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Clarifying the structures of imidines: using crystallographic characterization to identify tautomers and localized systems of π-bonding

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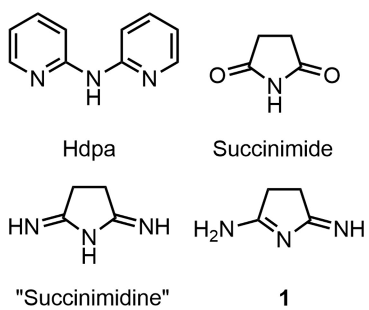
Nitrogen heterocycles are a class of organic compounds with extremely versatile functionality. Imidines, HN[C(NH)*R*]$_2$, are a rare class of heterocycles related to imides, HN[C(O)*R*]$_2$, in which the O atoms of the carbonyl groups are replaced by N—H groups. The useful synthesis of the imidine compounds succinimidine and glutarimidine, as well as their partially hydrolyzed imino–imide congeners, was first described in the mid-1950s, though structural characterization is presented for the first time in this article. In the solid state, these structures are different from the proposed imidine form: succinimidine crystallizes as an imino–amine, 2-imino-3,4-dihydro-2*H*-pyrrol-5-amine, $C_4H_7N_2$ (**1**), glutarimidine as 6-imino-3,4,5,6-tetrahydropyridin-2-amine methanol monosolvate, $C_5H_9N_3{\cdot}CH_3OH$ (**2**), and the corresponding hydrolyzed imino–imide compounds as amino–amides 5-amino-3,4-dihydro-2*H*-pyrrol-2-one, $C_4H_6N_2O$ (**3**), and 6-amino-4,5-dihydropyridin-2(3*H*)-one, $C_5H_8N_2O$ (**4**). Imidine **1** was also determined as the hydrochloride salt solvate 5-amino-3,4-dihydro-2*H*-pyrrol-2-iminium chloride–2-imino-3,4-dihydro-2*H*-pyrrol-5-amine–water (1/1/1), $C_4H_8N_3^+{\cdot}Cl^-{\cdot}C_4H_7N_3{\cdot}H_2O$ (**1**·HCl). As such, **1** and **2** show alternating short and long C—N bonds across the molecule, revealing distinct imino (C═NH) and amine (C—NH$_2$) groups throughout the C—N backbone. These structures provide definitive evidence for the predominant imino–amine tautomer in the solid state, which serves to enrich the previously proposed imidine-focused structures that have appeared in organic chemistry textbooks since the discovery of this class of compounds in 1883.

1. Introduction

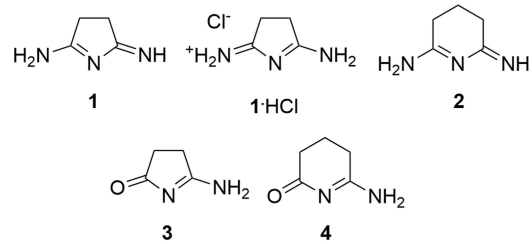
Nitrogen heterocycles are of considerable interest for their ability to act as ligands in coordination chemistry, notably supporting multimetallic compounds and, in particular, compounds having metal–metal bonds (Chipman & Berry, 2020; Beach *et al.*, 2021; Kerru *et al.*, 2020). Examples of these types of ligands can be seen in 2-naphthyridylphenylamine (Ding *et al.*, 2015; Liu, Wang *et al.*, 2009; Liu, Chen *et al.*, 2009; Tsai *et al.*, 2013), 1,8-naphthyridin-2(1*H*)-one (Chang *et al.*, 2017), 2-anilinopyridinate (Roy *et al.*, 2022) and 2,2′-dipyridylamine (Hdpa) (Chipman & Berry, 2018*a*,*b*; Lescouëzec *et al.*, 2001; Berry *et al.*, 2003; Hsiao *et al.*, 2008).

We have recently explored the ability of the ligand 2,2′-dipyridylamine (Scheme 1 shows the structures of Hdpa, succinimide, the proposed ‘succinimidine’ structure, and the observed structure of **1**) to support linear trimetallic metal–metal-bonded compounds (Brogden & Berry, 2016). In the search for other multitopic *N*-donor ligands that might support similar structures, our attention was drawn to the class of compounds called ‘imidines’, first described by Pinner in 1883 (Pinner, 1883) and then later by Elvidge and Linstead in the 1950s. In particular, we focus on the heterocyclic compounds ‘succinimidine’ and ‘glutarimidine’ (Elvidge *et al.*, 1959; Elvidge & Linstead, 1954). These compounds were so named because of their proposed structural analogy to succinimide (Scheme 1) and the corresponding six-membered-ring analog glutarimide. Since imidines represent a relatively rare functional group, these structures, proposed solely on the basis of elemental analysis results, have been propagated in prominent organic chemistry textbooks (March, 1992). We show here that although solution-based studies agree with the historically predicted imidine tautomers, in the solid state, the compounds ‘succinimidine’ and ‘glutarimidine’ adopt a different tautomeric form from those originally proposed. In the solid state, the structures are unsymmetric imino–amines and are better named systematically as 2-imino-3,4-dihydro-2*H*-pyrrol-5-amine (**1**) and 6-imino-3,4,5,6-tetrahydropyridin-2-amine (**2**).



Scheme 1

The 1950s syntheses involved the reaction of methanol solutions of terminal dinitriles (succinonitrile, glutaronitrile, or adiponitrile) with liquid ammonia before heating (Elvidge & Linstead, 1954; Elvidge *et al.*, 1959). We have found that similar results can be obtained by saturating a methanol solution of succinonitrile with anhydrous ammonia. This solution, when heated for 18 h in a sealed bomb flask, yielded **1** in >50% yield. The product is easily separated from the mother liquor by precipitation *via* the addition of excess diethyl ether. The synthesis of **2** was performed in an almost identical manner; however, to achieve a useful yield, the reaction mixture was heated for 40 h total. The solvent was then removed by rotary evaporation and yellow crystals separated from the residual oil, which was washed away with ether. The modified Pinner reaction conditions result in protio-neutral ring closing to yield the N-heterocycle with two additional N-atom-based functional groups. Both the original article from Pinner and the later articles from Elvidge and Linstead draw all three N-atom sites as being singly protonated in a symmetric ‘imidine’ form (Pinner, 1883; Elvidge & Linstead, 1954; Elvidge *et al.*, 1959). Elvidge and Linstead additionally reported that reaction of the imidines with water sequentially replace one and then both terminal N-atom functional groups with carbonyl groups, such that ‘succinimidine’ could be fully hydrolyzed to form succinimide (Elvidge & Linstead, 1954; Elvidge *et al.*, 1959). While the symmetric structure of succinimide in the solid state is well established (Yu *et al.*, 2012; Mason, 1961), the monohydrolyzed forms of **1** and **2** have not been investigated before, and they are structurally characterized here (Scheme 2 shows the structures of the most stable solid-phase tautomers of the species described .



Scheme 2

in this article, with only one resonance structure being shown for the protonated species found in **1**·HCl). A combination of solid state, solution, and computational studies are employed to best describe the various possible tautomers of these species.

2. Experimental

2.1. General methods

Methanol (Sigma–Aldrich) was distilled from CaH_2 under N_2 and used immediately. Succinonitrile and glutaronitrile were purchased from Sigma–Aldrich and used as received. Inhibitor-free anhydrous diethyl ether was purchased from Sigma–Aldrich and used as received. All deuterated solvents were purchased from Sigma–Aldrich, used as received, and stored long term in air. Unless otherwise noted, all manipulations were performed in air. Electrospray ionization mass spectrometry was performed with a Thermo Q Exactive Plus mass spectrometer. IR spectra were recorded with a Bruker Tenser 27 spectrometer using an ATR adapter. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer. **Caution!** The synthetic procedures for the preparation of **1** and **2** involve heating a sealed reaction vessel and should only be performed at or below the scale described here using rated thick-walled glassware, with a protective blast shield.

2.2. Synthesis and crystallization

2.2.1. Synthesis of 1. Imidine **1** was synthesized through a modification of the literature procedure of Elvidge & Linstead (1954). Anhydrous methanol (70 ml), succinonitrile (4.02 g, 50.1 mmol), and a Teflon stirrer bar were combined in a 250 ml heavy-walled threaded glass vessel. The solid was fully dissolved and the resulting solution was sparged with anhydrous ammonia gas until saturated. The flask was then tightly sealed and partially submerged in an oil bath. The oil bath was programmed to heat to 70 °C for 18 h before automatically cooling to room temperature. A blast shield was placed in front of the flask and the heating cycle was started. Upon cooling to room temperature, the pressure flask containing a

Table 1
Experimental details.

Experiments were carried out at 100 K using a Bruker SMART APEXII (Quasar) diffractometer. H atoms were treated by a mixture of independent and constrained refinement. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2016; Krause *et al.*, 2015).

	1	**1**·HCl	**2**
Crystal data			
Chemical formula	$C_4H_7N_3$	$C_4H_8N_3^+·Cl^-·C_4H_7N_3·H_2O$	$C_5H_9N_3·CH_4O$
M_r	97.13	248.72	143.19
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	5.9577 (4), 6.7494 (5), 6.8249 (5)	19.294 (3), 9.4173 (8), 13.7430 (12)	9.4887 (9), 14.5341 (11), 12.2828 (10)
α, β, γ (°)	101.641 (4), 104.225 (6), 111.425 (4)	90, 108.570 (5), 90	90, 111.320 (8), 90
V (Å^3)	234.36 (3)	2367.0 (5)	1578.0 (2)
Z	2	8	8
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.75	2.81	0.70
Crystal size (mm)	0.11 × 0.11 × 0.10	0.09 × 0.04 × 0.04	0.03 × 0.02 × 0.01
Data collection			
T_{min}, T_{max}	0.844, 0.901	0.852, 0.947	0.690, 0.754
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	3673, 892, 833	19987, 2322, 1934	26582, 3219, 2938
R_{int}	0.019	0.051	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618	0.621	0.625
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.092, 1.09	0.044, 0.116, 1.03	0.040, 0.108, 1.07
No. of reflections	892	2322	3219
No. of parameters	76	151	204
No. of restraints	0	0	5
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.27, −0.27	0.44, −0.24	0.35, −0.28

	3	**4**
Crystal data		
Chemical formula	$C_4H_6N_2O$	$C_5H_8N_2O$
M_r	98.11	112.13
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$
a, b, c (Å)	7.3685 (5), 8.0074 (7), 8.4211 (9)	6.3296 (19), 7.0222 (19), 7.351 (2)
α, β, γ (°)	90, 115.741 (5), 90	84.975 (13), 71.693 (13), 63.889 (12)
V (Å^3)	447.56 (7)	278.06 (14)
Z	4	2
Radiation type	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.91	0.10
Crystal size (mm)	0.1 × 0.09 × 0.04	0.16 × 0.05 × 0.01
Data collection		
T_{min}, T_{max}	0.853, 0.915	0.929, 0.991
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	7398, 886, 775	9023, 2048, 1680
R_{int}	0.042	0.034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.770
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.089, 1.03	0.043, 0.120, 1.06
No. of reflections	886	2048
No. of parameters	72	79
No. of restraints	0	0
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.23, −0.18	0.44, −0.27

Computer programs: *APEX3* (Bruker, 2016, 2017), *SAINT-Plus* (Bruker, 2016), *SAINT* (Bruker, 2017), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

black solution was removed from the oil bath. Activated carbon (~3 g) was added to the solution, which was sparged with nitrogen for 10 min. The solution was then filtered through Celite to yield a pale-yellow filtrate. This filtrate was added to diethyl ether (300 ml), resulting in precipitation of the product. The suspension was filtered through a glass frit and the off-white solid was washed several times with ether. The solid was dried under high-vacuum overnight and stored in a nitrogen glove-box without further purification. X-ray-quality crystals were obtained by slow diffusion of diethyl ether into a saturated solution of **1** in MeOH under an inert atmosphere. ESI (m/z): ($[M + H]^+$) 98.0712. IR (ATR, cm^{-1}): 3289, 3157, 3077, 2935, 2847, 1829, 1772, 1749, 1686, 1662, 1654, 1636, 1532, 1473, 1453, 1418, 1328, 1296, 1265, 1241, 1223, 1190, 1143, 1129, 1115, 996, 936, 919, 851, 822, 783, 665, 651, 641. ^{1}H NMR (400 MHz, DMSO): δ 7.37 (*s*, 3H), 2.46 (*s*, 4H). Crystals of **1**·HCl were fortuitously obtained by slow diffusion of diethyl ether into a deuterated chloroform solution containing **1** (yield: 2.46 g, 25.3 mmol, 50.6%).

2.2.2. Synthesis of 2. Imidine **2** was synthesized by a modified literature method (Elvidge & Linstead, 1954). Anhydrous methanol (70 ml), glutaronitrile (2.0299 g, 21.568 mmol), and an oven-dried stirrer bar were added to an oven-dried pressure flask under a constant stream of nitrogen gas. The resulting solution was sparged with nitrogen gas for 5 min and then saturated with ammonia gas. The flask was then sealed and heated at 70 °C for 40 h while stirring. Once the flask had cooled, the clear solution was sparged with nitrogen for ~20 min. The solvent was removed *via* rotary evaporation. The resulting yellow powder was washed with diethyl ether and filtered to remove residual glutaronitrile. X-ray-quality crystals were obtained by evaporation of a saturated MeOH solution (yield: 0.760 g, 31.7%). ESI (*m*/*z*): ([*M* + H]$^{+}$) 112.0868. IR (ATR, cm^{-1}): 3254, 3004, 2954, 1666, 1605, 1543, 1457, 1418, 1373, 1334, 1316, 1316, 1187, 1145, 1103, 1061, 967, 909, 886, 791, 758, 676. ^{1}H NMR (400 MHz, DMSO): δ 7.05 (*s*, 3H), 2.20 (*t*, J = 6.5 Hz, 4H), 1.80–1.57 (*q*, 2H).

2.2.3. Synthesis of 3. A scintillation vial was charged with **1** (1.0 g, 0.010 mol). Milli-Q water (3.4 ml, 0 °C) was then added to the vial, immediately turning the solution faint brown. The vial was stored in a 0 °C refrigerator overnight. The next day, white crystals (yield: 0.68 g, 0.0069 mol, 69%) suitable for X-ray diffraction analysis were collected from the solution. ESI (*m*/*z*): ([*M* + H]$^{+}$) 99.0552. IR (ATR, cm^{-1}): 3220, 3135, 3019, 2938, 2918, 2851, 2360, 2341, 1686, 1627, 1526, 1456, 1437, 1418, 1397, 1338, 1294, 1251, 1221, 1161, 1009, 929, 866, 852, 827, 765, 677. ^{1}H NMR (400 MHz, DMSO): δ 8.30 (*s*, 1H), 8.07 (*s*, 1H), 2.67–2.56 (*m*, 2H), 2.34–2.25 (*m*, 2H).

2.2.4. Synthesis of 4. A scintillation vial was filled with **2** (0.10 g, 0.90 mmol) and the solid was subsequently dissolved in a minimal amount of Milli-Q water. The resulting solution was cooled overnight before allowing ether vapor to diffuse into the solution. The product precipitated out as white crystals (yield 0.048 g, 47%) suitable for X-ray diffraction, with a minor impurity of 6-hydroxy-4,5-dihydropyridin-2(3*H*)-one. ESI (*m*/*z*): ([*M* + NH_4]$^{+}$): 130.0975. IR (ATR, cm^{-1}): 3381, 3185, 2967, 2947, 2920, 2886, 2823, 2774, 1644, 1534, 1506, 1458, 1426, 1418, 1349, 1299, 1274, 1222, 1153, 1120, 1071, 1056, 948, 917, 864, 807, 756, 671, 638. ^{1}H NMR (400 MHz, DMSO-d_6): δ, 7.35 (*s*, 1H), 6.80 (*s*, 1H), 2.24 (*t*, J = 7.7 Hz, 2H), 1.88 (*t*, J = 7.3 Hz, 2H), 1.78 (quint, J = 7.4 Hz, 2H).

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For the structures of **1** and **4**, the diffraction data were consistent with a triclinic unit cell.

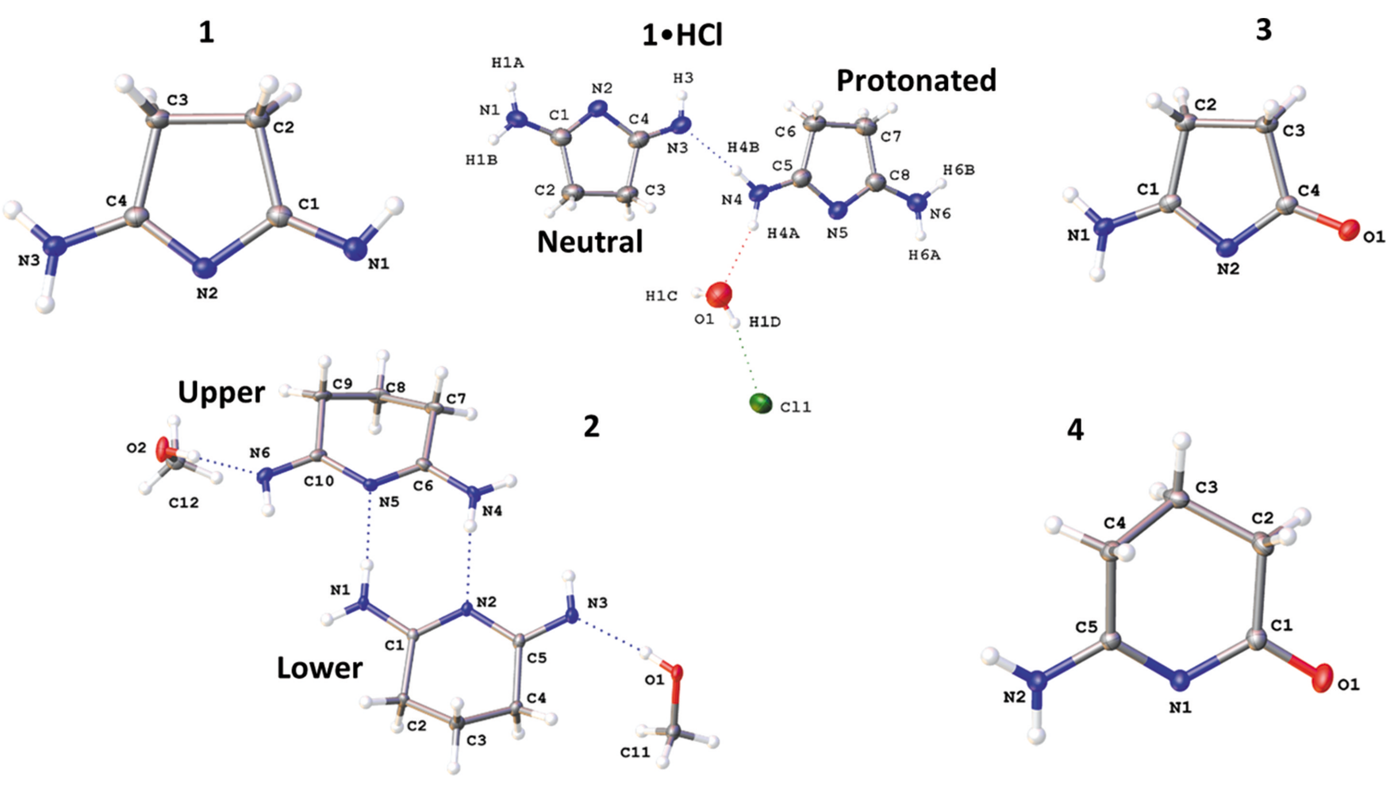


Figure 1
The asymmetric units of **1** (top left), **1**·HCl (top middle), **3** (top right), **2** (bottom left) and **4** (bottom right), shown with 50% probability displacement ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. Only the major disorder component of the ring in **2** is shown. Additional labels for **1**·HCl and **2** are included for clarification in later discussion.

Table 2
Selected bond lengths and comparisons (Å) of the structures.

See Fig. 2 for definitions of distances A–D.

Compound	A	B	C	D	Δ(A–D)	Δ(C—B)
1	1.318 (2)	1.320 (2)	1.387 (2)	1.275 (2)	0.043 (4)	0.067 (4)
1·HCl (protonated species)	1.299 (3)	1.343 (3)	1.349 (3)	1.294 (2)	0.005 (5)	0.006 (6)
1·HCl (neutral species)	1.314 (3)	1.323 (3)	1.393 (3)	1.274 (3)	0.040 (6)	0.070 (6)
2 (upper)	1.329 (2)	1.316 (2)	1.386 (1)	1.280 (2)	0.049 (4)	0.070 (3)
2 (lower)	1.325 (2)	1.323 (2)	1.381 (2)	1.289 (2)	0.036 (4)	0.058 (4)
3	1.311 (2)	1.333 (1)	1.379 (2)	1.231 (1)	–	0.046 (3)
4	1.315 (2)	1.334 (1)	1.366 (2)	1.238 (1)	–	0.032 (3)

The *E*-statistics for **1** and **4** strongly suggested the centrosymmetric space group $P\bar{1}$, which yielded chemically reasonable and computationally stable refinements. For the structures of **2**, **3**, and **1**·HCl, a combination of systematic absences in the diffraction data and the *E*-statistics were used to assign the centrosymmetric space groups $P2_1/c$, $P2_1/n$, and $C2/c$, respectively.

The structures were solved *via* intrinsic phasing and refined by least-squares refinement on F^2, followed by difference Fourier synthesis. All non-H atoms above 70% occupancy were refined with anisotropic displacement parameters. Unless otherwise stated, all H atoms were included in the final structure-factor calculations at idealized positions and were allowed to ride on their neighboring atoms with relative isotropic displacement coefficients. In the structure **1**·HCl, all amine H atoms were fixed at idealized locations, where as the imidine and water H atoms were allowed to freely refine.

The coordinates of the H atoms bound to N atoms in **1**, **3**, and **4** were allowed to refine freely. In **2**, residual electron density provided strong evidence for the coordinates of the N-atom-bound H atoms; however, there was not sufficient electron density to allow the H atoms to refine freely. As such, the coordinates of the H atoms bound to N atoms in **2** were fixed at idealized positions.

In the structure of **2**, the three methylene C atoms of the ring are disordered over two positions, with a major occupancy of 85.4 (6)%. The lesser fraction of the disordered part of the ring was restrained to the geometry of the major fraction of the same ring. One of the methanol solvent molecules exhibited disorder of the CH_3 protons.

3. Results and discussion

3.1. Structural commentary

Three of the title N-heterocycles, namely, **1**, **3**, and **4**, crystalize with only one molecule in the asymmetric unit, with no disorder or solvent molecules. The crystal structure for **2** includes two N-heterocycles and two methanol solvent molecules in the asymmetric unit. The two independent molecules of **2** (denoted 'upper' and 'lower') interact *via* a set of two N—H···N hydrogen bonds to form a dimeric structure. A similar structural motif is seen in the structure of succinimide (Yu *et al.*, 2012; Mason, 1961) and for some of the other compounds described here, when looking at the structures beyond just the asymmetric unit (*vide infra*). Additionally, one of the molecules of **2** displays disorder across the three $–CH_2–$ units in the backbone, and one methanol molecule shows disorder of the H atoms on the $–CH_3$ group. The structure of **1**·HCl contains one neutral five-membered heterocycle, its protonated species, a Cl^- counter-ion, and one solvent water molecule. The asymmetric unit of each structure is shown in Fig. 1.

In **1**, the NH protons are distributed such that one terminal N atom is doubly protonated as an amine, the N atom in the ring is not protonated, and the other terminal N atom is singly protonated, as an imine, with the proton pointing towards the hydrophobic backbone. In **2**, the H atoms are distributed in a nearly identical manner. However, due to intermolecular O—H···N hydrogen-bonding interactions with the solvent methanol molecules, the imine N atom of each of the two independent molecules of **2** has its single H atom pointed away from the hydrophobic backbone. In both **3** and **4**, the O atom binds as a carbonyl group, as indicated by the short C═O distances of 1.231 (1) and 1.238 (1) Å. As in the NNN structures, the N atom in the ring is not protonated, and the terminal N atom is doubly protonated as an amine. Crystals of **1**·HCl were obtained fortuitously from slow diffusion of diethyl ether into a solution of deuterated chloroform containing **1**. In the structure of **1**·HCl, there exists both a neutral species, comparable to the heterocycle found in **1**, and a protonated cationic species where both terminal N atoms are doubly protonated, with the N atom in the ring being left unprotonated. The protonated species in **1**·HCl is balanced by a Cl^- anion. The protonation states of all the complexes can be seen in Fig. 1. Notably, the protonation states of all the compounds differ from the structure of succinimide, which remains symmetric despite forming similarly asymmetric hydrogen-bonded dimers (Yu *et al.*, 2012; Mason, 1961). The structures of **1** and **2** are also notably inconsistent with their earlier structural proposals as 'succinimidine' and 'glutarimidine', and it is particularly notable that protonation of **1** to form the HCl salt occurs at a terminal imine rather than the

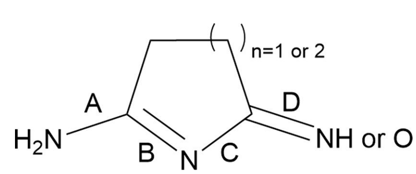


Figure 2
A generic structure used to define the bonds of interest.

Table 3
Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2^{i}	0.890 (18)	2.061 (18)	2.9414 (15)	169.6 (15)
N3—H3B···N1^{ii}	0.868 (19)	2.083 (19)	2.9238 (16)	162.6 (15)

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

Table 4
Hydrogen-bond geometry (Å, °) for **1**·HCl.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N5^{i}	0.88	2.12	2.984 (3)	168
N1—H1B···Cl1^{i}	0.88	2.37	3.2432 (18)	173
N3—H3···Cl1^{ii}	0.79 (3)	2.59 (3)	3.367 (2)	168 (3)
N4—H4A···O1	0.88	2.07	2.931 (3)	164
N4—H4B···N3	0.88	1.92	2.795 (3)	171
N6—H6A···N2^{iii}	0.88	2.02	2.903 (3)	177

Symmetry codes: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $x-\frac{1}{2}, y+\frac{1}{2}, z$.

internal ring position. These observations are consistent with pK_a data for terminal *versus* internal imines: $(Ph)_2C{=}NH$ (pK_a = 31.0) (Bordwell & Ji, 1991) and $PhCH_2N{=}C(Ph)_2$ (pK_a = 24.3) (Bordwell, 1988).

The proposed protonation states of **1**–**4** are further supported by the bond lengths across the heteroatoms, as seen in Fig. 2. These bond distances, as well as relevant comparisons, are given in Table 2. We note the neutral compounds show statistically meaningful differences between the A/D and B/C bond pairs defined in Fig. 2. Specifically, these differences appear to indicate a localized π-system with alternating single and double bonds, where the shorter bonds are localized to B

Table 5
Hydrogen-bond geometry (Å, °) for **2**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N3	0.84	1.87	2.7051 (14)	174
O2—H2···N6	0.84	1.89	2.7312 (14)	178
N1—H1A···N5	0.88	2.13	2.9896 (14)	164
N1—H1B···O1^{i}	0.88	1.94	2.8233 (13)	176
N4—H4A···N2	0.88	2.10	2.9739 (14)	173
N4—H4B···O2^{ii}	0.88	2.00	2.8639 (14)	167
C9—H9A···O1^{iii}	0.99	2.55	3.439 (2)	150

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

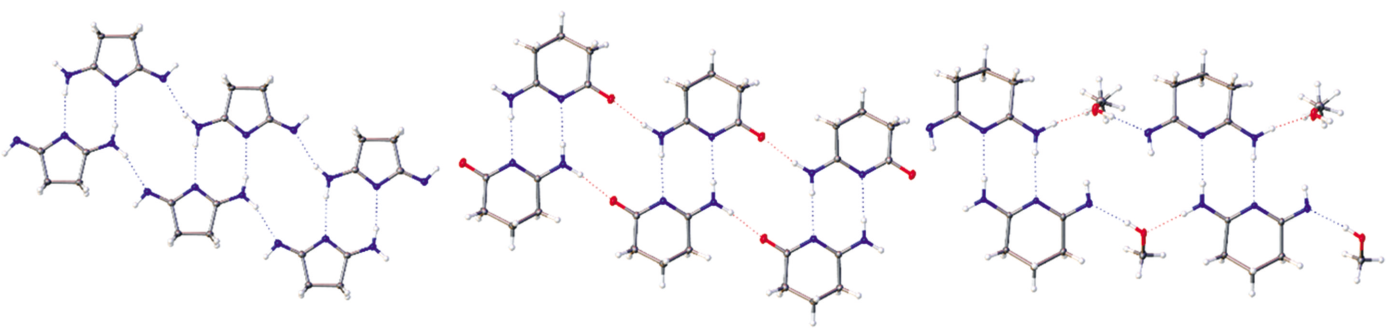


Figure 3
A comparison of the planar dimers formed by **1** (left), **4** (middle) and **2** (right), shown with 50% probability displacement ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. Only the major disorder component of the ring in **2** is shown.

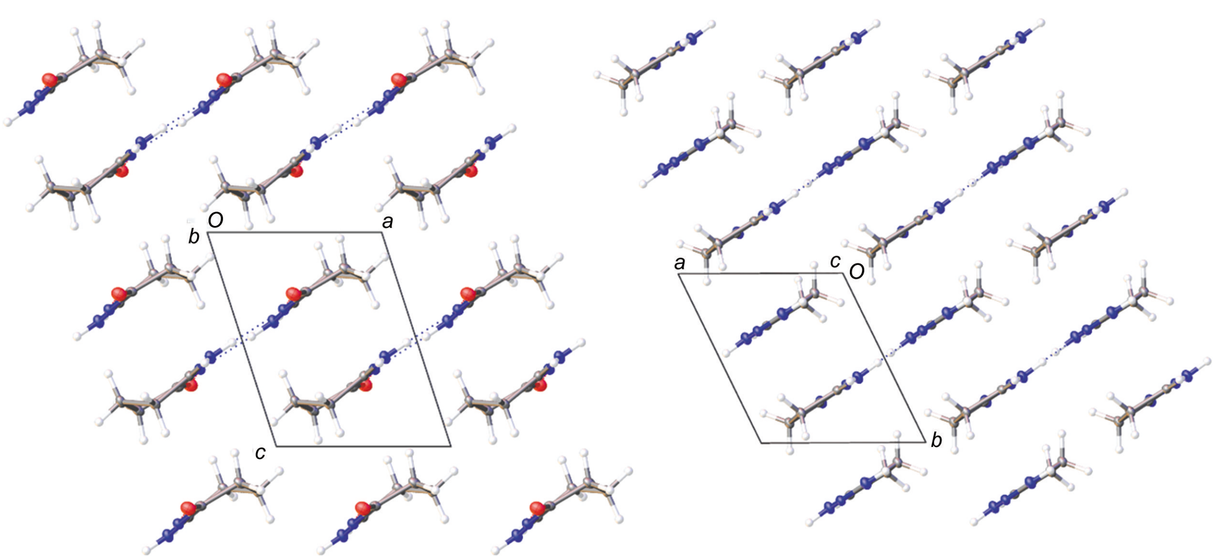


Figure 4
(Left) A molecular drawing of **4**, viewed along the crystallographic *b* axis. (Right) A molecular drawing of **1**, viewed along the crystallographic *c* axis. Both structures are drawn with 50% probability displacement ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions.

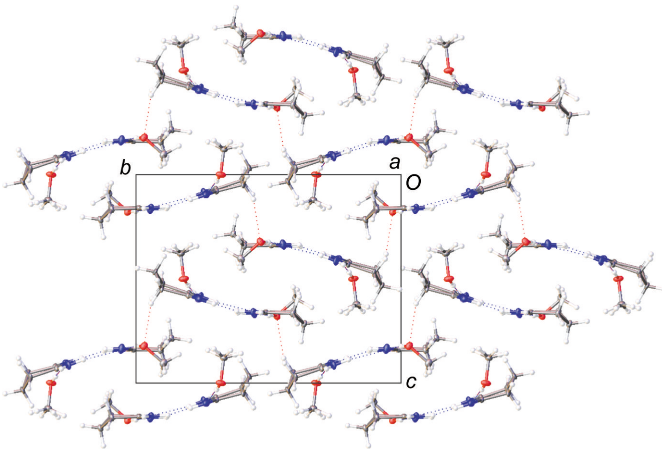


Figure 5
A molecular drawing of **2**, viewed along the crystallographic *a* axis, drawn with 50% probability displacement ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions.

Table 6
Hydrogen-bond geometry (Å, °) for **3**.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N2^{i}	0.861 (18)	2.099 (19)	2.9454 (16)	167.6 (15)
N1—H1B···O1^{ii}	0.882 (19)	2.01 (2)	2.8832 (15)	170.9 (17)

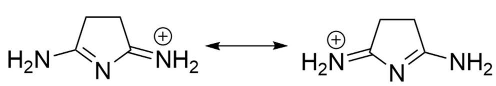
Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Table 7
Hydrogen-bond geometry (Å, °) for **4**.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.89 (2)	2.07 (2)	2.9550 (15)	178 (1)
N2—H2B···O1^{ii}	0.90 (2)	1.97 (2)	2.8588 (14)	170 (1)

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

and D. In contrast, these differences in the structure of the protonated species of **1**·HCl are statistically insignificant. Thus, the structure of the protonated species in **1**·HCl is best described by a delocalized electronic structure which could be represented by the two limiting resonance forms shown in Scheme 3. Notably, the neutral species in **1**·HCl shows nearly identical differences in the bond lengths to those in **1**. Notably, the neutral molecule in **1**·HCl and in **2** show an alternate binding motif for the imine-bound proton observed in **1**. This alternative binding motif likely arises from the hydrogen-bonding interaction blocking the other side of the imine.



Scheme 3

To gain further insights into the protonation states of **1**, computational studies were performed. All calculations were carried out using *GAUSSIAN16* (Frisch *et al.*, 2016), Hartree–Fock theory, and the 6-31g(d) basis set. Input geometries were constructed from modified crystallographic coordinates. The geometry-optimized *xyz* coordinates for all structures are provided in the supporting information (Tables S1 and S2). The calculations indicate that, in the gas phase, the Gibbs free energy of the symmetric 'succinimidine' tautomer is ~1.9 kcal mol^{-1} more stable than the asymmetric form observed crystallographically. The energy difference is small enough to allow for the network of hydrogen bonds in the crystal structure to dictate which tautomer of the compound is observed in the solid state. This packing-influenced tautomerization also aligns with previous tautomer-based studies that utilized variable-temperature crystallography and thermal evolution to better understand the tautomer ratios in keto–amine/iminoenol systems (Godsi *et al.*, 2004). To examine which tautomer is preferred in solution, we examined a solution of **1** in DMSO-d_6 by ^{1}H NMR spectroscopy. The main signal observed is a singlet at 2.46 ppm assignable to the CH_2 protons, consistent with the symmetric 'succinimidine' tautomer. This provides evidence that in solution, the imidine structure, as historically drawn in textbooks (March, 1992), dominates, yet in the solid state, the asymmetric tautomer is prevalent. Additionally, the singlet at 7.37 ppm likely indicates rapid exchange between all three of the NH protons. For reference, the ^{1}H NMR spectrum of succinimide in $CDCl_3$-d_1

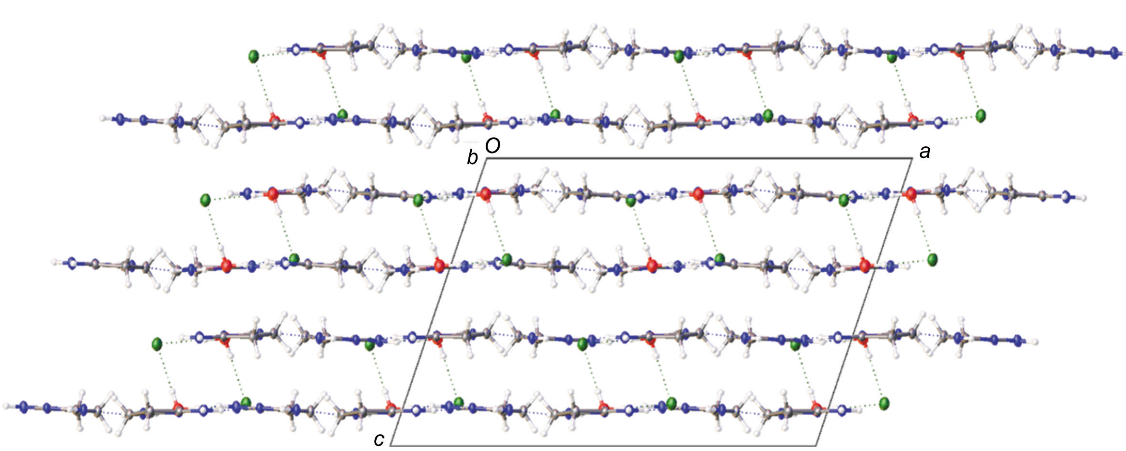


Figure 6
A molecular drawing of **1**·HCl, viewed along the crystallographic *b* axis, shown with 50% probability displacement ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. The figure depicts hydrogen-bonding interactions between sheets, bridging pairs of these sheets.

consists of a singlet at 2.769 ppm (https://www.chemicalbook.com/SpectrumEN_123-56-8_1HNMR.htm).

3.2. Crystal packing

Unsurprisingly, the large number of hydrogen-bond donors and acceptors in the molecules examined here result in significant intermolecular hydrogen-bonding interactions throughout the crystal structures (Tables 3–7). In **1**, **2**, and **4**, the hydrogen-bonding interactions result in oligomerization of the planar dimer units formed by the hydrophilic section of the molecules being paired together (Fig. 3). Each pair involves a double-hydrogen-bonded eight-membered ring reminiscent of the structural motifs seen for carboxylic acid dimers in the solid (Jasinski *et al.*, 2009), solution (Kolbe *et al.*, 1997), or gas phase (Emmeluth *et al.*, 2003). The linking of these hydrogen-bonded dimers through further lateral hydrogen bonds creates long two-dimensional ribbons throughout the crystal lattice. These ribbons stack together to form the three-dimensional crystal structures. For both **1** and **4**, there are no hydrogen-bonding interactions between ribbons either in the same plane or in between planes, as seen in Fig. 4. This pattern is broken with **2**, where the methanol solvent molecule hydrogen bonds in between sheets. This additional hydrogen-bonding interaction perpetuates throughout the packed crystal structure, making a series of interlaced sheets, as seen in Fig. 5. Compounds **1** and **2** contain a mismatch in the number of hydrogen-bond-donating and -accepting groups, leading to structures in which one of the potential hydrogen-bond donors remains unsatisfied.

In the structure of **1**·HCl, hydrophobic backbone and hydrophilic heteroatoms alternate in the plane, as seen in Fig. 1. Additionally, the solvent water molecule in **1**·HCl hydrogen bonds between sheets, bridging pairs of these sheets, as seen in Fig. 6. The major exception to the planar molecular sheets stabilized by a hydrogen-bond network is found in the crystal packing of **3**. Compound **3** does not form discrete carboxylic acid-style dimers. Instead, each molecule of **3** has hydrogen-bonding interactions with four other molecules of **3** that form an interconnected three-dimensional lattice as the molecules stack perpendicular to each other, as seen in Fig. 7. The introduction of the three-dimensional hydrogen-bonding lattice is likely what aids in the crystallization of **3** from aqueous conditions.

4. Summary

Through careful analysis of solid-state and solution phase measurements of the historical imidines, the apparent experimental disagreement between whether their structures are asymmetric or symmetric tautomers has been resolved. The crystallographic data provide evidence for the solid-state asymmetric tautomer for both the five- and six-membered ring compounds, whereas solution phase NMR spectroscopy data strongly indicate a more symmetric form. The energetic differences between the symmetric and asymmetric forms were calculated to be sufficiently small to allow for tautomerization to reasonably occur in solution at room temperature. The synthetic methods and characterization of these compounds have been modernized and safety issues associated with the synthesis have been clarified.

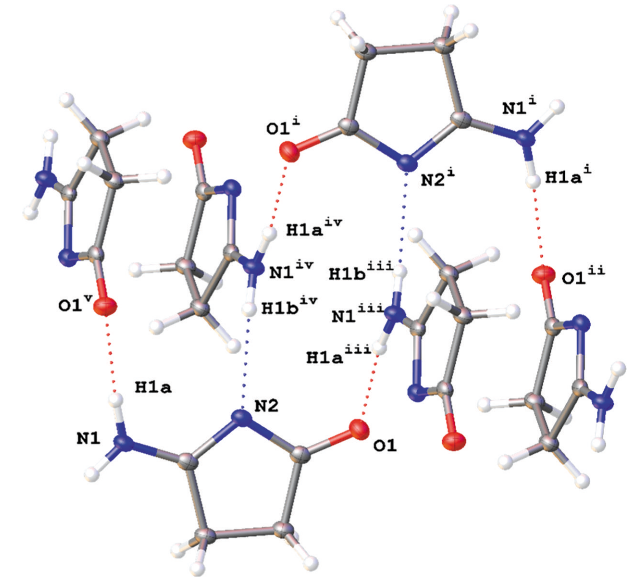


Figure 7
The stacked hydrogen-bonding network observed in **3**. All atoms are drawn with 50% probability displacement ellipsoids and dotted lines are used to indicate hydrogen-bonding interactions. [Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+2, -y+1, -z+2$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.]

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MMA would like to thank Marilyn Olmstead and Ilia Guzei for the years of assistance with crystallography. NMR spectrometers were supported by an NSF grant and a generous gift from Paul J. and Margaret M. Bender. The mass spectrometer was supported by an NIH grant. The Bruker D8 VENTURE Photon III X-ray diffractometer was partially funded by an NSF Award to the UW–Madison Department of Chemistry. The Bruker Quazar APEXII diffractometer was purchased by the UW–Madison Department of Chemistry with a portion of a generous gift from Paul J. and Margaret M. Bender.

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supporting information

Acta Cryst. (2023). C**79**, 133-141   [https://doi.org/10.1107/S2053229623002036]

Clarifying the structures of imidines: using crystallographic characterization to identify tautomers and localized systems of *π*-bonding

Michael M. Aristov, Han Geng, James W. Harris and John F. Berry

Computing details

Data collection: *APEX3* (Bruker, 2016) for 1HCl, (1), (3), (4); *APEX3* (Bruker, 2017) for (2). Cell refinement: *SAINT-Plus* (Bruker, 2016) for 1HCl, (1), (3), (4); *SAINT* (Bruker, 2017) for (2). Data reduction: *SAINT-Plus* (Bruker, 2016) for 1HCl, (1), (3), (4); *SAINT* (Bruker, 2017) for (2). Program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015*a*) for 1HCl, (3), (4); olex2.solve (Bourhis *et al.*, 2015) for (1); SHELXT2018 (Sheldrick, 2015*a*) for (2). For all structures, program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015*b*); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

5-Amino-3,4-dihydro-2*H*-pyrrol-2-iminium chloride; 2-imino-3,4-dihydro-2*H*-pyrrol-5-amine monohydrate (1HCl)

Crystal data

$C_4H_8N_3^+·Cl^-·C_4H_7N_3·H_2O$
M_r = 248.72
Monoclinic, $C2/c$
a = 19.294 (3) Å
b = 9.4173 (8) Å
c = 13.7430 (12) Å
$β$ = 108.570 (5)°
V = 2367.0 (5) Å^3
Z = 8
F(000) = 1056
D_x = 1.396 Mg m^{-3}
Cu $Kα$ radiation, $λ$ = 1.54178 Å
Cell parameters from 3499 reflections
$θ$ = 5.3–72.6°
$μ$ = 2.81 mm^{-1}
T = 100 K
Plate, yellow
0.09 × 0.04 × 0.04 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: sealed X-ray tube, Siemens, K FFCU 2K 90
Equatorially mounted graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
0.5\ $ω$ and 0.5\ $φ$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.852, T_{max} = 0.947
19987 measured reflections
2322 independent reflections
1934 reflections with $I > 2σ(I)$
R_{int} = 0.051
$θ_{max}$ = 73.4°, $θ_{min}$ = 4.8°
h = −19→22
k = −11→11
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2σ(F^2)]$ = 0.044
$wR(F^2)$ = 0.116
S = 1.03
2322 reflections
151 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 3.8293P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.37230 (3)	0.13946 (5)	0.64679 (4)	0.02616 (18)
O1	0.52636 (10)	0.20000 (19)	0.62586 (13)	0.0323 (4)
H1C	0.554123	0.178738	0.687537	0.048*
H1D	0.482073	0.195192	0.628768	0.048*
N1	0.89152 (10)	−0.01953 (19)	0.63459 (14)	0.0213 (4)
H1A	0.933610	0.020351	0.638718	0.026*
H1B	0.887512	−0.112645	0.633330	0.026*
N2	0.83658 (9)	0.20054 (18)	0.63183 (13)	0.0177 (4)
N3	0.74838 (10)	0.3797 (2)	0.62504 (15)	0.0209 (4)
H3	0.7811 (15)	0.432 (3)	0.6270 (19)	0.025*
C1	0.83466 (11)	0.0600 (2)	0.63030 (16)	0.0181 (4)
C2	0.76165 (11)	−0.0043 (2)	0.62353 (17)	0.0216 (5)
H2A	0.765060	−0.063498	0.684413	0.026*
H2B	0.742135	−0.062511	0.560730	0.026*
C3	0.71463 (12)	0.1278 (2)	0.61988 (18)	0.0227 (5)
H3A	0.672930	0.131175	0.555355	0.027*
H3B	0.695671	0.129967	0.678861	0.027*
C4	0.76720 (11)	0.2500 (2)	0.62531 (16)	0.0186 (4)
N4	0.60620 (10)	0.45993 (19)	0.61180 (14)	0.0203 (4)
H4A	0.574901	0.392743	0.613477	0.024*
H4B	0.649751	0.437282	0.608902	0.024*
N5	0.52247 (9)	0.63443 (18)	0.61803 (14)	0.0187 (4)
N6	0.46620 (10)	0.84956 (19)	0.62318 (14)	0.0212 (4)
H6A	0.426125	0.805334	0.623645	0.025*
H6B	0.467938	0.942936	0.624638	0.025*
C5	0.58819 (11)	0.5920 (2)	0.61361 (16)	0.0180 (4)
C6	0.63821 (12)	0.7130 (2)	0.60916 (17)	0.0211 (5)
H6C	0.648152	0.714642	0.542801	0.025*
H6D	0.685130	0.707256	0.665851	0.025*
C7	0.59372 (12)	0.8428 (2)	0.62085 (17)	0.0218 (5)
H7A	0.617624	0.893340	0.686113	0.026*
H7B	0.586458	0.909687	0.562868	0.026*
C8	0.52279 (11)	0.7770 (2)	0.62033 (16)	0.0181 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0235 (3)	0.0165 (3)	0.0389 (3)	−0.0026 (2)	0.0105 (2)	0.0008 (2)
O1	0.0272 (9)	0.0335 (10)	0.0368 (10)	0.0017 (7)	0.0111 (8)	0.0031 (8)
N1	0.0191 (9)	0.0132 (9)	0.0347 (11)	−0.0021 (7)	0.0131 (8)	−0.0006 (7)
N2	0.0132 (9)	0.0168 (9)	0.0249 (9)	−0.0006 (7)	0.0084 (7)	−0.0009 (7)
N3	0.0139 (9)	0.0185 (10)	0.0321 (11)	−0.0006 (7)	0.0099 (8)	−0.0003 (7)
C1	0.0179 (11)	0.0175 (10)	0.0201 (10)	−0.0023 (8)	0.0079 (8)	−0.0007 (8)
C2	0.0174 (11)	0.0193 (11)	0.0287 (12)	−0.0040 (8)	0.0083 (9)	−0.0007 (9)
C3	0.0148 (11)	0.0217 (12)	0.0324 (12)	−0.0029 (8)	0.0086 (9)	0.0013 (9)
C4	0.0142 (10)	0.0209 (11)	0.0209 (11)	−0.0016 (8)	0.0062 (8)	−0.0003 (9)
N4	0.0124 (9)	0.0194 (9)	0.0311 (10)	−0.0001 (7)	0.0096 (7)	0.0004 (7)
N5	0.0141 (9)	0.0173 (9)	0.0253 (10)	0.0008 (7)	0.0072 (7)	0.0012 (7)
N6	0.0179 (9)	0.0147 (9)	0.0320 (11)	−0.0009 (7)	0.0091 (8)	0.0003 (7)
C5	0.0146 (10)	0.0206 (11)	0.0181 (10)	−0.0010 (8)	0.0042 (8)	0.0009 (8)
C6	0.0166 (11)	0.0211 (11)	0.0262 (12)	−0.0045 (8)	0.0076 (9)	0.0003 (9)
C7	0.0199 (11)	0.0185 (11)	0.0268 (12)	−0.0048 (8)	0.0072 (9)	0.0005 (9)
C8	0.0168 (10)	0.0178 (10)	0.0186 (10)	−0.0024 (8)	0.0041 (8)	−0.0001 (8)

Geometric parameters (Å, º)

O1—H1C	0.8697	N4—H4A	0.8800
O1—H1D	0.8693	N4—H4B	0.8800
N1—H1A	0.8800	N4—C5	1.294 (3)
N1—H1B	0.8800	N5—C5	1.349 (3)
N1—C1	1.314 (3)	N5—C8	1.343 (3)
N2—C1	1.324 (3)	N6—H6A	0.8800
N2—C4	1.393 (3)	N6—H6B	0.8800
N3—H3	0.79 (3)	N6—C8	1.299 (3)
N3—C4	1.274 (3)	C5—C6	1.507 (3)
C1—C2	1.508 (3)	C6—H6C	0.9900
C2—H2A	0.9900	C6—H6D	0.9900
C2—H2B	0.9900	C6—C7	1.531 (3)
C2—C3	1.531 (3)	C7—H7A	0.9900
C3—H3A	0.9900	C7—H7B	0.9900
C3—H3B	0.9900	C7—C8	1.500 (3)
C3—C4	1.520 (3)		
H1C—O1—H1D	104.6	C5—N4—H4A	120.0
H1A—N1—H1B	120.0	C5—N4—H4B	120.0
C1—N1—H1A	120.0	C8—N5—C5	107.43 (18)
C1—N1—H1B	120.0	H6A—N6—H6B	120.0
C1—N2—C4	108.14 (17)	C8—N6—H6A	120.0
C4—N3—H3	112 (2)	C8—N6—H6B	120.0
N1—C1—N2	123.37 (19)	N4—C5—N5	123.19 (19)
N1—C1—C2	121.61 (19)	N4—C5—C6	123.14 (19)
N2—C1—C2	115.02 (18)	N5—C5—C6	113.67 (19)

C1—C2—H2A	111.4	C5—C6—H6C	111.3
C1—C2—H2B	111.4	C5—C6—H6D	111.3
C1—C2—C3	102.00 (17)	C5—C6—C7	102.22 (17)
H2A—C2—H2B	109.2	H6C—C6—H6D	109.2
C3—C2—H2A	111.4	C7—C6—H6C	111.3
C3—C2—H2B	111.4	C7—C6—H6D	111.3
C2—C3—H3A	111.1	C6—C7—H7A	111.3
C2—C3—H3B	111.1	C6—C7—H7B	111.3
H3A—C3—H3B	109.0	H7A—C7—H7B	109.2
C4—C3—C2	103.54 (17)	C8—C7—C6	102.16 (17)
C4—C3—H3A	111.1	C8—C7—H7A	111.3
C4—C3—H3B	111.1	C8—C7—H7B	111.3
N2—C4—C3	111.29 (18)	N5—C8—C7	114.24 (19)
N3—C4—N2	125.99 (19)	N6—C8—N5	121.94 (19)
N3—C4—C3	122.71 (19)	N6—C8—C7	123.82 (19)
H4A—N4—H4B	120.0		

N1—C1—C2—C3	−179.69 (19)	N4—C5—C6—C7	−176.4 (2)
N2—C1—C2—C3	0.5 (2)	N5—C5—C6—C7	4.6 (2)
C1—N2—C4—N3	179.7 (2)	C5—N5—C8—N6	179.0 (2)
C1—N2—C4—C3	0.6 (2)	C5—N5—C8—C7	−1.9 (2)
C1—C2—C3—C4	−0.1 (2)	C5—C6—C7—C8	−5.0 (2)
C2—C3—C4—N2	−0.2 (2)	C6—C7—C8—N5	4.6 (2)
C2—C3—C4—N3	−179.4 (2)	C6—C7—C8—N6	−176.2 (2)
C4—N2—C1—N1	179.5 (2)	C8—N5—C5—N4	179.1 (2)
C4—N2—C1—C2	−0.7 (3)	C8—N5—C5—C6	−1.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N5^{i}	0.88	2.12	2.984 (3)	168
N1—H1*B*···Cl1^{i}	0.88	2.37	3.2432 (18)	173
N3—H3···Cl1^{ii}	0.79 (3)	2.59 (3)	3.367 (2)	168 (3)
N4—H4*A*···O1	0.88	2.07	2.931 (3)	164
N4—H4*B*···N3	0.88	1.92	2.795 (3)	171
N6—H6*A*···N2^{iii}	0.88	2.02	2.903 (3)	177

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

2-Imino-3,4-dihydro-2*H*-pyrrol-5-amine (1)

Crystal data

$C_4H_7N_3$	γ = 111.425 (4)°
M_r = 97.13	V = 234.36 (3) Å^3
Triclinic, $P\overline{1}$	Z = 2
a = 5.9577 (4) Å	F(000) = 104
b = 6.7494 (5) Å	D_x = 1.376 Mg m^{-3}
c = 6.8249 (5) Å	Cu $K\alpha$ radiation, λ = 1.54178 Å
α = 101.641 (4)°	Cell parameters from 2253 reflections
β = 104.225 (6)°	θ = 7.1–72.2°

μ = 0.75 mm^{-1}
T = 100 K

Plate, colourless
0.11 × 0.11 × 0.10 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: sealed X-ray tube, Siemens, K FFCU 2K 90
Equatorially mounted graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
0.60\ ω and 0.6\ φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)

T_{min} = 0.844, T_{max} = 0.901
3673 measured reflections
892 independent reflections
833 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 72.2°, θ_{min} = 7.1°
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.092
S = 1.09
892 reflections
76 parameters
0 restraints
Primary atom site location: iterative

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.0676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.48601 (19)	0.24030 (16)	0.74167 (16)	0.0172 (3)
N2	0.68866 (18)	0.34098 (16)	0.50208 (16)	0.0139 (3)
N3	0.7801 (2)	0.38375 (17)	0.19741 (18)	0.0162 (3)
C1	0.4720 (2)	0.23523 (18)	0.55105 (19)	0.0139 (3)
C2	0.2300 (2)	0.11734 (19)	0.35125 (19)	0.0149 (3)
H2A	0.1018	0.1747	0.3654	0.018*
H2B	0.1508	−0.0473	0.3228	0.018*
C3	0.3297 (2)	0.17603 (19)	0.17466 (19)	0.0151 (3)
H3C	0.2900	0.0390	0.0601	0.018*
H3D	0.2563	0.2685	0.1118	0.018*
C4	0.6171 (2)	0.30852 (18)	0.29488 (19)	0.0134 (3)
H3A	0.946 (3)	0.471 (3)	0.274 (3)	0.022 (4)*
H1	0.329 (4)	0.168 (3)	0.741 (3)	0.032 (4)*
H3B	0.723 (3)	0.362 (3)	0.061 (3)	0.025 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0139 (5)	0.0206 (6)	0.0146 (6)	0.0048 (4)	0.0049 (4)	0.0061 (4)
N2	0.0116 (5)	0.0142 (5)	0.0134 (5)	0.0041 (4)	0.0027 (4)	0.0040 (4)
N3	0.0122 (5)	0.0199 (5)	0.0119 (6)	0.0042 (4)	0.0019 (4)	0.0043 (4)
C1	0.0135 (6)	0.0114 (5)	0.0159 (7)	0.0056 (4)	0.0038 (5)	0.0039 (4)
C2	0.0118 (6)	0.0159 (6)	0.0146 (6)	0.0044 (5)	0.0031 (5)	0.0049 (5)
C3	0.0120 (5)	0.0162 (6)	0.0126 (6)	0.0038 (4)	0.0012 (4)	0.0037 (4)
C4	0.0129 (6)	0.0116 (5)	0.0137 (6)	0.0053 (4)	0.0026 (5)	0.0030 (4)

Geometric parameters (Å, º)

N1—C1	1.2756 (15)	C1—C2	1.5260 (16)
N1—H1	0.88 (2)	C2—H2A	0.9900
N2—C1	1.3865 (15)	C2—H2B	0.9900
N2—C4	1.3191 (16)	C2—C3	1.5279 (16)
N3—C4	1.3177 (16)	C3—H3C	0.9900
N3—H3A	0.890 (18)	C3—H3D	0.9900
N3—H3B	0.868 (19)	C3—C4	1.5164 (16)
C1—N1—H1	108.4 (12)	C3—C2—H2A	111.1
C4—N2—C1	108.59 (10)	C3—C2—H2B	111.1
C4—N3—H3A	119.6 (11)	C2—C3—H3C	111.4
C4—N3—H3B	119.8 (11)	C2—C3—H3D	111.4
H3A—N3—H3B	120.1 (15)	H3C—C3—H3D	109.2
N1—C1—N2	121.78 (11)	C4—C3—C2	101.95 (9)
N1—C1—C2	127.03 (10)	C4—C3—H3C	111.4
N2—C1—C2	111.20 (10)	C4—C3—H3D	111.4
C1—C2—H2A	111.1	N2—C4—C3	114.74 (10)
C1—C2—H2B	111.1	N3—C4—N2	123.35 (11)
C1—C2—C3	103.42 (9)	N3—C4—C3	121.91 (11)
H2A—C2—H2B	109.0		
N1—C1—C2—C3	178.09 (11)	C2—C3—C4—N2	−3.05 (13)
N2—C1—C2—C3	−2.51 (12)	C2—C3—C4—N3	176.82 (10)
C1—N2—C4—N3	−178.30 (10)	C4—N2—C1—N1	−179.87 (10)
C1—N2—C4—C3	1.57 (13)	C4—N2—C1—C2	0.68 (13)
C1—C2—C3—C4	3.04 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2^{i}	0.890 (18)	2.061 (18)	2.9414 (15)	169.6 (15)
N3—H3*B*···N1^{ii}	0.868 (19)	2.083 (19)	2.9238 (16)	162.6 (15)

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

5-Amino-3,4-dihydro-2*H*-pyrrol-2-one (3)

Crystal data

$C_4H_6N_2O$
M_r = 98.11
Monoclinic, $P2_1/n$
a = 7.3685 (5) Å
b = 8.0074 (7) Å
c = 8.4211 (9) Å
β = 115.741 (5)°
V = 447.56 (7) Å^3
Z = 4
F(000) = 208
D_x = 1.456 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2533 reflections
θ = 6.7–71.6°
μ = 0.91 mm^{-1}
T = 100 K
Block, colourless
0.1 × 0.09 × 0.04 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: sealed X-ray tube, Siemens, K FFCU 2K 90
Equatorially mounted graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
0.60\ ω and 0.6\ φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.853, T_{max} = 0.915
7398 measured reflections
886 independent reflections
775 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 72.0°, θ_{min} = 6.7°
h = −9→9
k = −9→9
l = −9→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.089
S = 1.03
886 reflections
72 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.1366P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.60985 (13)	0.63368 (12)	0.91223 (11)	0.0184 (3)
N1	0.47862 (17)	0.21160 (14)	0.51216 (14)	0.0166 (3)
N2	0.59548 (16)	0.41138 (14)	0.73439 (13)	0.0148 (3)
C1	0.44758 (18)	0.33546 (16)	0.59918 (15)	0.0144 (3)
C2	0.23969 (18)	0.40567 (16)	0.55086 (16)	0.0160 (3)
H2A	0.146793	0.318525	0.555478	0.019*
H2B	0.182063	0.456487	0.431893	0.019*
C3	0.28201 (18)	0.53733 (17)	0.69360 (16)	0.0165 (3)
H3A	0.232171	0.648419	0.641205	0.020*

H3B	0.218560	0.506897	0.771872	0.020*
C4	0.51048 (18)	0.53586 (16)	0.79326 (15)	0.0145 (3)
H1A	0.377 (3)	0.172 (2)	0.422 (2)	0.020 (4)*
H1B	0.602 (3)	0.177 (2)	0.540 (2)	0.021 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0156 (5)	0.0202 (5)	0.0177 (5)	−0.0026 (4)	0.0056 (4)	−0.0035 (4)
N1	0.0116 (6)	0.0185 (6)	0.0156 (5)	−0.0003 (4)	0.0022 (4)	−0.0009 (4)
N2	0.0129 (5)	0.0164 (6)	0.0131 (5)	0.0000 (4)	0.0036 (4)	0.0020 (4)
C1	0.0134 (6)	0.0156 (6)	0.0130 (6)	−0.0013 (5)	0.0047 (4)	0.0044 (5)
C2	0.0122 (6)	0.0189 (7)	0.0149 (6)	0.0003 (5)	0.0040 (5)	0.0020 (5)
C3	0.0118 (6)	0.0199 (7)	0.0163 (6)	0.0005 (5)	0.0047 (5)	0.0013 (5)
C4	0.0142 (6)	0.0158 (6)	0.0126 (6)	0.0001 (5)	0.0051 (5)	0.0034 (5)

Geometric parameters (Å, º)

O1—C4	1.2313 (16)	C2—H2A	0.9900
N1—C1	1.3110 (17)	C2—H2B	0.9900
N1—H1A	0.861 (18)	C2—C3	1.5257 (18)
N1—H1B	0.882 (19)	C3—H3A	0.9900
N2—C1	1.3326 (16)	C3—H3B	0.9900
N2—C4	1.3788 (17)	C3—C4	1.5204 (17)
C1—C2	1.5122 (17)		
C1—N1—H1A	118.3 (12)	C3—C2—H2A	111.4
C1—N1—H1B	119.9 (11)	C3—C2—H2B	111.4
H1A—N1—H1B	121.5 (16)	C2—C3—H3A	111.1
C1—N2—C4	107.84 (10)	C2—C3—H3B	111.1
N1—C1—N2	123.11 (11)	H3A—C3—H3B	109.1
N1—C1—C2	122.22 (11)	C4—C3—C2	103.18 (10)
N2—C1—C2	114.66 (11)	C4—C3—H3A	111.1
C1—C2—H2A	111.4	C4—C3—H3B	111.1
C1—C2—H2B	111.4	O1—C4—N2	123.36 (12)
C1—C2—C3	102.03 (10)	O1—C4—C3	124.67 (11)
H2A—C2—H2B	109.2	N2—C4—C3	111.97 (11)
N1—C1—C2—C3	177.20 (11)	C2—C3—C4—O1	174.20 (12)
N2—C1—C2—C3	−3.93 (14)	C2—C3—C4—N2	−5.57 (13)
C1—N2—C4—O1	−176.49 (11)	C4—N2—C1—N1	179.39 (11)
C1—N2—C4—C3	3.29 (14)	C4—N2—C1—C2	0.53 (14)
C1—C2—C3—C4	5.22 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N2^{i}	0.861 (18)	2.099 (19)	2.9454 (16)	167.6 (15)

N1—H1*B*···O1[ii]	0.882 (19)	2.01 (2)	2.8832 (15)	170.9 (17)

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

6-Amino-4,5-dihydropyridin-2(3*H*)-one (4)

Crystal data

$C_5H_8N_2O$
M_r = 112.13
Triclinic, $P\overline{1}$
a = 6.3296 (19) Å
b = 7.0222 (19) Å
c = 7.351 (2) Å
α = 84.975 (13)°
β = 71.693 (13)°
γ = 63.889 (12)°
V = 278.06 (14) Å^3
Z = 2
F(000) = 120
D_x = 1.339 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2665 reflections
θ = 2.9–32.7°
µ = 0.10 mm^{-1}
T = 100 K
Plate, colourless
0.16 × 0.05 × 0.01 mm

Data collection

Bruker APEXII Quazar diffractometer
Radiation source: microfocus sealed X-ray tube, Incoatec Iµs
Mirror optics monochromator
Detector resolution: 7.9 pixels mm-1
0.5\ *ω* and 0.5\ *φ* scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.929, T_{max} = 0.991
9023 measured reflections
2048 independent reflections
1680 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 33.2°, θ_{min} = 2.9°
h = −9→9
k = −10→10
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.120
S = 1.06
2048 reflections
79 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.1043P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.37974 (15)	0.77854 (12)	0.28900 (12)	0.01953 (18)
N1	0.29468 (15)	0.49662 (13)	0.36116 (12)	0.01259 (17)
N2	0.21326 (16)	0.20840 (14)	0.41622 (13)	0.01446 (18)
H2A	0.061 (3)	0.295 (2)	0.486 (2)	0.017*
H2B	0.256 (3)	0.071 (2)	0.390 (2)	0.017*

C1	0.45505 (18)	0.58343 (16)	0.27751 (14)	0.01306 (19)
C2	0.72439 (18)	0.44644 (17)	0.16905 (15)	0.0158 (2)
H2C	0.828777	0.499108	0.204319	0.019*
H2D	0.749196	0.461186	0.029656	0.019*
C3	0.80909 (17)	0.21259 (16)	0.20960 (15)	0.0150 (2)
H3A	0.828669	0.190240	0.339314	0.018*
H3B	0.970881	0.126647	0.114773	0.018*
C4	0.61686 (17)	0.14393 (15)	0.19691 (14)	0.01348 (19)
H4A	0.610844	0.150894	0.063433	0.016*
H4B	0.661582	−0.004411	0.234345	0.016*
C5	0.36818 (17)	0.28965 (15)	0.32952 (13)	0.01144 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0242 (4)	0.0119 (3)	0.0217 (4)	−0.0092 (3)	−0.0036 (3)	−0.0007 (3)
N1	0.0127 (3)	0.0107 (4)	0.0140 (4)	−0.0056 (3)	−0.0025 (3)	−0.0007 (3)
N2	0.0124 (4)	0.0104 (4)	0.0198 (4)	−0.0055 (3)	−0.0026 (3)	−0.0016 (3)
C1	0.0157 (4)	0.0129 (4)	0.0113 (4)	−0.0073 (3)	−0.0031 (3)	−0.0005 (3)
C2	0.0151 (4)	0.0177 (5)	0.0148 (4)	−0.0097 (4)	−0.0002 (3)	−0.0017 (3)
C3	0.0106 (4)	0.0157 (4)	0.0171 (4)	−0.0052 (3)	−0.0020 (3)	−0.0037 (3)
C4	0.0124 (4)	0.0116 (4)	0.0145 (4)	−0.0043 (3)	−0.0020 (3)	−0.0032 (3)
C5	0.0114 (4)	0.0114 (4)	0.0118 (4)	−0.0046 (3)	−0.0043 (3)	−0.0001 (3)

Geometric parameters (Å, º)

O1—C1	1.2376 (12)	C2—H2D	0.9900
N1—C1	1.3663 (13)	C2—C3	1.5207 (15)
N1—C5	1.3338 (13)	C3—H3A	0.9900
N2—H2A	0.887 (16)	C3—H3B	0.9900
N2—H2B	0.903 (15)	C3—C4	1.5223 (14)
N2—C5	1.3151 (13)	C4—H4A	0.9900
C1—C2	1.5180 (15)	C4—H4B	0.9900
C2—H2C	0.9900	C4—C5	1.5060 (14)
C5—N1—C1	119.36 (9)	C2—C3—H3B	109.9
H2A—N2—H2B	121.2 (14)	C2—C3—C4	108.86 (8)
C5—N2—H2A	118.9 (9)	H3A—C3—H3B	108.3
C5—N2—H2B	119.3 (9)	C4—C3—H3A	109.9
O1—C1—N1	119.52 (9)	C4—C3—H3B	109.9
O1—C1—C2	118.85 (9)	C3—C4—H4A	109.9
N1—C1—C2	121.63 (9)	C3—C4—H4B	109.9
C1—C2—H2C	108.9	H4A—C4—H4B	108.3
C1—C2—H2D	108.9	C5—C4—C3	108.86 (8)
C1—C2—C3	113.27 (8)	C5—C4—H4A	109.9
H2C—C2—H2D	107.7	C5—C4—H4B	109.9
C3—C2—H2C	108.9	N1—C5—C4	123.80 (8)
C3—C2—H2D	108.9	N2—C5—N1	118.26 (9)

C2—C3—H3A	109.9	N2—C5—C4	117.93 (9)
O1—C1—C2—C3	164.67 (9)	C2—C3—C4—C5	−54.51 (11)
N1—C1—C2—C3	−15.73 (13)	C3—C4—C5—N1	35.61 (12)
C1—N1—C5—N2	177.95 (8)	C3—C4—C5—N2	−145.67 (9)
C1—N1—C5—C4	−3.33 (14)	C5—N1—C1—O1	172.09 (9)
C1—C2—C3—C4	46.55 (11)	C5—N1—C1—C2	−7.50 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1^{i}	0.89 (2)	2.07 (2)	2.9550 (15)	178 (1)
N2—H2*B*···O1^{ii}	0.90 (2)	1.97 (2)	2.8588 (14)	170 (1)

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

6-Imino-3,4,5,6-tetrahydropyridin-2-amine methanol monosolvate (2)

Crystal data

$C_5H_9N_3{\cdot}CH_4O$
M_r = 143.19
Monoclinic, $P2_1/c$
a = 9.4887 (9) Å
b = 14.5341 (11) Å
c = 12.2828 (10) Å
β = 111.320 (8)°
V = 1578.0 (2) Å^3
Z = 8
F(000) = 624
D_x = 1.205 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54178 Å
Cell parameters from 9930 reflections
θ = 4.9–74.4°
µ = 0.70 mm^{-1}
T = 100 K
Block, yellow
0.03 × 0.02 × 0.01 mm

Data collection

Bruker APEXII Quazar diffractometer
0.5° *ω* and 0.5° *φ* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.690, T_{max} = 0.754
26582 measured reflections
3219 independent reflections
2938 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 74.5°, θ_{min} = 4.9°
h = −11→9
k = −18→18
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.108
S = 1.07
3219 reflections
204 parameters
5 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.8148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.91809 (9)	0.53060 (6)	0.32228 (8)	0.0154 (2)	
H1	0.843291	0.500710	0.324261	0.023*	
C11	0.95021 (14)	0.60412 (9)	0.40431 (12)	0.0176 (3)	
H11A	0.914773	0.662174	0.362792	0.026*	
H11B	1.059570	0.607547	0.447497	0.026*	
H11C	0.898395	0.593247	0.459110	0.026*	
O2	−0.23850 (10)	0.18016 (7)	0.49986 (8)	0.0186 (2)	
H2	−0.177175	0.196182	0.468403	0.028*	
C12	−0.16048 (15)	0.16888 (9)	0.62137 (11)	0.0179 (3)	
H12A	−0.075415	0.126555	0.634784	0.021*	0.854 (6)
H12B	−0.229589	0.143625	0.656730	0.021*	0.854 (6)
H12C	−0.122367	0.228643	0.656828	0.021*	0.854 (6)
H12D	−0.209499	0.205994	0.664111	0.021*	0.146 (6)
H12E	−0.055325	0.188924	0.642165	0.021*	0.146 (6)
H12F	−0.162546	0.103905	0.642067	0.021*	0.146 (6)
N1	0.18981 (11)	0.44082 (7)	0.34103 (9)	0.0119 (2)	
H1A	0.193322	0.380372	0.345176	0.014*	
H1B	0.107360	0.470129	0.338113	0.014*	
N2	0.43078 (10)	0.44159 (7)	0.34367 (8)	0.0101 (2)	
N3	0.67078 (12)	0.44558 (8)	0.33472 (10)	0.0179 (2)	
H3	0.6580 (19)	0.3842 (13)	0.3373 (15)	0.022*	
N4	0.45550 (12)	0.24491 (7)	0.41496 (10)	0.0152 (2)	
H4A	0.441875	0.301552	0.387785	0.018*	
H4B	0.544157	0.218156	0.432102	0.018*	
N5	0.21070 (11)	0.24124 (7)	0.40385 (9)	0.0109 (2)	
N6	−0.03480 (12)	0.23502 (7)	0.40299 (9)	0.0145 (2)	
H6	−0.0302 (19)	0.2941 (12)	0.3799 (15)	0.017*	
C1	0.30862 (12)	0.48770 (8)	0.33917 (9)	0.0086 (2)	
C2	0.29419 (13)	0.59129 (8)	0.33369 (11)	0.0121 (2)	
H2A	0.314806	0.615714	0.413238	0.015*	
H2B	0.189341	0.608325	0.284329	0.015*	
C3	0.40331 (13)	0.63441 (8)	0.28387 (11)	0.0142 (2)	
H3A	0.407300	0.701797	0.296414	0.017*	
H3B	0.368326	0.622714	0.198743	0.017*	
C4	0.55968 (13)	0.59317 (8)	0.34406 (11)	0.0134 (2)	
H4C	0.628254	0.615835	0.305505	0.016*	
H4D	0.600702	0.613484	0.426622	0.016*	
C5	0.55477 (13)	0.48907 (8)	0.33947 (10)	0.0112 (2)	
C6	0.34220 (14)	0.19978 (8)	0.43011 (11)	0.0132 (2)	

C7	0.3718 (2)	0.10128 (11)	0.4725 (2)	0.0165 (4)	0.854 (6)
H7A	0.477899	0.095201	0.527129	0.020*	0.854 (6)
H7B	0.357403	0.060030	0.405148	0.020*	0.854 (6)
C8	0.26531 (19)	0.07255 (12)	0.53405 (16)	0.0189 (5)	0.854 (6)
H8A	0.275274	0.005791	0.551184	0.023*	0.854 (6)
H8B	0.290335	0.106319	0.608716	0.023*	0.854 (6)
C9	0.1044 (2)	0.09504 (10)	0.4530 (2)	0.0155 (4)	0.854 (6)
H9A	0.077210	0.056923	0.381497	0.019*	0.854 (6)
H9B	0.032970	0.080500	0.492550	0.019*	0.854 (6)
C9A	0.1419 (16)	0.1047 (10)	0.5033 (18)	0.040 (4)*	0.146 (6)
H9AA	0.166713	0.124120	0.585420	0.047*	0.146 (6)
H9AB	0.053918	0.062706	0.482943	0.047*	0.146 (6)
C7A	0.4042 (12)	0.1163 (7)	0.5095 (12)	0.022 (4)*	0.146 (6)
H7AA	0.482399	0.084901	0.487294	0.027*	0.146 (6)
H7AB	0.450947	0.136391	0.591897	0.027*	0.146 (6)
C8A	0.2746 (14)	0.0515 (8)	0.4957 (16)	0.043 (4)*	0.146 (6)
H8AA	0.306708	0.004182	0.557862	0.052*	0.146 (6)
H8AB	0.244586	0.019944	0.419149	0.052*	0.146 (6)
C10	0.09196 (14)	0.19534 (8)	0.42037 (10)	0.0128 (2)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0100 (4)	0.0182 (4)	0.0211 (5)	−0.0020 (3)	0.0093 (3)	−0.0038 (3)
C11	0.0131 (6)	0.0192 (6)	0.0228 (6)	−0.0031 (5)	0.0092 (5)	−0.0041 (5)
O2	0.0092 (4)	0.0341 (5)	0.0129 (4)	−0.0001 (4)	0.0044 (3)	0.0038 (4)
C12	0.0209 (6)	0.0198 (6)	0.0129 (6)	0.0010 (5)	0.0061 (5)	0.0014 (5)
N1	0.0080 (4)	0.0095 (5)	0.0199 (5)	0.0006 (3)	0.0072 (4)	0.0023 (4)
N2	0.0082 (5)	0.0102 (5)	0.0130 (5)	−0.0004 (3)	0.0051 (4)	0.0011 (4)
N3	0.0122 (5)	0.0139 (5)	0.0313 (6)	−0.0011 (4)	0.0122 (4)	−0.0030 (4)
N4	0.0125 (5)	0.0108 (5)	0.0244 (5)	0.0044 (4)	0.0095 (4)	0.0026 (4)
N5	0.0127 (5)	0.0078 (4)	0.0139 (5)	0.0000 (4)	0.0067 (4)	0.0004 (4)
N6	0.0140 (5)	0.0150 (5)	0.0151 (5)	−0.0043 (4)	0.0061 (4)	−0.0003 (4)
C1	0.0083 (5)	0.0105 (5)	0.0071 (5)	0.0005 (4)	0.0027 (4)	0.0011 (4)
C2	0.0100 (5)	0.0093 (5)	0.0174 (6)	0.0016 (4)	0.0054 (4)	0.0027 (4)
C3	0.0140 (6)	0.0113 (5)	0.0185 (6)	−0.0003 (4)	0.0074 (5)	0.0036 (4)
C4	0.0113 (5)	0.0123 (6)	0.0173 (6)	−0.0014 (4)	0.0059 (5)	0.0013 (4)
C5	0.0086 (5)	0.0136 (6)	0.0114 (5)	−0.0007 (4)	0.0036 (4)	0.0010 (4)
C6	0.0171 (6)	0.0092 (5)	0.0150 (6)	0.0025 (4)	0.0079 (5)	0.0005 (4)
C7	0.0159 (8)	0.0073 (7)	0.0213 (10)	0.0026 (6)	0.0010 (8)	0.0023 (7)
C8	0.0311 (9)	0.0087 (7)	0.0167 (8)	0.0020 (6)	0.0083 (7)	0.0063 (6)
C9	0.0228 (8)	0.0073 (7)	0.0205 (10)	−0.0037 (6)	0.0128 (8)	−0.0004 (6)
C10	0.0184 (6)	0.0096 (5)	0.0134 (6)	−0.0034 (4)	0.0092 (5)	−0.0017 (4)

Geometric parameters (Å, º)

O1—H1	0.8400	C2—H2B	0.9900
O1—C11	1.4236 (15)	C2—C3	1.5165 (16)

C11—H11A	0.9800	C3—H3A	0.9900
C11—H11B	0.9800	C3—H3B	0.9900
C11—H11C	0.9800	C3—C4	1.5197 (16)
O2—H2	0.8400	C4—H4C	0.9900
O2—C12	1.4139 (15)	C4—H4D	0.9900
C12—H12A	0.9800	C4—C5	1.5141 (16)
C12—H12B	0.9800	C6—C7	1.5143 (18)
C12—H12C	0.9800	C6—C7A	1.533 (8)
C12—H12D	0.9800	C7—H7A	0.9900
C12—H12E	0.9800	C7—H7B	0.9900
C12—H12F	0.9800	C7—C8	1.524 (2)
N1—H1A	0.8800	C8—H8A	0.9900
N1—H1B	0.8800	C8—H8B	0.9900
N1—C1	1.3245 (15)	C8—C9	1.524 (2)
N2—C1	1.3225 (15)	C9—H9A	0.9900
N2—C5	1.3810 (14)	C9—H9B	0.9900
N3—H3	0.902 (19)	C9—C10	1.5051 (17)
N3—C5	1.2890 (16)	C9A—H9AA	0.9900
N4—H4A	0.8800	C9A—H9AB	0.9900
N4—H4B	0.8800	C9A—C8A	1.510 (9)
N4—C6	1.3290 (16)	C9A—C10	1.627 (16)
N5—C6	1.3158 (16)	C7A—H7AA	0.9900
N5—C10	1.3863 (15)	C7A—H7AB	0.9900
N6—H6	0.910 (18)	C7A—C8A	1.509 (9)
N6—C10	1.2799 (17)	C8A—H8AA	0.9900
C1—C2	1.5111 (15)	C8A—H8AB	0.9900
C2—H2A	0.9900		

C11—O1—H1	109.5	C3—C4—H4D	109.4
O1—C11—H11A	109.5	H4C—C4—H4D	108.0
O1—C11—H11B	109.5	C5—C4—C3	111.38 (10)
O1—C11—H11C	109.5	C5—C4—H4C	109.4
H11A—C11—H11B	109.5	C5—C4—H4D	109.4
H11A—C11—H11C	109.5	N2—C5—C4	120.87 (10)
H11B—C11—H11C	109.5	N3—C5—N2	120.65 (11)
C12—O2—H2	109.5	N3—C5—C4	118.46 (10)
O2—C12—H12A	109.5	N4—C6—C7	117.14 (11)
O2—C12—H12B	109.5	N4—C6—C7A	109.7 (4)
O2—C12—H12C	109.5	N5—C6—N4	118.88 (11)
O2—C12—H12D	109.5	N5—C6—C7	123.93 (12)
O2—C12—H12E	109.5	N5—C6—C7A	128.9 (4)
O2—C12—H12F	109.5	C6—C7—H7A	109.5
H12A—C12—H12B	109.5	C6—C7—H7B	109.5
H12A—C12—H12C	109.5	C6—C7—C8	110.85 (12)
H12A—C12—H12D	141.1	H7A—C7—H7B	108.1
H12A—C12—H12E	56.3	C8—C7—H7A	109.5
H12A—C12—H12F	56.3	C8—C7—H7B	109.5
H12B—C12—H12C	109.5	C7—C8—H8A	110.2

H12B—C12—H12D	56.3	C7—C8—H8B	110.2
H12B—C12—H12E	141.1	H8A—C8—H8B	108.5
H12B—C12—H12F	56.3	C9—C8—C7	107.73 (15)
H12C—C12—H12D	56.3	C9—C8—H8A	110.2
H12C—C12—H12E	56.3	C9—C8—H8B	110.2
H12C—C12—H12F	141.1	C8—C9—H9A	109.6
H12D—C12—H12E	109.5	C8—C9—H9B	109.6
H12D—C12—H12F	109.5	H9A—C9—H9B	108.1
H12E—C12—H12F	109.5	C10—C9—C8	110.18 (14)
H1A—N1—H1B	120.0	C10—C9—H9A	109.6
C1—N1—H1A	120.0	C10—C9—H9B	109.6
C1—N1—H1B	120.0	H9AA—C9A—H9AB	107.4
C1—N2—C5	119.40 (10)	C8A—C9A—H9AA	108.3
C5—N3—H3	110.8 (11)	C8A—C9A—H9AB	108.3
H4A—N4—H4B	120.0	C8A—C9A—C10	115.8 (11)
C6—N4—H4A	120.0	C10—C9A—H9AA	108.3
C6—N4—H4B	120.0	C10—C9A—H9AB	108.3
C6—N5—C10	119.50 (10)	C6—C7A—H7AA	110.0
C10—N6—H6	109.1 (10)	C6—C7A—H7AB	110.0
N1—C1—C2	116.70 (10)	H7AA—C7A—H7AB	108.4
N2—C1—N1	118.50 (10)	C8A—C7A—C6	108.3 (8)
N2—C1—C2	124.79 (10)	C8A—C7A—H7AA	110.0
C1—C2—H2A	109.3	C8A—C7A—H7AB	110.0
C1—C2—H2B	109.3	C9A—C8A—H8AA	109.7
C1—C2—C3	111.45 (10)	C9A—C8A—H8AB	109.7
H2A—C2—H2B	108.0	C7A—C8A—C9A	109.7 (10)
C3—C2—H2A	109.3	C7A—C8A—H8AA	109.7
C3—C2—H2B	109.3	C7A—C8A—H8AB	109.7
C2—C3—H3A	109.8	H8AA—C8A—H8AB	108.2
C2—C3—H3B	109.8	N5—C10—C9	121.04 (11)
C2—C3—C4	109.26 (10)	N5—C10—C9A	114.5 (5)
H3A—C3—H3B	108.3	N6—C10—N5	121.55 (11)
C4—C3—H3A	109.8	N6—C10—C9	117.32 (11)
C4—C3—H3B	109.8	N6—C10—C9A	120.8 (4)
C3—C4—H4C	109.4		

N1—C1—C2—C3	−157.01 (10)	C6—N5—C10—N6	175.54 (11)
N2—C1—C2—C3	23.88 (16)	C6—N5—C10—C9	−7.94 (19)
N4—C6—C7—C8	155.78 (15)	C6—N5—C10—C9A	15.7 (7)
N4—C6—C7A—C8A	−162.9 (9)	C6—C7—C8—C9	51.6 (2)
N5—C6—C7—C8	−26.8 (3)	C6—C7A—C8A—C9A	−47.2 (19)
N5—C6—C7A—C8A	35.6 (14)	C7—C8—C9—C10	−56.0 (2)
C1—N2—C5—N3	−174.68 (11)	C8—C9—C10—N5	35.7 (2)
C1—N2—C5—C4	7.19 (16)	C8—C9—C10—N6	−147.66 (14)
C1—C2—C3—C4	−47.65 (13)	C8A—C9A—C10—N5	−33.4 (16)
C2—C3—C4—C5	52.55 (13)	C8A—C9A—C10—N6	166.6 (10)
C3—C4—C5—N2	−33.54 (15)	C10—N5—C6—N4	−179.33 (11)
C3—C4—C5—N3	148.29 (11)	C10—N5—C6—C7	3.3 (2)

C5—N2—C1—N1	178.71 (10)	C10—N5—C6—C7A	−19.3 (7)
C5—N2—C1—C2	−2.20 (17)	C10—C9A—C8A—C7A	50 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N3	0.84	1.87	2.7051 (14)	174
O2—H2···N6	0.84	1.89	2.7312 (14)	178
N1—H1*A*···N5	0.88	2.13	2.9896 (14)	164
N1—H1*B*···O1^{i}	0.88	1.94	2.8233 (13)	176
N4—H4*A*···N2	0.88	2.10	2.9739 (14)	173
N4—H4*B*···O2^{ii}	0.88	2.00	2.8639 (14)	167
C9—H9*A*···O1^{iii}	0.99	2.55	3.439 (2)	150

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