C5 | 0.6105 (17) | 0.4017 (4) | 0.0624 (3) | 0.0785 (19) |
| H5 | 0.6664 | 0.3839 | 0.0214 | 0.094* |

| | | | | |
|---|---|---|---|---|
| C6 | 0.4652 (16) | 0.3546 (3) | 0.1102 (3) | 0.0701 (17) |
| H6 | 0.4202 | 0.3063 | 0.0997 | 0.084* |
| C7 | 0.3858 (14) | 0.3762 (3) | 0.1717 (3) | 0.0623 (16) |
| H7A | 0.2963 | 0.3434 | 0.2036 | 0.075* |
| C8 | 0.5046 (17) | 0.6182 (3) | 0.2734 (3) | 0.0760 (18) |
| H8A | 0.2687 | 0.6396 | 0.2823 | 0.114* |
| H8B | 0.6421 | 0.6575 | 0.2556 | 0.114* |
| H8C | 0.6008 | 0.5966 | 0.3127 | 0.114* |
| C9 | 0.5569 (14) | −0.0599 (3) | 0.7229 (3) | 0.0559 (14) |
| C10 | 0.3580 (15) | 0.0550 (3) | 0.6869 (3) | 0.0590 (15) |
| C11 | 0.3466 (14) | 0.0050 (3) | 0.6392 (3) | 0.0575 (15) |
| C12 | 0.2216 (16) | 0.0290 (4) | 0.5784 (3) | 0.0707 (17) |
| H12 | 0.2144 | −0.0043 | 0.5455 | 0.085* |
| C13 | 0.1106 (17) | 0.1053 (4) | 0.5709 (3) | 0.087 (2) |
| H13 | 0.0230 | 0.1243 | 0.5318 | 0.104* |
| C14 | 0.1258 (16) | 0.1536 (4) | 0.6194 (4) | 0.0769 (19) |
| H14 | 0.0493 | 0.2048 | 0.6120 | 0.092* |
| C15 | 0.2482 (17) | 0.1302 (3) | 0.6784 (3) | 0.0769 (19) |
| H15 | 0.2562 | 0.1639 | 0.7110 | 0.092* |
| C16 | 0.6985 (15) | −0.1238 (3) | 0.7661 (3) | 0.0714 (17) |
| H16A | 0.5251 | −0.1588 | 0.7753 | 0.107* |
| H16B | 0.7597 | −0.1045 | 0.8058 | 0.107* |
| H16C | 0.9025 | −0.1496 | 0.7453 | 0.107* |
| C17 | 0.2781 (16) | 0.8892 (4) | 0.1390 (3) | 0.0648 (16) |
| C18 | −0.0014 (16) | 0.7282 (3) | 0.1088 (3) | 0.0624 (16) |
| C19 | 0.1934 (14) | 0.8627 (3) | 0.0755 (3) | 0.0533 (14) |
| C20 | 0.0778 (14) | 0.7921 (3) | 0.0617 (3) | 0.0546 (14) |
| C21 | 0.0164 (15) | 0.7799 (3) | −0.0009 (3) | 0.0617 (16) |
| H21 | −0.0674 | 0.7343 | −0.0097 | 0.074* |
| C22 | 0.0716 (16) | 0.8313 (3) | −0.0510 (3) | 0.0660 (16) |
| H22 | 0.0319 | 0.8201 | −0.0931 | 0.079* |
| C23 | 0.1877 (16) | 0.9002 (3) | −0.0384 (3) | 0.0663 (16) |
| H23 | 0.2251 | 0.9365 | −0.0717 | 0.080* |
| C24 | 0.2460 (15) | 0.9138 (3) | 0.0239 (3) | 0.0607 (15) |
| H24 | 0.3256 | 0.9601 | 0.0321 | 0.073* |
| C25 | 0.9394 (15) | 0.4004 (3) | 0.3595 (3) | 0.0584 (15) |
| C26 | 0.6405 (16) | 0.2354 (3) | 0.3930 (3) | 0.0621 (16) |
| C27 | 0.7972 (13) | 0.3692 (3) | 0.4231 (2) | 0.0479 (13) |
| C28 | 0.6743 (13) | 0.2974 (3) | 0.4380 (2) | 0.0476 (13) |
| C29 | 0.5680 (13) | 0.2802 (3) | 0.5007 (3) | 0.0493 (13) |
| H29 | 0.4900 | 0.2327 | 0.5110 | 0.059* |
| C30 | 0.5710 (15) | 0.3294 (3) | 0.5490 (3) | 0.0633 (16) |
| H30 | 0.4947 | 0.3153 | 0.5909 | 0.076* |
| C31 | 0.6872 (15) | 0.4000 (3) | 0.5354 (3) | 0.0612 (16) |
| H31 | 0.6900 | 0.4347 | 0.5673 | 0.073* |
| C32 | 0.7995 (14) | 0.4170 (3) | 0.4723 (3) | 0.0562 (15) |
| H32 | 0.8820 | 0.4642 | 0.4627 | 0.067* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.065 (3) | 0.060 (3) | 0.059 (3) | −0.019 (2) | 0.006 (3) | 0.008 (3) |
| N2 | 0.070 (3) | 0.051 (3) | 0.052 (3) | −0.015 (2) | −0.005 (2) | 0.005 (2) |
| N3 | 0.093 (4) | 0.053 (3) | 0.058 (3) | −0.028 (3) | −0.011 (3) | −0.007 (3) |
| N4 | 0.078 (4) | 0.063 (3) | 0.048 (3) | −0.020 (3) | −0.010 (3) | −0.008 (3) |
| O1 | 0.120 (4) | 0.070 (3) | 0.070 (3) | −0.035 (3) | −0.013 (3) | −0.017 (2) |
| O2 | 0.137 (4) | 0.085 (3) | 0.049 (3) | −0.033 (3) | −0.016 (3) | 0.003 (2) |
| O3 | 0.117 (4) | 0.077 (3) | 0.058 (3) | −0.031 (3) | −0.006 (3) | 0.014 (2) |
| O4 | 0.121 (4) | 0.066 (3) | 0.079 (3) | −0.045 (3) | −0.003 (3) | 0.005 (2) |
| O5 | 0.106 (3) | 0.069 (3) | 0.060 (3) | −0.043 (3) | 0.003 (2) | 0.003 (2) |
| O6 | 0.130 (4) | 0.078 (3) | 0.054 (3) | −0.028 (3) | 0.015 (3) | −0.004 (2) |
| O7 | 0.127 (4) | 0.068 (3) | 0.062 (3) | −0.034 (3) | 0.004 (3) | −0.012 (2) |
| O8 | 0.143 (4) | 0.061 (3) | 0.078 (3) | −0.048 (3) | 0.014 (3) | −0.015 (2) |
| C1 | 0.054 (4) | 0.060 (4) | 0.059 (4) | −0.013 (3) | 0.001 (3) | −0.002 (3) |
| C2 | 0.068 (4) | 0.056 (3) | 0.045 (3) | −0.013 (3) | −0.007 (3) | −0.002 (3) |
| C3 | 0.059 (4) | 0.053 (3) | 0.047 (4) | −0.010 (3) | −0.002 (3) | −0.001 (3) |
| C4 | 0.067 (4) | 0.074 (4) | 0.049 (4) | −0.002 (3) | 0.008 (3) | 0.005 (3) |
| C5 | 0.098 (5) | 0.080 (5) | 0.056 (4) | 0.001 (4) | −0.004 (4) | −0.011 (4) |
| C6 | 0.079 (5) | 0.062 (4) | 0.072 (5) | −0.007 (3) | −0.017 (4) | −0.011 (4) |
| C7 | 0.070 (4) | 0.058 (4) | 0.061 (4) | −0.017 (3) | −0.003 (3) | −0.005 (3) |
| C8 | 0.093 (5) | 0.072 (4) | 0.065 (4) | −0.019 (4) | −0.005 (4) | −0.007 (3) |
| C9 | 0.065 (4) | 0.050 (3) | 0.054 (4) | −0.012 (3) | −0.004 (3) | −0.008 (3) |
| C10 | 0.070 (4) | 0.060 (4) | 0.053 (4) | −0.034 (3) | −0.009 (3) | 0.001 (3) |
| C11 | 0.067 (4) | 0.062 (4) | 0.048 (4) | −0.033 (3) | −0.007 (3) | 0.008 (3) |
| C12 | 0.070 (4) | 0.082 (5) | 0.063 (4) | −0.026 (4) | −0.008 (3) | 0.001 (4) |
| C13 | 0.081 (5) | 0.106 (6) | 0.077 (5) | −0.030 (5) | −0.016 (4) | 0.020 (5) |
| C14 | 0.065 (4) | 0.067 (4) | 0.093 (5) | 0.001 (3) | 0.000 (4) | 0.020 (4) |
| C15 | 0.088 (5) | 0.052 (4) | 0.093 (5) | −0.026 (3) | −0.004 (4) | 0.002 (4) |
| C16 | 0.069 (4) | 0.074 (4) | 0.071 (4) | −0.009 (3) | −0.008 (3) | 0.003 (3) |
| C17 | 0.079 (5) | 0.069 (4) | 0.050 (4) | −0.023 (3) | −0.003 (3) | −0.006 (3) |
| C18 | 0.075 (4) | 0.063 (4) | 0.051 (4) | −0.016 (3) | −0.006 (3) | −0.002 (3) |
| C19 | 0.063 (4) | 0.049 (3) | 0.050 (4) | −0.016 (3) | −0.005 (3) | −0.003 (3) |
| C20 | 0.067 (4) | 0.045 (3) | 0.054 (4) | −0.017 (3) | −0.003 (3) | 0.004 (3) |
| C21 | 0.090 (5) | 0.048 (3) | 0.052 (4) | −0.022 (3) | −0.015 (3) | −0.002 (3) |
| C22 | 0.090 (5) | 0.064 (4) | 0.045 (4) | −0.011 (3) | −0.008 (3) | 0.000 (3) |
| C23 | 0.088 (5) | 0.053 (4) | 0.058 (4) | −0.018 (3) | 0.003 (3) | 0.012 (3) |
| C24 | 0.085 (4) | 0.044 (3) | 0.056 (4) | −0.022 (3) | −0.007 (3) | −0.002 (3) |
| C25 | 0.071 (4) | 0.053 (4) | 0.054 (4) | −0.013 (3) | −0.006 (3) | −0.010 (3) |
| C26 | 0.077 (4) | 0.068 (4) | 0.043 (4) | −0.017 (3) | −0.006 (3) | −0.001 (3) |
| C27 | 0.046 (3) | 0.049 (3) | 0.049 (3) | −0.007 (3) | −0.007 (3) | 0.001 (3) |
| C28 | 0.047 (3) | 0.046 (3) | 0.051 (3) | −0.010 (2) | −0.001 (3) | 0.001 (3) |
| C29 | 0.052 (3) | 0.041 (3) | 0.055 (4) | −0.005 (2) | −0.001 (3) | −0.001 (3) |
| C30 | 0.089 (5) | 0.062 (4) | 0.042 (3) | −0.023 (3) | −0.001 (3) | −0.001 (3) |
| C31 | 0.082 (4) | 0.051 (3) | 0.054 (4) | −0.016 (3) | −0.002 (3) | −0.012 (3) |
| C32 | 0.066 (4) | 0.049 (3) | 0.057 (4) | −0.017 (3) | −0.009 (3) | 0.001 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.312 (6) | C10—C15 | 1.360 (7) |
| N1—C3 | 1.389 (6) | C10—C11 | 1.370 (7) |
| N1—H1 | 0.8600 | C11—C12 | 1.404 (7) |
| N2—C1 | 1.323 (6) | C12—C13 | 1.376 (8) |
| N2—C2 | 1.376 (6) | C12—H12 | 0.9300 |
| N2—H2 | 0.8600 | C13—C14 | 1.365 (8) |
| N3—C9 | 1.312 (6) | C13—H13 | 0.9300 |
| N3—C11 | 1.358 (6) | C14—C15 | 1.365 (8) |
| N3—H3 | 0.8600 | C14—H14 | 0.9300 |
| N4—C9 | 1.323 (6) | C15—H15 | 0.9300 |
| N4—C10 | 1.380 (6) | C16—H16A | 0.9600 |
| N4—H4 | 0.8600 | C16—H16B | 0.9600 |
| O1—C17 | 1.234 (6) | C16—H16C | 0.9600 |
| O2—C17 | 1.263 (6) | C17—C19 | 1.487 (7) |
| O3—C18 | 1.278 (6) | C18—C20 | 1.494 (7) |
| O3—H3A | 0.8200 | C19—C24 | 1.380 (7) |
| O4—C18 | 1.237 (6) | C19—C20 | 1.418 (6) |
| O5—C25 | 1.222 (6) | C20—C21 | 1.366 (7) |
| O6—C25 | 1.271 (6) | C21—C22 | 1.364 (7) |
| O7—C26 | 1.269 (6) | C21—H21 | 0.9300 |
| O7—H7 | 0.8200 | C22—C23 | 1.385 (7) |
| O8—C26 | 1.230 (6) | C22—H22 | 0.9300 |
| C1—C8 | 1.480 (7) | C23—C24 | 1.365 (7) |
| C2—C3 | 1.359 (7) | C23—H23 | 0.9300 |
| C2—C7 | 1.382 (7) | C24—H24 | 0.9300 |
| C3—C4 | 1.369 (7) | C25—C27 | 1.496 (7) |
| C4—C5 | 1.377 (7) | C26—C28 | 1.500 (7) |
| C4—H4A | 0.9300 | C27—C32 | 1.362 (6) |
| C5—C6 | 1.386 (8) | C27—C28 | 1.411 (6) |
| C5—H5 | 0.9300 | C28—C29 | 1.369 (7) |
| C6—C7 | 1.361 (7) | C29—C30 | 1.364 (6) |
| C6—H6 | 0.9300 | C29—H29 | 0.9300 |
| C7—H7A | 0.9300 | C30—C31 | 1.377 (6) |
| C8—H8A | 0.9600 | C30—H30 | 0.9300 |
| C8—H8B | 0.9600 | C31—C32 | 1.381 (7) |
| C8—H8C | 0.9600 | C31—H31 | 0.9300 |
| C9—C16 | 1.483 (7) | C32—H32 | 0.9300 |
| | | | |
| C1—N1—C3 | 109.2 (5) | C15—C14—H14 | 118.5 |
| C1—N1—H1 | 125.4 | C10—C15—C14 | 116.4 (6) |
| C3—N1—H1 | 125.4 | C10—C15—H15 | 121.8 |
| C1—N2—C2 | 109.1 (4) | C14—C15—H15 | 121.8 |
| C1—N2—H2 | 125.4 | C9—C16—H16A | 109.5 |
| C2—N2—H2 | 125.4 | C9—C16—H16B | 109.5 |
| C9—N3—C11 | 109.3 (4) | H16A—C16—H16B | 109.5 |
| C9—N3—H3 | 125.3 | C9—C16—H16C | 109.5 |

| | | | |
|---|---|---|---|
| C11—N3—H3 | 125.3 | H16A—C16—H16C | 109.5 |
| C9—N4—C10 | 109.2 (4) | H16B—C16—H16C | 109.5 |
| C9—N4—H4 | 125.4 | O1—C17—O2 | 119.2 (5) |
| C10—N4—H4 | 125.4 | O1—C17—C19 | 119.4 (5) |
| C18—O3—H3A | 109.5 | O2—C17—C19 | 121.5 (5) |
| C26—O7—H7 | 109.5 | O4—C18—O3 | 118.7 (5) |
| N1—C1—N2 | 108.8 (5) | O4—C18—C20 | 119.3 (5) |
| N1—C1—C8 | 125.8 (5) | O3—C18—C20 | 122.0 (5) |
| N2—C1—C8 | 125.4 (5) | C24—C19—C20 | 117.2 (5) |
| C3—C2—N2 | 106.8 (5) | C24—C19—C17 | 114.3 (5) |
| C3—C2—C7 | 120.8 (5) | C20—C19—C17 | 128.4 (5) |
| N2—C2—C7 | 132.4 (5) | C21—C20—C19 | 118.3 (5) |
| C2—C3—C4 | 123.6 (5) | C21—C20—C18 | 114.3 (5) |
| C2—C3—N1 | 106.2 (5) | C19—C20—C18 | 127.4 (5) |
| C4—C3—N1 | 130.2 (5) | C22—C21—C20 | 123.4 (5) |
| C3—C4—C5 | 115.8 (5) | C22—C21—H21 | 118.3 |
| C3—C4—H4A | 122.1 | C20—C21—H21 | 118.3 |
| C5—C4—H4A | 122.1 | C21—C22—C23 | 119.0 (5) |
| C4—C5—C6 | 120.6 (6) | C21—C22—H22 | 120.5 |
| C4—C5—H5 | 119.7 | C23—C22—H22 | 120.5 |
| C6—C5—H5 | 119.7 | C24—C23—C22 | 118.5 (5) |
| C7—C6—C5 | 122.8 (6) | C24—C23—H23 | 120.7 |
| C7—C6—H6 | 118.6 | C22—C23—H23 | 120.7 |
| C5—C6—H6 | 118.6 | C23—C24—C19 | 123.6 (5) |
| C6—C7—C2 | 116.2 (5) | C23—C24—H24 | 118.2 |
| C6—C7—H7A | 121.9 | C19—C24—H24 | 118.2 |
| C2—C7—H7A | 121.9 | O5—C25—O6 | 119.9 (6) |
| C1—C8—H8A | 109.5 | O5—C25—C27 | 119.6 (5) |
| C1—C8—H8B | 109.5 | O6—C25—C27 | 120.5 (5) |
| H8A—C8—H8B | 109.5 | O8—C26—O7 | 119.9 (5) |
| C1—C8—H8C | 109.5 | O8—C26—C28 | 118.4 (5) |
| H8A—C8—H8C | 109.5 | O7—C26—C28 | 121.8 (5) |
| H8B—C8—H8C | 109.5 | C32—C27—C28 | 117.7 (5) |
| N3—C9—N4 | 108.7 (5) | C32—C27—C25 | 113.9 (5) |
| N3—C9—C16 | 125.9 (5) | C28—C27—C25 | 128.4 (5) |
| N4—C9—C16 | 125.4 (5) | C29—C28—C27 | 118.0 (5) |
| C15—C10—C11 | 122.2 (6) | C29—C28—C26 | 113.9 (5) |
| C15—C10—N4 | 132.4 (5) | C27—C28—C26 | 128.2 (5) |
| C11—C10—N4 | 105.4 (5) | C30—C29—C28 | 123.2 (5) |
| N3—C11—C10 | 107.4 (5) | C30—C29—H29 | 118.4 |
| N3—C11—C12 | 131.1 (5) | C28—C29—H29 | 118.4 |
| C10—C11—C12 | 121.5 (6) | C29—C30—C31 | 119.7 (5) |
| C13—C12—C11 | 115.4 (6) | C29—C30—H30 | 120.1 |
| C13—C12—H12 | 122.3 | C31—C30—H30 | 120.1 |
| C11—C12—H12 | 122.3 | C30—C31—C32 | 117.2 (5) |
| C14—C13—C12 | 121.6 (6) | C30—C31—H31 | 121.4 |
| C14—C13—H13 | 119.2 | C32—C31—H31 | 121.4 |
| C12—C13—H13 | 119.2 | C27—C32—C31 | 124.2 (5) |

| | | | |
|---|---|---|---|
| C13—C14—C15 | 122.9 (6) | C27—C32—H32 | 117.9 |
| C13—C14—H14 | 118.5 | C31—C32—H32 | 117.9 |
| | | | |
| C3—N1—C1—N2 | −0.6 (6) | O1—C17—C19—C24 | 5.5 (8) |
| C3—N1—C1—C8 | 178.7 (5) | O2—C17—C19—C24 | −174.2 (6) |
| C2—N2—C1—N1 | 0.1 (6) | O1—C17—C19—C20 | −176.5 (6) |
| C2—N2—C1—C8 | −179.1 (5) | O2—C17—C19—C20 | 3.8 (10) |
| C1—N2—C2—C3 | 0.4 (6) | C24—C19—C20—C21 | −1.9 (8) |
| C1—N2—C2—C7 | 177.6 (6) | C17—C19—C20—C21 | −179.8 (6) |
| N2—C2—C3—C4 | −178.8 (5) | C24—C19—C20—C18 | −179.2 (5) |
| C7—C2—C3—C4 | 3.6 (8) | C17—C19—C20—C18 | 2.9 (9) |
| N2—C2—C3—N1 | −0.7 (6) | O4—C18—C20—C21 | −2.2 (8) |
| C7—C2—C3—N1 | −178.3 (5) | O3—C18—C20—C21 | 176.7 (6) |
| C1—N1—C3—C2 | 0.8 (6) | O4—C18—C20—C19 | 175.3 (6) |
| C1—N1—C3—C4 | 178.8 (6) | O3—C18—C20—C19 | −5.9 (9) |
| C2—C3—C4—C5 | −2.7 (8) | C19—C20—C21—C22 | 2.3 (9) |
| N1—C3—C4—C5 | 179.6 (5) | C18—C20—C21—C22 | 179.9 (6) |
| C3—C4—C5—C6 | 1.8 (8) | C20—C21—C22—C23 | −1.6 (9) |
| C4—C5—C6—C7 | −1.8 (9) | C21—C22—C23—C24 | 0.7 (9) |
| C5—C6—C7—C2 | 2.4 (8) | C22—C23—C24—C19 | −0.5 (9) |
| C3—C2—C7—C6 | −3.2 (8) | C20—C19—C24—C23 | 1.1 (9) |
| N2—C2—C7—C6 | 179.9 (6) | C17—C19—C24—C23 | 179.3 (5) |
| C11—N3—C9—N4 | 0.1 (6) | O5—C25—C27—C32 | 1.3 (7) |
| C11—N3—C9—C16 | 179.0 (5) | O6—C25—C27—C32 | −178.2 (5) |
| C10—N4—C9—N3 | −0.6 (6) | O5—C25—C27—C28 | −176.7 (5) |
| C10—N4—C9—C16 | −179.5 (5) | O6—C25—C27—C28 | 3.7 (8) |
| C9—N4—C10—C15 | 179.7 (6) | C32—C27—C28—C29 | −0.5 (7) |
| C9—N4—C10—C11 | 0.8 (6) | C25—C27—C28—C29 | 177.5 (5) |
| C9—N3—C11—C10 | 0.4 (6) | C32—C27—C28—C26 | 179.1 (5) |
| C9—N3—C11—C12 | −179.6 (6) | C25—C27—C28—C26 | −2.9 (9) |
| C15—C10—C11—N3 | −179.7 (5) | O8—C26—C28—C29 | 0.7 (7) |
| N4—C10—C11—N3 | −0.7 (6) | O7—C26—C28—C29 | −179.1 (5) |
| C15—C10—C11—C12 | 0.3 (9) | O8—C26—C28—C27 | −178.9 (5) |
| N4—C10—C11—C12 | 179.3 (5) | O7—C26—C28—C27 | 1.3 (9) |
| N3—C11—C12—C13 | 179.5 (6) | C27—C28—C29—C30 | 1.0 (8) |
| C10—C11—C12—C13 | −0.5 (9) | C26—C28—C29—C30 | −178.7 (5) |
| C11—C12—C13—C14 | 0.6 (9) | C28—C29—C30—C31 | −0.4 (8) |
| C12—C13—C14—C15 | −0.5 (10) | C29—C30—C31—C32 | −0.5 (8) |
| C11—C10—C15—C14 | −0.1 (9) | C28—C27—C32—C31 | −0.5 (8) |
| N4—C10—C15—C14 | −178.8 (6) | C25—C27—C32—C31 | −178.8 (5) |
| C13—C14—C15—C10 | 0.2 (9) | C30—C31—C32—C27 | 1.0 (8) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O4$^{i}$ | 0.86 | 1.81 | 2.649 (6) | 166 |
| N2—H2···O5$^{ii}$ | 0.86 | 1.91 | 2.750 (6) | 165 |
| N2—H2···O6$^{ii}$ | 0.86 | 2.58 | 3.226 (6) | 133 |

| | | | | |
|---|---|---|---|---|
| N3—H3···O8$^{iii}$ | 0.86 | 1.79 | 2.631 (6) | 166 |
| N4—H4···O1$^{iv}$ | 0.86 | 1.83 | 2.680 (6) | 168 |
| N4—H4···O2$^{iv}$ | 0.86 | 2.58 | 3.232 (6) | 133 |
| O3—H3*A*···O2 | 0.82 | 1.55 | 2.372 (5) | 175 |
| O7—H7···O6 | 0.82 | 1.56 | 2.379 (5) | 179 |
| C7—H7*A*···O6$^{ii}$ | 0.93 | 2.53 | 3.244 (7) | 134 |

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