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# 4,4′-Iminodipyridinium bis(hydrogen phthalate)

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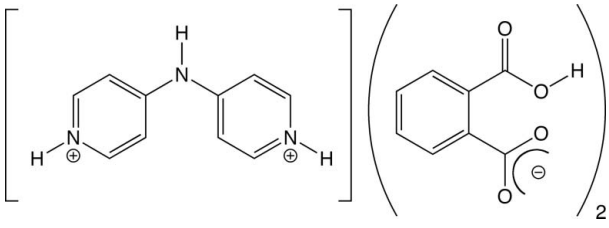
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.008 Å; $R$ factor = 0.060; $wR$ factor = 0.170; data-to-parameter ratio = 7.2.

In the title salt, $C_{10}H_{11}N_3^{2+}\cdot 2C_8H_5O_4^-$, doubly protonated 4,4′-dipyridylamine (dpa) cations participate in N—H···O hydrogen bonding with two hydrogen phthalate anions to form a neutral unit. Both anions contain an intramolecular O—H···O hydrogen bond. In the crystal structure, these units form two-dimensional layers through $\pi$–$\pi$ stacking interactions with a centroid-to-centroid distance of 3.763 (3) Å. In turn, these layers aggregate in three dimensions by additional N—H···O hydrogen bonding. The assignment to the noncentrosymmetric space group $P1$ is corroborated by chemically unreasonable aromatic ring bond distances and poor $K$ scale factor distributions for a disordered model in the centrosymmetric $P\overline{1}$ space group.

## Related literature

For the crystal structure of dpa, see: Cordes *et al.* (2006). For a chiral dpa-containing coordination polymer, see: Montney *et al.* (2007). For carboxylic acid/imine co-crystals, see: Horiuchi *et al.* (2005); Bhogala & Nangia (2003). For charge-separated hydrogen bonding, see: Steiner (2002). For the preparation of dpa, see: Zapf *et al.* (1998).



## Experimental

### Crystal data

$C_{10}H_{11}N_3^{2+}\cdot 2C_8H_5O_4^-$
$M_r$ = 503.46
Triclinic, $P1$
$a$ = 7.858 (2) Å
$b$ = 8.101 (2) Å
$c$ = 9.601 (3) Å
$\alpha$ = 85.673 (5)°
$\beta$ = 85.186 (5)°
$\gamma$ = 68.834 (4)°
$V$ = 567.3 (3) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 0.11 mm$^{-1}$
$T$ = 293 (2) K
0.75 × 0.60 × 0.30 mm

### Data collection

Bruker SMART 1K diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.831, $T_{max}$ = 0.967
6282 measured reflections
2513 independent reflections
2269 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.014

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.170
$S$ = 1.06
2513 reflections
349 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.32 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3$A$···O2 | 1.07 (9) | 1.37 (9) | 2.386 (6) | 155 (7) |
| O6—H7$A$···O7 | 1.03 (8) | 1.37 (8) | 2.396 (6) | 172 (7) |
| N1—H1N···O1 | 0.86 (6) | 1.90 (6) | 2.757 (6) | 177 (7) |
| N2—H2N···O6 | 0.85 (6) | 2.00 (6) | 2.834 (5) | 167 (7) |
| N3—H3N···O8$^{i}$ | 0.92 (5) | 1.88 (5) | 2.794 (5) | 172 (5) |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2702).

## References

Bhogala, B. R. & Nangia, A. (2003). *Cryst. Growth Des.* **3**, 547–554.
Bruker (2001). *SMART* . Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cordes, D. B., Hanton, L. R. & Spicer, M. D. (2006). *Inorg. Chem.* **45**, 7651–7664.
Horiuchi, S., Ishii, F., Kumai, R., Okimoto, Y., Tachibana, H., Nagaora, N. & Tokura, Y. (2005). *Nat. Mater.* **4**, 163–166.
Montney, M. R., Mallika Krishnan, S., Patel, N. M., Supkowski, R. M. & LaDuca, R. L. (2007). *Cryst. Growth Des.* **7**, 1145–1153.
Palmer, D. (2005). *CrystalMaker*. CrystalMaker Software Ltd, Bicester, Oxfordshire, England.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Zapf, P. J., LaDuca, R. L., Rarig, R. S., Johnson, K. M. III & Zubieta, J. (1998). *Inorg. Chem.* **37**, 3411–3414.

# supporting information

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## 4,4′-Iminodipyridinium bis(hydrogen phthalate)

**David P. Martin and Robert L. LaDuca**

### S1. Comment

Co-crystals containing carboxylic acids and imines have exhibited enticing physical properties such as ferroelectricity (Horiuchi *et al.*, 2005). Proton transfer between carboxylic acid and pyridine components has been observed in this class of co-crystals (Bhogala & Nangia, 2003). Charge-separated hydrogen bonding interactions serve to promote the stability of these co-crystals (Steiner, 2002). Because of locked conformation between its pyridyl rings in the solid-state, crystals of pure dpa are noncentrosymmetric (Cordes *et al.*, 2006). Coordination polymers containing dpa have been observed to crystallize in noncentrosymmetric space groups (Montney *et al.*, 2007). Thus we have sought to prepare chiral dpa-containing co-crystals.

The asymmetric unit of the title salt contains a doubly protonated $[H_2dpa]^{2+}$ dication, and two hydrogen phthalate ($[phtH]^-$) ions (Fig. 1). The similar C—O bond lengths at the carboxylate termini marked by C17 and C28 indicate the presence of delocalized $\pi$ bonds. On the other hand the C—O bond distances at C18 and C27 show greater C═O and C—O single bond character.

Each $[H_2dpa]^{2+}$ dication is linked to $[Hpht]^-$ anions on either side to form neutral $[H_2dpa][[Hpht]_2$ units, *via* N—H···O hydrogen bonding donation from both of its pyridinium termini to $[Hpht]^-$ carboxylate oxygen atoms. These neutral units then engage in $\pi$–$\pi$ stacking between pyridyl and benzene rings (centroid-to-centroid distance = 3.763 Å) to construct *pseudo* two-dimensional layer patterns that lie parallel to the (101) crystal planes (Fig. 2).

The $[H_2dpa][[Hpht]_2$ layers are connected into the *pseudo* three-dimensional structure of the title compound *via* N—H···O hydrogen bonding mechanisms instilled by the central amine units of the $[H_2dpa]^{2+}$ dications (Fig. 3). Geometric parameters for the hydrogen bonding interactions are given in Table 1.

The assignment to the noncentrosymmetric space group *P*1 is corroborated by chemically unreasonable aromatic ring bond distances (1.0 and 1.7 Å) and poor *K* scale factors distributions for a disordered model in the centrosymmetric $P\bar{1}$ space group.

### S2. Experimental

Phthalic acid was obtained commercially. 4,4′-dipyridylamine was prepared *via* a published procedure (Zapf *et al.*, 1998). A mixture of phthalic acid (96 mg, 0.58 mmol) and 4,4′-dipyridylamine (50 mg, 0.29 mmol) was placed in 10.0 g water (550 mmol) in a 25 ml beaker. The solution was then heated to boiling. Large colourless blocks of the title compound were isolated after the solution was cooled to 298K and allowed to stand undisturbed for 3 d.

### S3. Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.95 Å and refined in riding mode with $U_{iso} = 1.2U_{eq}$(C). All H atoms bound to O and N atoms were found *via* Fourier difference map and refined with $U_{iso} = 1.2U_{eq}$(N) or $1.2U_{eq}$(O). The pyridinium N—H bonds were restrained with N—H = 0.89 (2) Å and the amine N—H bond

was restrained with N—H = 0.85 (2) Å. The O—H distances were allowed to refine. In the absence of significant anomalous dispersion effects Friedel pairs were merged prior to the final refinement.

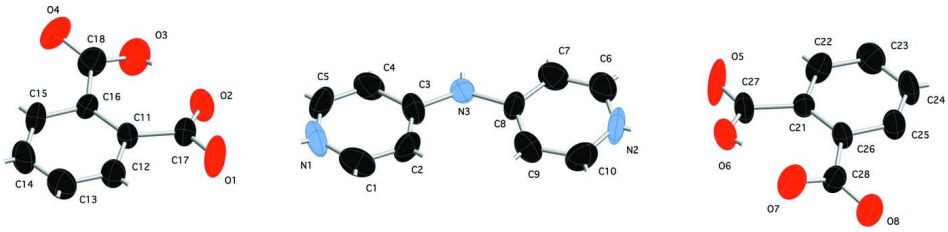


**Figure 1**

Asymmetric unit of the title compound, showing 50% probability ellipsoids and atom numbering scheme. Hydrogen atoms are represented as short gray sticks. Color codes: light-blue N, red O, black C. Hydrogen bonding is shown as dashed lines.

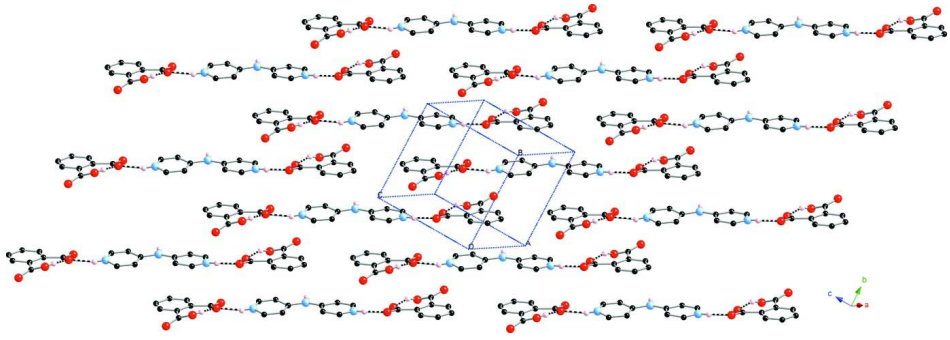

**Figure 2**

A *pseudo* layer in the title compound. Color codes: light-blue N, red O, black C, pink H. Hydrogen bonding is shown as dashed lines.

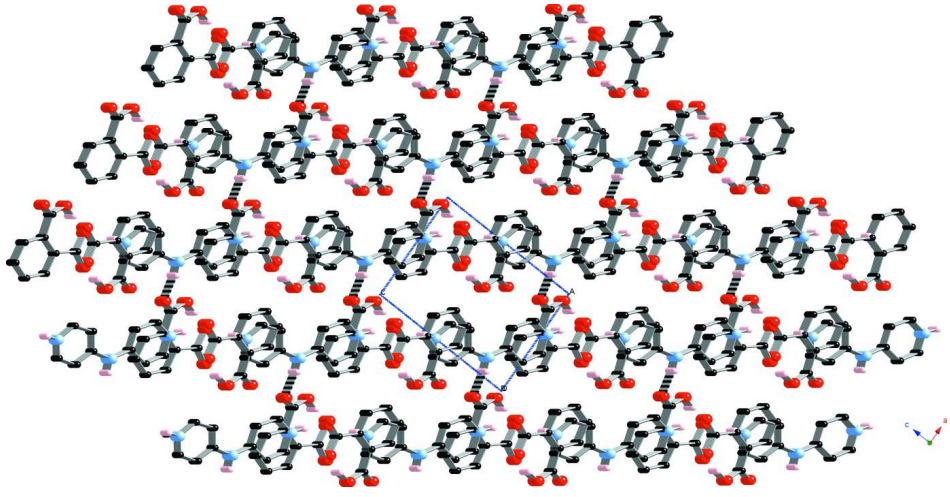

**Figure 3**

Packing diagram illustrating the stacking of layers to form the 3-D crystal structure of the title compound. Hydrogen bonding is shown as dashed lines.

## 4,4′-Iminodipyridinium bis(hydrogen phthalate)

*Crystal data*

$C_{10}H_{11}N_3^{2+}\cdot 2C_8H_5O_4^-$
$M_r = 503.46$
Triclinic, $P\overline{1}$
Hall symbol: P 1
$a = 7.858$ (2) Å
$b = 8.101$ (2) Å
$c = 9.601$ (3) Å
$\alpha = 85.673$ (5)°
$\beta = 85.186$ (5)°
$\gamma = 68.834$ (4)°
$V = 567.3$ (3) Å$^3$
$Z = 1$
$F(000) = 262$
$D_x = 1.474$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6282 reflections
$\theta = 2.1$–$28.0°$
$\mu = 0.11$ mm$^{-1}$
$T = 293$ K
Block, colourless
0.75 × 0.60 × 0.30 mm

*Data collection*

Bruker SMART 1K diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.831$, $T_{max} = 0.967$
6282 measured reflections
2513 independent reflections
2269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.1°$
$h = -10\rightarrow10$
$k = -10\rightarrow10$
$l = -12\rightarrow12$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.170$
$S = 1.06$
2513 reflections
349 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 0.2863P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å$^{-3}$
$\Delta\rho_{min} = -0.32$ 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | −0.9711 (7) | 0.8965 (7) | 1.1049 (4) | 0.0832 (14) |
| O2 | −0.7469 (5) | 0.7612 (6) | 1.2383 (5) | 0.0712 (12) |
| O3 | −0.6750 (5) | 0.5656 (7) | 1.4411 (6) | 0.0824 (14) |

| | | | | |
|---|---|---|---|---|
| H3A | −0.691 (11) | 0.624 (10) | 1.337 (9) | 0.099* |
| O4 | −0.8021 (6) | 0.3983 (6) | 1.5649 (5) | 0.0780 (13) |
| O5 | 0.3019 (7) | 1.2225 (8) | 0.2453 (5) | 0.0926 (17) |
| O6 | 0.0684 (5) | 1.3566 (6) | 0.1220 (5) | 0.0709 (12) |
| H7A | 0.043 (9) | 1.430 (9) | 0.028 (8) | 0.085* |
| O7 | −0.0087 (5) | 1.5473 (6) | −0.0843 (5) | 0.0802 (13) |
| O8 | 0.1036 (5) | 1.7269 (5) | −0.2062 (4) | 0.0654 (10) |
| N1 | −0.6896 (8) | 0.9599 (7) | 0.9469 (5) | 0.0655 (14) |
| H1N | −0.780 (6) | 0.944 (9) | 0.995 (6) | 0.079* |
| N2 | −0.0792 (9) | 1.2304 (7) | 0.3688 (5) | 0.0760 (18) |
| H2N | −0.047 (10) | 1.285 (8) | 0.299 (5) | 0.091* |
| N3 | −0.2299 (5) | 0.9798 (5) | 0.7185 (4) | 0.0495 (8) |
| H3N | −0.121 (5) | 0.902 (6) | 0.751 (6) | 0.059* |
| C1 | −0.7118 (7) | 1.0624 (9) | 0.8305 (7) | 0.0714 (17) |
| H1 | −0.8289 | 1.1282 | 0.8031 | 0.086* |
| C2 | −0.5601 (8) | 1.0716 (7) | 0.7497 (5) | 0.0605 (14) |
| H2 | −0.5747 | 1.1424 | 0.6674 | 0.073* |
| C3 | −0.3924 (6) | 0.9770 (7) | 0.7916 (5) | 0.0533 (12) |
| C4 | −0.3767 (8) | 0.8754 (8) | 0.9177 (6) | 0.0689 (16) |
| H4 | −0.2625 | 0.8122 | 0.9517 | 0.083* |
| C5 | −0.5320 (10) | 0.8709 (8) | 0.9894 (6) | 0.0713 (16) |
| H5 | −0.5226 | 0.8009 | 1.0718 | 0.086* |
| C6 | 0.0413 (8) | 1.1117 (8) | 0.4402 (7) | 0.0668 (15) |
| H6 | 0.1643 | 1.0811 | 0.4115 | 0.080* |
| C7 | −0.0060 (7) | 1.0321 (7) | 0.5539 (6) | 0.0607 (13) |
| H7 | 0.0843 | 0.9471 | 0.6042 | 0.073* |
| C8 | −0.1878 (8) | 1.0729 (6) | 0.5996 (5) | 0.0517 (11) |
| C9 | −0.3186 (7) | 1.1998 (8) | 0.5237 (6) | 0.0618 (14) |
| H9 | −0.4424 | 1.2313 | 0.5500 | 0.074* |
| C10 | −0.2574 (9) | 1.2797 (8) | 0.4051 (6) | 0.0697 (15) |
| H10 | −0.3414 | 1.3673 | 0.3517 | 0.084* |
| C11 | −1.0440 (6) | 0.7547 (6) | 1.3134 (4) | 0.0392 (9) |
| C12 | −1.2276 (6) | 0.8392 (7) | 1.2857 (5) | 0.0508 (11) |
| H12 | −1.2573 | 0.9150 | 1.2065 | 0.061* |
| C13 | −1.3670 (7) | 0.8140 (8) | 1.3720 (7) | 0.0642 (14) |
| H13 | −1.4881 | 0.8714 | 1.3502 | 0.077* |
| C14 | −1.3265 (7) | 0.7059 (8) | 1.4877 (6) | 0.0639 (15) |
| H14 | −1.4203 | 0.6922 | 1.5477 | 0.077* |
| C15 | −1.1462 (7) | 0.6149 (7) | 1.5178 (5) | 0.0547 (12) |
| H15 | −1.1207 | 0.5380 | 1.5967 | 0.066* |
| C16 | −1.0025 (6) | 0.6360 (5) | 1.4328 (4) | 0.0384 (9) |
| C17 | −0.9122 (7) | 0.8067 (6) | 1.2125 (5) | 0.0493 (11) |
| C18 | −0.8166 (7) | 0.5225 (7) | 1.4825 (6) | 0.0586 (12) |
| C21 | 0.3638 (5) | 1.3702 (5) | 0.0345 (4) | 0.0391 (9) |
| C22 | 0.5473 (7) | 1.2878 (7) | 0.0605 (5) | 0.0535 (12) |
| H22 | 0.5797 | 1.2125 | 0.1396 | 0.064* |
| C23 | 0.6836 (7) | 1.3158 (8) | −0.0294 (7) | 0.0640 (14) |
| H23 | 0.8060 | 1.2567 | −0.0120 | 0.077* |

| | | | | |
|---|---|---|---|---|
| C24 | 0.6362 (7) | 1.4317 (9) | −0.1449 (6) | 0.0632 (14) |
| H24 | 0.7259 | 1.4535 | −0.2048 | 0.076* |
| C25 | 0.4570 (7) | 1.5131 (7) | −0.1694 (5) | 0.0539 (12) |
| H25 | 0.4265 | 1.5892 | −0.2483 | 0.065* |
| C26 | 0.3158 (6) | 1.4886 (6) | −0.0825 (4) | 0.0420 (9) |
| C27 | 0.2367 (8) | 1.3142 (7) | 0.1443 (5) | 0.0548 (12) |
| C28 | 0.1238 (6) | 1.5967 (6) | −0.1279 (5) | 0.0488 (10) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.080 (3) | 0.110 (4) | 0.055 (2) | −0.037 (3) | 0.000 (2) | 0.034 (2) |
| O2 | 0.044 (2) | 0.090 (3) | 0.076 (3) | −0.0278 (18) | 0.0088 (17) | 0.023 (2) |
| O3 | 0.0427 (19) | 0.099 (3) | 0.106 (3) | −0.030 (2) | −0.022 (2) | 0.032 (3) |
| O4 | 0.081 (3) | 0.072 (3) | 0.072 (3) | −0.020 (2) | −0.018 (2) | 0.032 (2) |
| O5 | 0.083 (3) | 0.134 (5) | 0.058 (2) | −0.047 (3) | 0.000 (2) | 0.048 (3) |
| O6 | 0.046 (2) | 0.083 (3) | 0.079 (3) | −0.0271 (18) | 0.0162 (18) | 0.022 (2) |
| O7 | 0.0424 (18) | 0.088 (3) | 0.108 (3) | −0.0269 (18) | −0.0145 (19) | 0.040 (2) |
| O8 | 0.054 (2) | 0.064 (2) | 0.071 (2) | −0.0164 (17) | −0.0107 (17) | 0.0269 (18) |
| N1 | 0.071 (3) | 0.081 (3) | 0.061 (3) | −0.051 (3) | 0.032 (2) | −0.020 (2) |
| N2 | 0.125 (5) | 0.062 (3) | 0.051 (2) | −0.054 (3) | 0.037 (3) | 0.000 (2) |
| N3 | 0.0458 (17) | 0.056 (2) | 0.0426 (18) | −0.0175 (15) | 0.0023 (14) | 0.0135 (15) |
| C1 | 0.040 (3) | 0.084 (4) | 0.082 (4) | −0.008 (3) | −0.013 (2) | −0.014 (3) |
| C2 | 0.084 (4) | 0.056 (3) | 0.039 (2) | −0.024 (3) | −0.011 (2) | 0.018 (2) |
| C3 | 0.045 (2) | 0.070 (3) | 0.050 (3) | −0.028 (2) | 0.0135 (19) | −0.015 (2) |
| C4 | 0.063 (3) | 0.066 (3) | 0.051 (3) | 0.006 (2) | −0.005 (2) | 0.010 (2) |
| C5 | 0.098 (5) | 0.059 (3) | 0.049 (3) | −0.025 (3) | 0.005 (3) | 0.018 (2) |
| C6 | 0.054 (3) | 0.066 (3) | 0.083 (4) | −0.028 (2) | 0.018 (3) | −0.015 (3) |
| C7 | 0.049 (3) | 0.067 (3) | 0.057 (3) | −0.009 (2) | −0.007 (2) | −0.003 (2) |
| C8 | 0.076 (3) | 0.043 (2) | 0.038 (2) | −0.027 (2) | 0.011 (2) | 0.0008 (17) |
| C9 | 0.044 (2) | 0.078 (4) | 0.063 (3) | −0.021 (2) | 0.007 (2) | −0.014 (3) |
| C10 | 0.082 (4) | 0.058 (3) | 0.058 (3) | −0.012 (3) | −0.018 (3) | 0.014 (2) |
| C11 | 0.037 (2) | 0.048 (2) | 0.0359 (19) | −0.0200 (17) | −0.0010 (16) | 0.0031 (16) |
| C12 | 0.040 (2) | 0.059 (3) | 0.051 (3) | −0.016 (2) | −0.0064 (19) | 0.009 (2) |
| C13 | 0.036 (2) | 0.077 (4) | 0.077 (4) | −0.018 (2) | −0.004 (2) | 0.002 (3) |
| C14 | 0.047 (3) | 0.078 (4) | 0.076 (4) | −0.037 (3) | 0.015 (2) | −0.001 (3) |
| C15 | 0.060 (3) | 0.065 (3) | 0.048 (3) | −0.036 (2) | 0.006 (2) | 0.009 (2) |
| C16 | 0.041 (2) | 0.041 (2) | 0.038 (2) | −0.0194 (17) | −0.0055 (16) | 0.0053 (16) |
| C17 | 0.054 (3) | 0.055 (3) | 0.041 (2) | −0.025 (2) | 0.0030 (19) | 0.0045 (19) |
| C18 | 0.054 (3) | 0.057 (3) | 0.064 (3) | −0.019 (2) | −0.012 (2) | 0.009 (2) |
| C21 | 0.038 (2) | 0.040 (2) | 0.039 (2) | −0.0150 (16) | −0.0002 (16) | 0.0020 (16) |
| C22 | 0.051 (3) | 0.058 (3) | 0.052 (3) | −0.020 (2) | −0.016 (2) | 0.014 (2) |
| C23 | 0.034 (2) | 0.077 (3) | 0.083 (4) | −0.024 (2) | −0.004 (2) | 0.002 (3) |
| C24 | 0.047 (3) | 0.088 (4) | 0.061 (3) | −0.037 (3) | 0.015 (2) | 0.004 (3) |
| C25 | 0.050 (3) | 0.065 (3) | 0.049 (3) | −0.027 (2) | −0.001 (2) | 0.014 (2) |
| C26 | 0.0350 (19) | 0.052 (2) | 0.041 (2) | −0.0199 (17) | 0.0055 (16) | −0.0010 (18) |
| C27 | 0.062 (3) | 0.058 (3) | 0.045 (2) | −0.026 (2) | 0.015 (2) | 0.004 (2) |
| C28 | 0.042 (2) | 0.051 (2) | 0.051 (2) | −0.0165 (18) | −0.0068 (18) | 0.013 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C17 | 1.238 (6) | C7—C8 | 1.385 (7) |
| O2—C17 | 1.257 (6) | C7—H7 | 0.9300 |
| O2—H3A | 1.37 (9) | C8—C9 | 1.376 (8) |
| O3—C18 | 1.305 (7) | C9—C10 | 1.403 (8) |
| O3—H3A | 1.07 (9) | C9—H9 | 0.9300 |
| O4—C18 | 1.210 (6) | C10—H10 | 0.9300 |
| O5—C27 | 1.206 (7) | C11—C12 | 1.395 (6) |
| O6—C27 | 1.273 (7) | C11—C16 | 1.420 (6) |
| O6—H7A | 1.03 (8) | C11—C17 | 1.507 (6) |
| O7—C28 | 1.273 (6) | C12—C13 | 1.383 (7) |
| O7—H7A | 1.37 (8) | C12—H12 | 0.9300 |
| O8—C28 | 1.218 (6) | C13—C14 | 1.347 (8) |
| N1—C5 | 1.271 (9) | C13—H13 | 0.9300 |
| N1—C1 | 1.325 (9) | C14—C15 | 1.385 (8) |
| N1—H1N | 0.86 (6) | C14—H14 | 0.9300 |
| N2—C6 | 1.282 (9) | C15—C16 | 1.391 (6) |
| N2—C10 | 1.333 (9) | C15—H15 | 0.9300 |
| N2—H2N | 0.85 (6) | C16—C18 | 1.513 (7) |
| N3—C8 | 1.403 (5) | C21—C22 | 1.388 (6) |
| N3—C3 | 1.411 (5) | C21—C26 | 1.404 (6) |
| N3—H3N | 0.92 (5) | C21—C27 | 1.547 (6) |
| C1—C2 | 1.389 (9) | C22—C23 | 1.391 (7) |
| C1—H1 | 0.9300 | C22—H22 | 0.9300 |
| C2—C3 | 1.342 (8) | C23—C24 | 1.382 (9) |
| C2—H2 | 0.9300 | C23—H23 | 0.9300 |
| C3—C4 | 1.400 (7) | C24—C25 | 1.355 (8) |
| C4—C5 | 1.361 (9) | C24—H24 | 0.9300 |
| C4—H4 | 0.9300 | C25—C26 | 1.394 (6) |
| C5—H5 | 0.9300 | C25—H25 | 0.9300 |
| C6—C7 | 1.321 (9) | C26—C28 | 1.527 (6) |
| C6—H6 | 0.9300 | | |

| | | | |
|---|---|---|---|
| C17—O2—H3A | 114 (4) | C13—C12—C11 | 122.2 (4) |
| C18—O3—H3A | 110 (4) | C13—C12—H12 | 118.9 |
| C27—O6—H7A | 109 (4) | C11—C12—H12 | 118.9 |
| C28—O7—H7A | 109 (3) | C14—C13—C12 | 119.7 (5) |
| C5—N1—C1 | 121.9 (5) | C14—C13—H13 | 120.2 |
| C5—N1—H1N | 116 (5) | C12—C13—H13 | 120.2 |
| C1—N1—H1N | 122 (5) | C13—C14—C15 | 120.4 (5) |
| C6—N2—C10 | 122.0 (5) | C13—C14—H14 | 119.8 |
| C6—N2—H2N | 120 (5) | C15—C14—H14 | 119.8 |
| C10—N2—H2N | 118 (5) | C14—C15—C16 | 121.4 (5) |
| C8—N3—C3 | 135.3 (4) | C14—C15—H15 | 119.3 |
| C8—N3—H3N | 108 (4) | C16—C15—H15 | 119.3 |
| C3—N3—H3N | 117 (4) | C15—C16—C11 | 118.6 (4) |
| N1—C1—C2 | 119.9 (5) | C15—C16—C18 | 113.1 (4) |

| | | | |
|---|---|---|---|
| N1—C1—H1 | 120.0 | C11—C16—C18 | 128.3 (4) |
| C2—C1—H1 | 120.0 | O1—C17—O2 | 121.0 (5) |
| C3—C2—C1 | 119.2 (5) | O1—C17—C11 | 118.5 (5) |
| C3—C2—H2 | 120.4 | O2—C17—C11 | 120.5 (4) |
| C1—C2—H2 | 120.4 | O4—C18—O3 | 120.8 (5) |
| C2—C3—C4 | 118.6 (5) | O4—C18—C16 | 119.8 (5) |
| C2—C3—N3 | 123.6 (5) | O3—C18—C16 | 119.3 (5) |
| C4—C3—N3 | 117.8 (5) | C22—C21—C26 | 118.9 (4) |
| C5—C4—C3 | 118.6 (5) | C22—C21—C27 | 112.6 (4) |
| C5—C4—H4 | 120.7 | C26—C21—C27 | 128.5 (4) |
| C3—C4—H4 | 120.7 | C21—C22—C23 | 121.3 (4) |
| N1—C5—C4 | 121.8 (5) | C21—C22—H22 | 119.4 |
| N1—C5—H5 | 119.1 | C23—C22—H22 | 119.4 |
| C4—C5—H5 | 119.1 | C24—C23—C22 | 119.6 (5) |
| N2—C6—C7 | 121.3 (5) | C24—C23—H23 | 120.2 |
| N2—C6—H6 | 119.4 | C22—C23—H23 | 120.2 |
| C7—C6—H6 | 119.4 | C25—C24—C23 | 118.9 (4) |
| C6—C7—C8 | 121.1 (5) | C25—C24—H24 | 120.5 |
| C6—C7—H7 | 119.4 | C23—C24—H24 | 120.5 |
| C8—C7—H7 | 119.4 | C24—C25—C26 | 123.4 (4) |
| C9—C8—C7 | 118.2 (4) | C24—C25—H25 | 118.3 |
| C9—C8—N3 | 123.2 (5) | C26—C25—H25 | 118.3 |
| C7—C8—N3 | 118.5 (5) | C25—C26—C21 | 117.8 (4) |
| C8—C9—C10 | 117.3 (5) | C25—C26—C28 | 114.7 (4) |
| C8—C9—H9 | 121.4 | C21—C26—C28 | 127.5 (3) |
| C10—C9—H9 | 121.4 | O5—C27—O6 | 121.4 (5) |
| N2—C10—C9 | 120.1 (5) | O5—C27—C21 | 119.0 (5) |
| N2—C10—H10 | 119.9 | O6—C27—C21 | 119.4 (4) |
| C9—C10—H10 | 119.9 | O8—C28—O7 | 122.3 (5) |
| C12—C11—C16 | 117.7 (4) | O8—C28—C26 | 118.4 (4) |
| C12—C11—C17 | 114.6 (4) | O7—C28—C26 | 119.3 (4) |
| C16—C11—C17 | 127.7 (4) | | |

| | | | |
|---|---|---|---|
| C5—N1—C1—C2 | 1.5 (9) | C12—C11—C16—C18 | 177.2 (5) |
| N1—C1—C2—C3 | −0.6 (9) | C17—C11—C16—C18 | −4.8 (8) |
| C1—C2—C3—C4 | −1.4 (8) | C12—C11—C17—O1 | −10.2 (7) |
| C1—C2—C3—N3 | −178.7 (5) | C16—C11—C17—O1 | 171.7 (5) |
| C8—N3—C3—C2 | 3.8 (8) | C12—C11—C17—O2 | 169.0 (5) |
| C8—N3—C3—C4 | −173.6 (5) | C16—C11—C17—O2 | −9.0 (8) |
| C2—C3—C4—C5 | 2.7 (9) | C15—C16—C18—O4 | 17.3 (7) |
| N3—C3—C4—C5 | −179.9 (5) | C11—C16—C18—O4 | −162.1 (5) |
| C1—N1—C5—C4 | −0.2 (10) | C15—C16—C18—O3 | −159.4 (5) |
| C3—C4—C5—N1 | −1.9 (10) | C11—C16—C18—O3 | 21.3 (8) |
| C10—N2—C6—C7 | 0.1 (10) | C26—C21—C22—C23 | −2.2 (8) |
| N2—C6—C7—C8 | 0.5 (9) | C27—C21—C22—C23 | 177.6 (5) |
| C6—C7—C8—C9 | −0.4 (8) | C21—C22—C23—C24 | 1.9 (9) |
| C6—C7—C8—N3 | 178.0 (5) | C22—C23—C24—C25 | −1.3 (10) |
| C3—N3—C8—C9 | 1.6 (8) | C23—C24—C25—C26 | 1.2 (10) |

| | | | |
|---|---|---|---|
| C3—N3—C8—C7 | −176.7 (5) | C24—C25—C26—C21 | −1.4 (8) |
| C7—C8—C9—C10 | −0.3 (8) | C24—C25—C26—C28 | 178.6 (5) |
| N3—C8—C9—C10 | −178.6 (5) | C22—C21—C26—C25 | 1.9 (7) |
| C6—N2—C10—C9 | −0.8 (9) | C27—C21—C26—C25 | −177.9 (5) |
| C8—C9—C10—N2 | 0.9 (9) | C22—C21—C26—C28 | −178.1 (5) |
| C16—C11—C12—C13 | 1.7 (7) | C27—C21—C26—C28 | 2.1 (8) |
| C17—C11—C12—C13 | −176.5 (5) | C22—C21—C27—O5 | 6.8 (7) |
| C11—C12—C13—C14 | 0.6 (9) | C26—C21—C27—O5 | −173.4 (6) |
| C12—C13—C14—C15 | −2.4 (9) | C22—C21—C27—O6 | −168.9 (5) |
| C13—C14—C15—C16 | 1.9 (9) | C26—C21—C27—O6 | 10.9 (8) |
| C14—C15—C16—C11 | 0.4 (7) | C25—C26—C28—O8 | −20.4 (7) |
| C14—C15—C16—C18 | −179.0 (5) | C21—C26—C28—O8 | 159.6 (5) |
| C12—C11—C16—C15 | −2.2 (6) | C25—C26—C28—O7 | 158.8 (5) |
| C17—C11—C16—C15 | 175.9 (5) | C21—C26—C28—O7 | −21.2 (8) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*A*···O2 | 1.07 (9) | 1.37 (9) | 2.386 (6) | 155 (7) |
| O6—H7*A*···O7 | 1.03 (8) | 1.37 (8) | 2.396 (6) | 172 (7) |
| N1—H1*N*···O1 | 0.86 (6) | 1.90 (6) | 2.757 (6) | 177 (7) |
| N2—H2*N*···O6 | 0.85 (6) | 2.00 (6) | 2.834 (5) | 167 (7) |
| N3—H3*N*···O8$^{i}$ | 0.92 (5) | 1.88 (5) | 2.794 (5) | 172 (5) |

Symmetry code: (i) *x*, *y*−1, *z*+1.