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N,*N*,*N*′,*N*′-Tetrakis(pyridin-4-yl)methanediamine monohydrate

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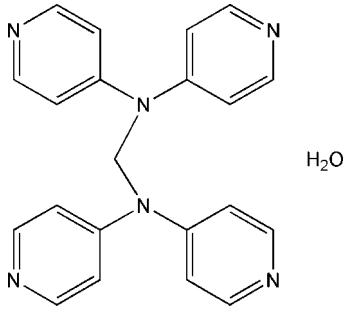
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.003 Å; disorder in solvent or counterion; R factor = 0.051; wR factor = 0.163; data-to-parameter ratio = 17.2.

In the title compound, $C_{21}H_{18}N_6\cdot H_2O$, two 4,4′-dipyridylamine groups are linked by a methylene C atom, which sits on a twofold axis. The lattice water molecule is located slightly off a twofold axis, and is therefore disordered over two positions. In the crystal, the organic molecules and the water molecule are linked by O—H···N hydrogen bonds. The organic molecules exhibit extensive offset face-to-face π–π interactions to symmetry equivalents [centroid–centroid distances = 3.725 (3) and 4.059 (3) Å].

Related literature

For metal-organic frameworks including 4,4′-dipyridylamine, see: Braverman & LaDuca (2007); Shyu *et al.* (2009). For the catalysis of multidimensional metal-organic frameworks, see: Welbes & Borovik (2005). For self-assembled metal-organic networks and their luminescent properties, see: Shin *et al.* (2012); Zeng *et al.* (2010).



Experimental

Crystal data

$C_{21}H_{18}N_6\cdot H_2O$ M_r = 372.42
Monoclinic, $C2/c$
a = 13.9048 (11) Å
b = 13.7637 (11) Å
c = 10.0569 (8) Å
β = 109.142 (2)°
V = 1818.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 200 K
0.34 × 0.26 × 0.25 mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.973, T_{max} = 0.978
6540 measured reflections
2241 independent reflections
1313 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.163
S = 1.09
2241 reflections
130 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1W···N2^{i}	1.02	1.88	2.869 (2)	161

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); 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: PK2409).

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supplementary materials

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N,N,N′,N′-Tetrakis(pyridin-4-yl)methanediamine monohydrate

Jong Won Shin and Kil Sik Min

Comment

Polypyridyl ligands have attracted considerable attention in materials science because they can be used for the construction of multidimensional metal-organic frameworks. These have potential applications in catalysis and as luminescent materials (Shin *et al.*, 2012; Welbes & Borovik, 2005; Zeng *et al.*, 2010). For example, as a building block, bis(4-pyridyl)amine (bpa) has been extensively used for self-assembly of multidimensional coordination polymers, because the ligand has significant functionalities, *e.g.* hydrogen bonding capability (Braverman & LaDuca, 2007; Shyu, *et al.*, 2009). Thus, we have made a new ligand, *N,N,N′,N′*-tetra-4-pyridyl-methylenediamine (TPMD), which can be used as a building unit for self-assembly of potential luminescent materials and catalysts. Here, we report the synthesis and crystal structure of *N,N,N′,N′*-tetra-4-pyridyl-methylenediamine monohydrate.

The title compound in its crystalline state is centrosymmetric (Fig. 1). The dihedral angle between neighboring pyridyl rings is 63.74 (7)°, and the angle of N1—C11—N1(-*x*, *y*, 1.5 - *z*) is 114.5 (2)°. The water molecule appears to be slightly off a 2-fold axis, and was refined using a disordered model, which gave a lower *R* value and a flatter difference map compared to a non-disordered model. The crystal packing is stabilized by strong intermolecular O—H···N hydrogen bonds (Table 1) that connect pairs of organic molecules by water molecules into chains along the (101) direction (Fig. 2). The crystal is also stabilized by intermolecular offset face-to-face π-π interactions [centroid-centroid distances = 3.725 (3) Å (-*x* + 1/2, -*y* + 1/2, 2 - *z*) and 4.059 (3) Å (-*x* + 1/2, -*y* + 1/2, 1 - *z*)] (Fig. 3).

Experimental

The title compound was prepared as follows. NaH (0.561 g, 0.0234 mol) was added carefully to a DMF solution (50 ml) of 4,4′-dipyridylamine (2.00 g, 0.0117 mol) and stirred for 2 days at room temperature. To the mixture was added dropwise dichloromethane (20 ml) and the mixture solution was again stirred for 2 days, which resulted in a dark red solution. Then the mixture was quenched with H_2O (50 ml), and the organic layer was extracted with $CHCl_3$ (3 times, 100 ml). The extract was washed with NaCl solution to purify and then dried with Na_2SO_4. After removing the organic solvent, a pale yellow oil was obtained, from which colorless crystals formed in 1 day. The crystals were filtered and washed with *n*-hexane and acetonitrile. Yield: 0.86 g (42%). Anal. Calcd. for $C_{21}H_{20}N_6O$: C, 67.73; H, 5.41; N, 22.57. Found: C, 67.63; H, 5.23; N, 22.51. ^{1}H NMR (400 MHz, DMSO-d^6, 300 K): δ = 8.35 (dd, J = 1.52, 1.52 Hz, 8 H), 6.91 (dd, J = 1.56, 1.60 Hz, 8 H), 5.95 (s, 2H). GC—MS: m/*z* = 354.1 (M^+). IR (KBr, cm^{-1}): 3425, 3050, 3024, 1601, 1581, 1497, 1207, 1068, 850, 602.

Refinement

The H atom of O1 was located in a difference Fourier map and refined isotropically. The remaining H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) Å and 0.99 (open chain H atoms) Å, and with U_{iso}(H) values of 1.2 times the equivalent anisotropic displacement

parameters of the parent C atoms.

Computing details

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

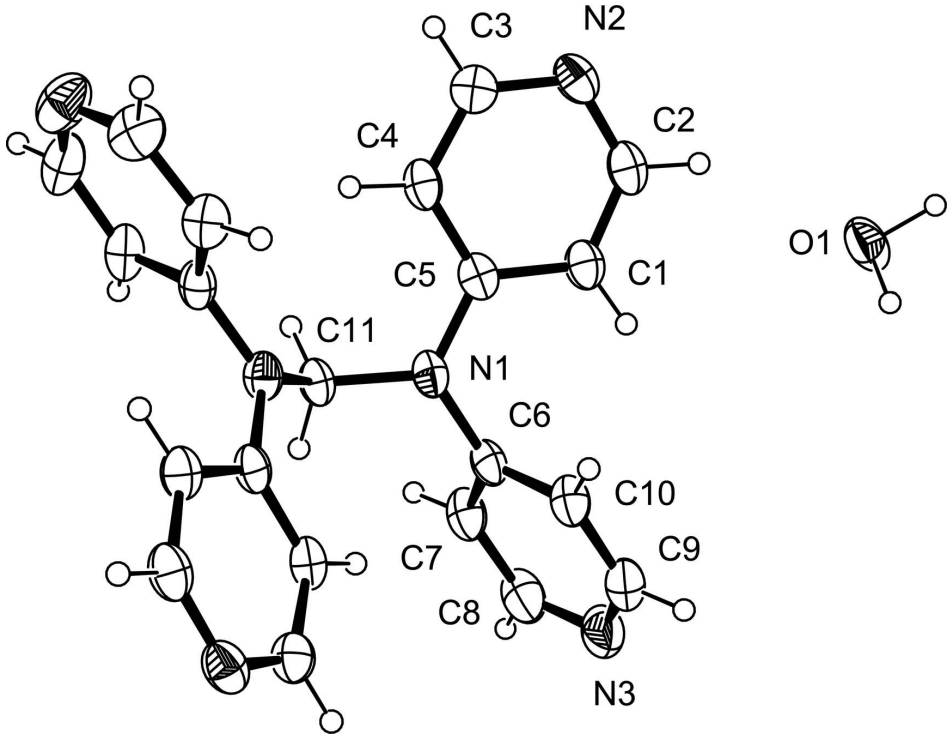

Figure 1

An ellipsoid plot (40% probability) of the title compound. The unlabelled half of the molecule is related by a crystallographic 2-fold axis. The water molecule is disordered about a 2-fold axis (for clarity, only one component is shown).

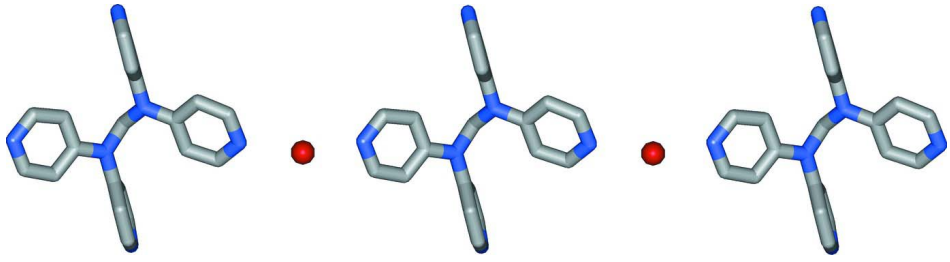

Figure 2

A view of the title compound showing a one-dimensional chain formed by O—H···N hydrogen bonding interactions. The chain extends along the (101) direction.

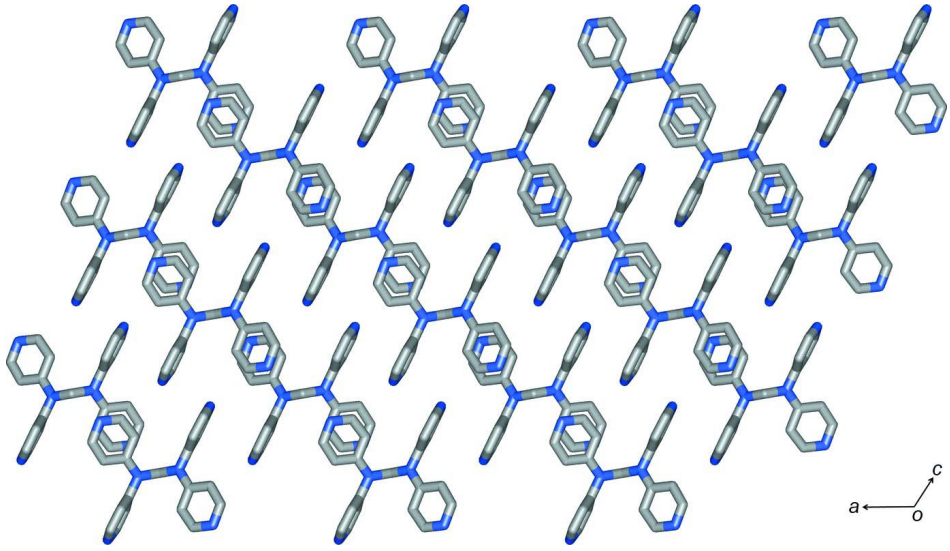

Figure 3

A view of the title compound showing offset face-to-face π-π interactions.

N,*N*,*N*′,*N*′-Tetrakis(pyridin-4-yl)methanediamine monohydrate

Crystal data

$C_{21}H_{18}N_6 \cdot H_2O$
$M_r = 372.42$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 13.9048$ (11) Å
$b = 13.7637$ (11) Å
$c = 10.0569$ (8) Å
$\beta = 109.142$ (2)°
$V = 1818.3$ (3) Å^3
$Z = 4$
$F(000) = 784$
$D_x = 1.360$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2155 reflections
$\theta = 2.7$–$28.2°$
$\mu = 0.09$ mm^{-1}
$T = 200$ K
Block, colorless
0.34 × 0.26 × 0.25 mm

Data collection

Siemens SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.973$, $T_{max} = 0.978$
6540 measured reflections
2241 independent reflections
1313 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$
$h = -14 \rightarrow 18$
$k = -18 \rightarrow 16$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.163$
$S = 1.09$
2241 reflections
130 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

$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.1675P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ 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}	Occ. (<1)
N1	0.08225 (11)	0.18977 (10)	0.72834 (16)	0.0378 (4)	
N2	0.32207 (12)	0.08225 (11)	1.07690 (17)	0.0456 (4)	
N3	0.12205 (15)	0.19990 (14)	0.3297 (2)	0.0627 (6)	
C1	0.24926 (14)	0.11276 (13)	0.8290 (2)	0.0415 (5)	
H1	0.2569	0.1085	0.7387	0.050*	
C2	0.32458 (14)	0.07990 (13)	0.9453 (2)	0.0455 (5)	
H2	0.3836	0.0532	0.9315	0.055*	
C3	0.23734 (15)	0.12101 (13)	1.0907 (2)	0.0444 (5)	
H3	0.2327	0.1249	1.1827	0.053*	
C4	0.15609 (14)	0.15572 (12)	0.9798 (2)	0.0388 (5)	
H4	0.0977	0.1813	0.9966	0.047*	
C5	0.16063 (13)	0.15281 (11)	0.84383 (19)	0.0356 (4)	
C6	0.09476 (13)	0.19319 (12)	0.5933 (2)	0.0373 (4)	
C7	0.09792 (15)	0.28090 (13)	0.5269 (2)	0.0461 (5)	
H7	0.0918	0.3406	0.5708	0.055*	
C8	0.11000 (16)	0.28004 (16)	0.3965 (2)	0.0569 (6)	
H8	0.1097	0.3407	0.3512	0.068*	
C9	0.11687 (16)	0.11622 (16)	0.3940 (2)	0.0555 (6)	
H9	0.1238	0.0577	0.3480	0.067*	
C10	0.10220 (14)	0.10896 (14)	0.5221 (2)	0.0452 (5)	
H10	0.0972	0.0471	0.5613	0.054*	
C11	0.0000	0.24732 (13)	0.7500	0.0355 (6)	
H11A	0.0293	0.2898	0.8329	0.043*	0.50
H11B	−0.0293	0.2898	0.6671	0.043*	0.50
O1	0.4878 (6)	0.01031 (13)	0.7761 (8)	0.0617 (12)	0.50
H1W	0.5532	−0.0300	0.8088	0.130 (11)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0315 (8)	0.0354 (8)	0.0500 (9)	0.0046 (6)	0.0180 (7)	0.0039 (6)
N2	0.0331 (9)	0.0417 (9)	0.0577 (11)	0.0006 (7)	0.0089 (8)	0.0033 (7)
N3	0.0592 (13)	0.0774 (13)	0.0613 (12)	0.0230 (10)	0.0331 (10)	0.0175 (10)
C1	0.0353 (11)	0.0379 (10)	0.0547 (12)	0.0007 (8)	0.0193 (9)	0.0021 (8)

C2	0.0335 (11)	0.0403 (10)	0.0650 (14)	0.0014 (8)	0.0190 (9)	−0.0005 (9)
C3	0.0454 (12)	0.0394 (10)	0.0498 (12)	−0.0056 (9)	0.0175 (9)	0.0005 (8)
C4	0.0315 (10)	0.0314 (9)	0.0577 (12)	−0.0013 (7)	0.0203 (9)	0.0024 (8)
C5	0.0319 (10)	0.0260 (8)	0.0497 (11)	−0.0037 (7)	0.0146 (8)	0.0022 (7)
C6	0.0262 (9)	0.0382 (10)	0.0498 (11)	0.0035 (7)	0.0158 (8)	0.0066 (8)
C7	0.0407 (12)	0.0382 (10)	0.0663 (14)	0.0027 (8)	0.0270 (10)	0.0090 (9)
C8	0.0490 (14)	0.0604 (14)	0.0709 (15)	0.0124 (10)	0.0326 (11)	0.0269 (11)
C9	0.0514 (14)	0.0595 (13)	0.0595 (14)	0.0176 (10)	0.0235 (11)	0.0006 (10)
C10	0.0433 (12)	0.0387 (10)	0.0572 (12)	0.0078 (8)	0.0214 (10)	0.0033 (8)
C11	0.0285 (13)	0.0291 (12)	0.0509 (15)	0.000	0.0158 (11)	0.000
O1	0.052 (2)	0.0452 (13)	0.072 (2)	0.0162 (17)	−0.0008 (17)	−0.0107 (16)

Geometric parameters (Å, º)

N1—C5	1.402 (2)	C4—H4	0.9500
N1—C6	1.425 (2)	C6—C10	1.384 (3)
N1—C11	1.4649 (17)	C6—C7	1.387 (2)
N2—C2	1.335 (2)	C7—C8	1.376 (3)
N2—C3	1.341 (2)	C7—H7	0.9500
N3—C8	1.330 (3)	C8—H8	0.9500
N3—C9	1.335 (3)	C9—C10	1.373 (3)
C1—C2	1.366 (3)	C9—H9	0.9500
C1—C5	1.402 (2)	C10—H10	0.9500
C1—H1	0.9500	C11—N1^{i}	1.4649 (17)
C2—H2	0.9500	C11—H11A	0.9900
C3—C4	1.387 (3)	C11—H11B	0.9900
C3—H3	0.9500	O1—O1^{ii}	0.7127
C4—C5	1.390 (2)	O1—H1W	1.0230
C5—N1—C6	119.78 (14)	C10—C6—N1	121.22 (15)
C5—N1—C11	120.38 (13)	C7—C6—N1	121.38 (16)
C6—N1—C11	117.96 (12)	C8—C7—C6	118.99 (18)
C2—N2—C3	114.92 (16)	C8—C7—H7	120.5
C8—N3—C9	115.77 (19)	C6—C7—H7	120.5
C2—C1—C5	119.54 (18)	N3—C8—C7	124.30 (18)
C2—C1—H1	120.2	N3—C8—H8	117.8
C5—C1—H1	120.2	C7—C8—H8	117.8
N2—C2—C1	125.35 (19)	N3—C9—C10	124.49 (19)
N2—C2—H2	117.3	N3—C9—H9	117.8
C1—C2—H2	117.3	C10—C9—H9	117.8
N2—C3—C4	124.43 (18)	C9—C10—C6	118.94 (17)
N2—C3—H3	117.8	C9—C10—H10	120.5
C4—C3—H3	117.8	C6—C10—H10	120.5
C3—C4—C5	119.59 (17)	N1^{i}—C11—N1	114.54 (16)
C3—C4—H4	120.2	N1^{i}—C11—H11A	108.6
C5—C4—H4	120.2	N1—C11—H11A	108.6
C4—C5—C1	116.16 (16)	N1^{i}—C11—H11B	108.6
C4—C5—N1	122.06 (16)	N1—C11—H11B	108.6
C1—C5—N1	121.76 (17)	H11A—C11—H11B	107.6
C10—C6—C7	117.39 (18)	O1^{ii}—O1—H1W	69.5

C3—N2—C2—C1	−0.3 (3)	C11—N1—C6—C10	−129.57 (17)
C5—C1—C2—N2	0.0 (3)	C5—N1—C6—C7	−115.35 (19)
C2—N2—C3—C4	0.8 (3)	C11—N1—C6—C7	49.1 (2)
N2—C3—C4—C5	−1.1 (3)	C10—C6—C7—C8	−1.2 (3)
C3—C4—C5—C1	0.7 (2)	N1—C6—C7—C8	−179.92 (17)
C3—C4—C5—N1	−177.87 (15)	C9—N3—C8—C7	3.2 (3)
C2—C1—C5—C4	−0.2 (2)	C6—C7—C8—N3	−2.1 (3)
C2—C1—C5—N1	178.37 (16)	C8—N3—C9—C10	−1.2 (3)
C6—N1—C5—C4	174.20 (15)	N3—C9—C10—C6	−1.8 (3)
C11—N1—C5—C4	10.1 (2)	C7—C6—C10—C9	2.9 (3)
C6—N1—C5—C1	−4.3 (2)	N1—C6—C10—C9	−178.31 (17)
C11—N1—C5—C1	−168.41 (15)	C5—N1—C11—N1^{i}	−82.93 (13)
C5—N1—C6—C10	65.9 (2)	C6—N1—C11—N1^{i}	112.69 (14)

Symmetry codes: (i) −*x*, *y*, −*z*+3/2; (ii) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*W*···N2^{iii}	1.02	1.88	2.869 (2)	161

Symmetry code: (iii) −*x*+1, −*y*, −*z*+2.