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Neutral 4-phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazide and its salt forms with inorganic anions

Vinicius Oliveira Araujo,[a] Bárbara Tirloni,[b] Lívia Streit[c] and Vânia Denise Schwade[a]*

[a]Faculdade de Ciências Exatas e Tecnologia, Universidade Federal da Grande Dourados, Rodovia Dourados/Itahum, km 12, Dourados, Mato Grosso do Sul 79804-970, Brazil, [b]Departamento de Química, Universidade Federal de Santa Maria, Avenida Roraima, n. 1000, Santa Maria, Rio Grande do Sul 97105-900, Brazil, and [c]Department of Chemistry and Biochemistry, University of North Georgia, 3820 Mundy Mill Rd, Oakwood, GA 30566, USA. *Correspondence e-mail: vaniaschwade@gmail.com

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Semicarbazones can exist in two tautomeric forms. In the solid state, they are found in the keto form. This work presents the synthesis, structures and spectroscopic characterization (IR and NMR spectroscopy) of four such compounds, namely the neutral molecule 4-phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazide, $C_{19}H_{16}N_4O$, (I), abbreviated as HBzPyS, and three different hydrated salts, namely the chloride dihydrate, $C_{19}H_{17}N_4O^+\cdot Cl^-\cdot 2H_2O$, (II), the nitrate dihydrate, $C_{19}H_{17}N_4O^+\cdot NO_3^-\cdot 2H_2O$, (III), and the thiocyanate 2.5-hydrate, $C_{19}H_{17}N_4O^+\cdot SCN^-\cdot 2.5H_2O$, (IV), of 2-[phenyl({[(phenylcarbamoyl)amino]imino})methyl]pyridinium, abbreviated as $[H_2BzPyS]^+\cdot X^-\cdot nH_2O$, with $X = Cl^-$ and $n = 2$ for (II), $X = NO_3^-$ and $n = 2$ for (III), and $X = SCN^-$ and $n = 2.5$ for (IV), showing the influence of the anionic form in the intermolecular interactions. Water molecules and counter-ions (chloride or nitrate) are involved in the formation of a two-dimensional arrangement by the establishment of hydrogen bonds with the N—H groups of the cation, stabilizing the *E* isomers in the solid state. The neutral HBzPyS molecule crystallized as the *E* isomer due to the existence of weak π–π interactions between pairs of molecules. The calculated IR spectrum of the hydrated $[H_2BzPyS]^+$ cation is in good agreement with the experimental results.

1. Introduction

Hydrazones belong to a class of organic compounds with the structure $R_1R_2C{=}NNH_2$. These compounds possess diverse biological and pharmacological properties, such as antimicrobial, anti-inflammatory, analgesic, antifungal, antiviral, anticancer, antimalarial, antitrypanosomal *etc*. (Verma *et al.*, 2014). The biological properties of this class of compounds are often related to metal ion coordination (Beraldo & Gambino, 2004). Recently, Ag^I complexes with 2-benzoylpyridine-derived hydrazones have shown cytotoxic activity (Santos *et al.*, 2018). There are several studies concerning the hydrazone derived from 2-benzoylpyridine and 4-phenylsemicarbazide based on Cu^{II} complexes (Patel, 2009, 2010*a*,*b*; Patel *et al.*, 2009, 2010; Kurup *et al.*, 2011; Aiswarya *et al.*, 2013). In these Cu^{II} complexes, the hydrazone coordinates as a tridentate *N*,*N*′,*O*-chelating ligand, mainly without deprotonation.

Semicarbazone can exist in two tautomeric forms, namely keto and enol, or in an equilibrium mixture of the two forms due to the amide –NH—C(=O) function. In the solid state, it is well established by IR spectroscopy that the keto form remains (Kurup *et al.*, 2011). The rearrangement of the electron density in the whole molecule and, consequently, signif-

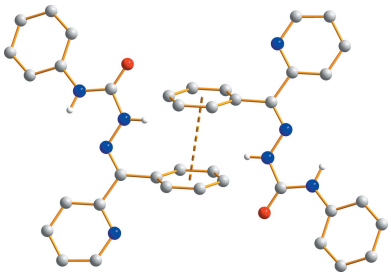


Table 1
Experimental details.

For all determinations, the temperature was 100 K, Z was 4, the radiation type was Mo $K\alpha$, the diffractometer was a Bruker D8 Venture Photon 100 and the absorption correction was multi-scan (*SADABS*; Bruker, 2015).

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$C_{19}H_{16}N_4O$	$C_{19}H_{17}N_4O^+\cdot Cl^-\cdot 2H_2O$	$C_{19}H_{17}N_4O^+\cdot NO_3^-\cdot 2H_2O$	$C_{19}H_{17}N_4O^+\cdot NCS^-\cdot 2.5H_2O$
M_r	316.36	388.85	415.41	420.48
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, b, c (Å)	5.6126 (3), 10.0683 (4), 27.2349 (12)	9.4452 (19), 9.5489 (19), 21.039 (4)	9.5556 (4), 9.3050 (4), 22.2715 (10)	13.0053 (4), 7.7965 (2), 20.8703 (7)
β (°)	90.095 (2)	95.26 (3)	96.048 (2)	107.887 (1)
V (Å^3)	1539.02 (12)	1889.5 (7)	1969.24 (15)	2013.87 (11)
μ (mm^{-1})	0.09	0.23	0.11	0.20
Crystal size (mm)	0.31 × 0.13 × 0.07	0.28 × 0.23 × 0.13	0.21 × 0.10 × 0.08	0.24 × 0.10 × 0.05
Data collection				
T_{min}, T_{max}	0.715, 0.746	0.724, 0.745	0.683, 0.746	0.707, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37458, 4693, 3813	66072, 5794, 4889	42340, 6023, 3810	31447, 6146, 4590
R_{int}	0.039	0.119	0.068	0.040
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715	0.716	0.716	0.716
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.130, 1.02	0.041, 0.112, 1.04	0.058, 0.140, 1.03	0.049, 0.131, 1.02
No. of reflections	4693	5794	6023	6146
No. of parameters	217	256	293	326
No. of restraints	0	0	0	6
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.24	0.42, −0.39	0.37, −0.54	0.4, −0.41

Computer programs: *APEX3* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2012) and *WinGX* (Farrugia, 2012).

icant changes in the spectral and photophysical behaviours are possible once tautomerism can occur by proton exchange between two or more forms, a process of great importance for dyes (Rauf *et al.*, 2015).

In this article, we present the synthesis, structure and spectroscopic characterization of four compounds, namely neutral 4-phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazide, (I) (see Scheme), denoted HBzPyS, and three different salts of $[H_2BzPyS]^+$ with chloride, (II), nitrate, (III), and thiocyanate, (IV), showing the influence of the anionic form in the intermolecular interactions.

2. Experimental

2.1. Synthesis and crystallization

All chemicals and the solvent (ethanol) were used without further purification. Single crystals suitable for X-ray analyses were obtained from the mother solution of the reactions after about one week by slow evaporation of the solvent.

2.1.1. Synthesis of $[H_2BzPyS]Cl\cdot 2H_2O$, (II). Hydrated salt (II) was obtained by the condensation reaction of 2-benzoylpyridine (916 mg, 5 mmol) and 4-phenylsemicarbazide hydrochloride (938 mg, 5 mmol) in ethanol (15 ml). The mixture was refluxed with stirring for 6 h. After cooling to room temperature, the solution was set aside for a few hours until a yellow microcrystalline compound formed, which was filtered off and dried (yield 98%).

2.1.2. Synthesis of [HBzPyS], (I). Hydrated salt (II) (176 mg, 0.45 mmol) was added to ethanol (4 ml) and to the resulting suspension, deionized water (2 ml) was added, giving a clear yellow solution. Solid sodium acetate (62 mg, 0.75 mmol) was added. Immediately, the solution became colourless and a white solid appeared. After 1 h of stirring at room temperature, the solid was filtered off and dried in air, affording (I) in 92% yield.

2.1.3. Synthesis of $[H_2BzPyS]X\cdot nH_2O$ [X = NO_3 and n = 2 for (III); X= SCN and n = 2.5 for (IV)]. Hydrated salts (III) and (IV) were prepared by adding sodium nitrate or potassium thiocyanate (0.75 mmol) to a solution of (II) (176 mg, 0.45 mmol) in ethanol (4 ml) and deionized water (2 ml). Slowly, a yellow solid appeared while the mixture was stirred for 1 h. The solid was filtered off and dried in air, giving (III) and (IV) in yields of 82 and 74%, respectively.

2.2. Spectroscopic data

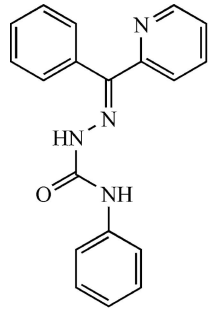
For (I): IR (KBr pellet, ν, cm^{-1}): 3375 (*m*), 3341 (*m*), 3048 (*w*), 3029 (*w*), 1698 (*s*), 1600 (*m*), 1535 (*s*), 1446 (*m*), 1418 (*m*), 1310 (*m*), 1268 (*m*), 1234 (*m*), 1189 (*m*), 1132 (*m*), 794 (*w*), 756 (*m*), 694 (*m*), 614 (*m*), 555 (*m*), 508 (*m*). ^{1}H NMR (600 MHz, DMSO-d_6, ppm): δ 9.26 (*s*, 1H), 8.92 (*s*, 1H), 8.44 (*ddd*, J = 4.8, 1.7, 0.9 Hz, 1H), 8.31–8.24 (*m*, 1H), 7.90–7.85 (*m*, 1H), 7.61–

Table 2
Selected geometric parameters (Å, °) for compounds (I)–(IV).

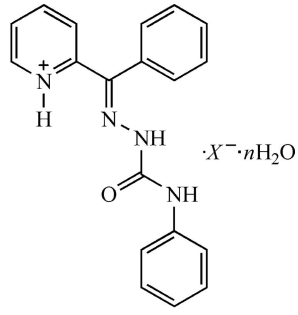
Compound (I)			
O1—C13	1.2173 (15)	N3—C13	1.3839 (15)
N1—C1	1.3385 (16)	N4—C13	1.3610 (15)
N1—C5	1.3462 (14)	N4—C14	1.4066 (14)
N2—C6	1.2919 (14)	C5—C6	1.4804 (16)
N2—N3	1.3615 (14)	C6—C7	1.4949 (15)
C6—N2—N3	117.67 (9)	N2—C6—C7	123.52 (10)
N2—N3—C13	121.17 (9)	C5—C6—C7	120.45 (9)
C13—N4—C14	127.66 (10)	O1—C13—N4	126.70 (11)
N1—C5—C6	116.36 (10)	O1—C13—N3	120.02 (10)
N2—C6—C5	116.03 (10)	N4—C13—N3	113.28 (10)
Compound (II)			
O1—C13	1.2298 (14)	N3—C13	1.3910 (14)
N1—C1	1.3384 (15)	N4—C13	1.3507 (14)
N1—C5	1.3575 (15)	N4—C14	1.4081 (14)
N2—C6	1.2902 (15)	C5—C6	1.4775 (15)
N2—N3	1.3447 (13)	C6—C7	1.4927 (16)
C6—N2—N3	119.08 (10)	N2—C6—C7	125.44 (10)
N2—N3—C13	117.20 (9)	C5—C6—C7	120.68 (10)
C13—N4—C14	127.57 (10)	O1—C13—N4	126.05 (10)
N1—C5—C6	117.58 (10)	O1—C13—N3	122.53 (10)
N2—C6—C5	113.87 (10)	N4—C13—N3	111.42 (10)
Compound (III)			
O1—C13	1.224 (2)	N4—C14	1.408 (2)
N1—C1	1.339 (2)	C5—C6	1.477 (2)
N1—C5	1.354 (2)	C6—C7	1.490 (2)
N2—C6	1.293 (2)	N5—O4	1.185 (2)
N2—N3	1.3451 (18)	N5—O3	1.224 (2)
N3—C13	1.391 (2)	N5—O5*B*	1.353 (3)
N4—C13	1.350 (2)	N5—O5*A*	1.363 (3)
C6—N2—N3	118.62 (14)	O1—C13—N3	122.58 (14)
N2—N3—C13	117.15 (13)	N4—C13—N3	111.39 (14)
C13—N4—C14	128.13 (14)	O4—N5—O3	126.39 (16)
N1—C5—C6	117.94 (14)	O4—N5—O5*B*	106.1 (2)
N2—C6—C5	114.14 (14)	O3—N5—O5*B*	118.2 (2)
N2—C6—C7	125.70 (14)	O4—N5—O5*A*	104.9 (2)
C5—C6—C7	120.16 (14)	O3—N5—O5*A*	114.96 (19)
O1—C13—N4	126.03 (15)		
Compound (IV)			
O1—C13	1.2232 (17)	N4—C14	1.4081 (18)
N1—C1	1.3431 (17)	C5—C6	1.4798 (18)
N1—C5	1.3542 (17)	C6—C7	1.4855 (18)
N2—C6	1.2895 (18)	S1*A*—C20*A*	1.650 (5)
N2—N3	1.3492 (15)	C20*A*—N5*A*	1.166 (6)
N3—C13	1.3902 (18)	S1*B*—C20*B*	1.616 (8)
N4—C13	1.3585 (17)	C20*B*—N5*B*	1.159 (8)
C6—N2—N3	119.00 (12)	C5—C6—C7	118.65 (12)
N2—N3—C13	117.37 (11)	O1—C13—N4	125.70 (13)
C13—N4—C14	127.43 (12)	O1—C13—N3	122.73 (12)
N1—C5—C6	118.07 (12)	N4—C13—N3	111.57 (12)
N2—C6—C5	114.46 (12)	N5*A*—C20*A*—S1*A*	177.1 (5)
N2—C6—C7	126.82 (12)	N5*B*—C20*B*—S1*B*	177.7 (5)

7.55 (*m*, 2H), 7.55–7.49 (*m*, 3H), 7.35 (*ddd*, *J* = 7.4, 4.8, 1.1 Hz, 1H), 7.33–7.27 (*m*, 4H), 7.01 (*t*, *J* = 7.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6, ppm): δ 155.32, 151.94, 148.58, 148.39, 139.02, 136.58, 132.06, 129.13, 129.11, 128.88, 128.76, 123.57, 122.66, 121.39, 119.40.

For (II): IR (KBr pellet, ν, cm^{-1}): 3373 (*m*), 3239 (*m*), 3197 (*m*), 3017 (*m*), 1701 (*s*), 1616 (*s*), 1599 (*s*), 1560 (*s*), 1536 (*s*), 1493 (*s*), 1446 (*s*), 1375 (*m*), 1321 (*s*), 1200 (*vs*), 1134 (*s*), 760 (*m*), 712 (*m*), 694 (*m*), 618 (*m*). ^{1}H NMR (600 MHz, DMSO-d_6, ppm): δ 10.08 (*s*, 1H), 9.71 (*s*, 1H), 8.87 (*d*, *J* = 5.0 Hz, 1H), 8.39 (*t*, *J* = 7.6 Hz, 1H), 7.90 (*t*, *J* = 6.1 Hz, 1H), 7.77 (*d*, *J* = 7.9 Hz, 2H), 7.68–7.60 (*m*, 3H), 7.53 (*d*, *J* = 6.3 Hz, 1H), 7.48–7.45 (*m*, 2H), 7.33–7.29 (*m*, 2H), 7.05 (*tt*, *J* = 7.5, 1.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6, ppm): δ 151.98, 148.99, 144.14, 143.70, 140.70, 138.74, 130.42, 129.79, 129.16, 129.03, 128.45, 125.73, 125.10, 123.02, 120.50.



(I)



(II) X = Cl , n = 2
(III) X = NO_3, n = 2
(IV) X = SCN, n = 2.5

For (III): IR (KBr pellet, ν, cm^{-1}): 3394 (*m*), 3092 (*w*), 3051 (*w*), 3033 (*w*), 1704 (*s*), 1617 (*m*), 1558 (*vs*), 1519 (*s*), 1502 (*s*), 1446 (*m*), 1383 (*s*), 1321 (*s*), 1250 (*m*), 1199 (*vs*), 1135 (*s*), 785 (*m*), 759 (*m*), 741 (*m*), 710 (*m*), 692 (*m*), 510 (*m*).

For (IV): IR (KBr pellet, ν, cm^{-1}): 3420 (*m*), 3327 (*m*), 3276 (*m*), 3036 (*w*), 2056 (*s*), 1699 (*s*), 1617 (*m*), 1559 (*s*), 1498 (*s*), 1445 (*m*), 1381 (*m*), 1320 (*m*), 1252 (*m*), 1204 (*s*), 1161 (*m*), 1135 (*m*), 782 (*m*), 758 (*m*), 740 (*m*), 698 (*m*), 506 (*m*).

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bonded to phenyl-ring C atoms were placed at calculated positions, with C—H = 0.98 Å, and treated as riding on the parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). The highest remaining electron densities are not attributable to any additional atom. Hydrated salts (III) and (IV) showed positional disorder in the anion which was handled with *SHELXL* (Sheldrick, 2015*b*) PART instructions which ensure that geometrical calculations do not simultaneously involve atoms from different disordered congeners. The O5 atom in the nitrate anion and the N5≡C20—S1 thiocyanate anion were calculated in two positions having almost 50% occupancy each. In (IV), a disordered water molecule was also successfully handled using PART instructions and restraints.

2.4. Computational details

Vibrational analysis of the $[H_2BzPyS]^+$ cation was carried out on the optimized structure using the density functional theory (DFT) formalism at the B3LYP/6-311G** level, including empirical dispersion corrections of Grimme at the D3 level. The *GAUSSIAN16* (Frisch *et al.*, 2016) suite of codes was used for all calculations. Optimization and frequency calculations were performed using *XSEDE* supercomputing resources (Towns *et al.*, 2014). Structure and IR spectrum

analyses, as well as band assignment, were carried out using *GaussView* (Dennington *et al.*, 2016).

3. Results and discussion

In the solid state, the asymmetric unit of (I) consists of one independent molecule of HBzPyS (Fig. 1). The compound crystallizes as the *E* isomer (where *E* refers to the configuration around the C=N bond), thus differing from the hydrazone derived from 2-benzoylpyridine and semicarbazide which crystallized as the *Z* isomer (Lima *et al.*, 2008). Due to the presence of the –NHPh group instead of an $–NH_2$ group, intermolecular hydrogen bonds between the –NHPh group and the carbonyl O atom are not observed in (I). Furthermore, as the orientation of the pyridine N atom also differs from that of the hydrazone derived from 2-benzoylpyridine and semicarbazide, intramolecular hydrogen bonding is also not present in (I). This may be due to the existence of weak π–π interactions between pairs of molecules, with a centroid–centroid distance of 4.0784 (7) Å (slippage ~1.37 Å) (Fig. 2). Aromatic π–π stacking interactions have been observed in Cu^{II} complexes (Patel, 2010*a*,*b*; Kurup *et al.*, 2011) and by us in Pb^{II} complexes with hydrazone-type ligands (Schwade *et al.*, 2016*a*,*b*). The imine N2=C6 bond length (Table 2) is in

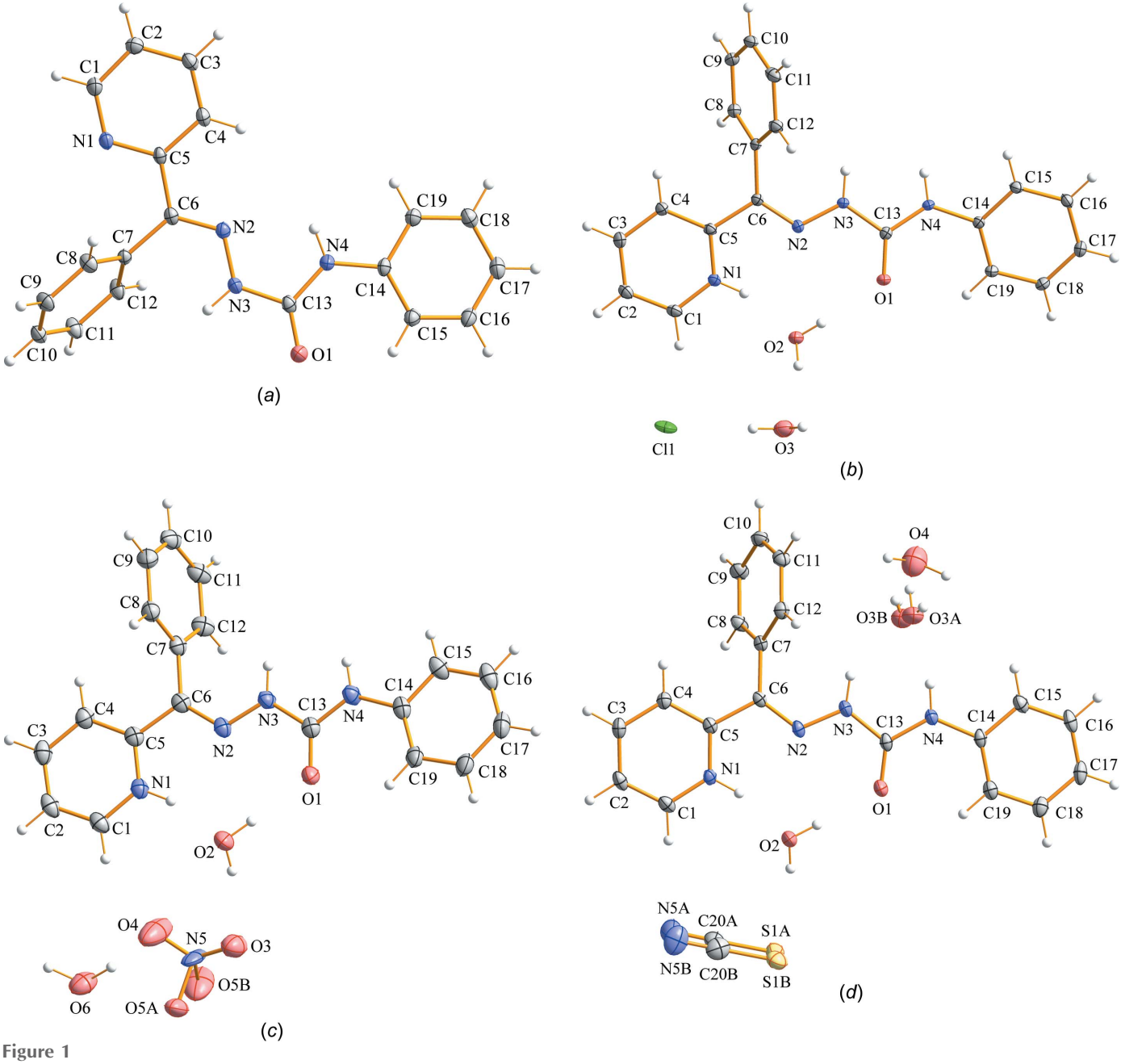


Figure 1
The molecular structures of (*a*) (I), (*b*) (II), (*c*) (III) and (*d*) (IV). Displacement ellipsoids are drawn at the 50% probability level. In (III) and (IV), disordered atoms are labelled with suffixes *A* and *B*.

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1W···O1	0.79 (2)	2.01 (2)	2.7905 (13)	169.6 (19)
N3—H3A···Cl1^{i}	0.86	2.52	3.2700 (12)	146
O3—H3W···Cl1^{ii}	0.92 (2)	2.25 (2)	3.1665 (14)	171.2 (19)
N1—H1A···O2	0.86	1.82	2.6533 (14)	163
N4—H4A···Cl1^{i}	0.86	2.31	3.1434 (13)	164
O3—H4W···Cl1	0.85 (2)	2.35 (2)	3.1974 (14)	178 (2)
O2—H2W···O3	0.86 (2)	1.90 (2)	2.7370 (15)	164.0 (18)

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

accordance with that reported for the hydrazone derived from 2-benzoylpyridine and semicarbazide (Lima *et al.*, 2008), which was obtained by the addition of an equimolar amount of sodium acetate to the reaction mixture (Pérez-Rebolledo *et al.*, 2006). In this work, (I) was obtained by the reaction of 4-phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazidium chloride, (II), with sodium acetate.

The direct reaction of 2-benzoylpyridine and 4-phenyl-semicarbazide hydrochloride gives as the product the hydrochloride derivative of (I) in good yield. The asymmetric unit of (II) consists of one $[H_2BzPyS]^+$ cation, a chloride anion and two solvent water molecules (Fig. 1). The water molecules are involved in hydrogen bonding producing a supramolecular two-dimensional arrangement in the crystallographic *bc* plane (Fig. 3). One of the water molecules participates in hydrogen bonding with the pyridinium H atom and the carbonyl O atom acting as donor and acceptor, respectively (Table 3).

Hydrated salts (III) and (IV) were prepared in an ethanolic/aqueous media of (I) and sodium nitrate or potassium thiocyanate. The same feature concerning hydrogen bonds with one water molecule is observed in the crystal structures of (III) (Fig. 3 and Table 4) and (IV) (Fig. 4 and Table 5). An analogous supramolecular two-dimensional arrangement has been observed for (III). Concerning the hydrazonium salts, it can be seen that the orientation of the cation is strongly

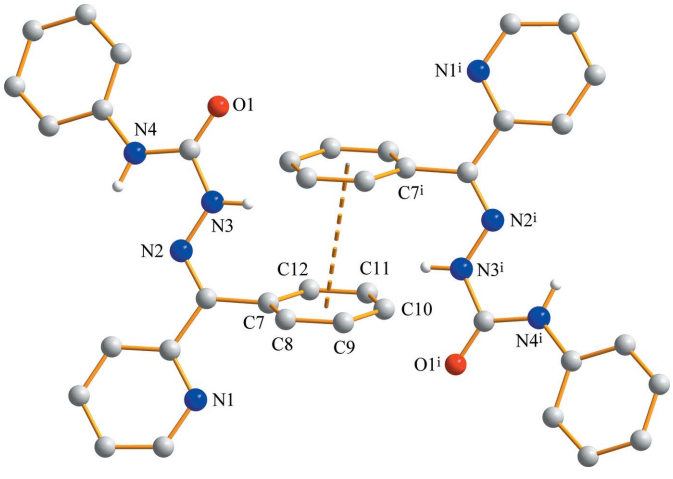


Figure 2
A view of the π-stacking interaction between two molecules in (I). Aromatic H atoms have been omitted for clarity. [Symmetry code: (i) $-x+1, -y, -z+1$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.88	1.81	2.6639 (19)	164
N3—H3A···O6^{i}	0.88	2.08	2.8794 (19)	150
N4—H4A···O6^{i}	0.88	2.03	2.875 (2)	159
O2—H1W···O1	0.86 (3)	1.92 (3)	2.7756 (17)	174 (2)
O2—H2W···O3	0.84 (3)	1.96 (3)	2.783 (2)	165 (2)
O6—H3W···O4	0.91 (3)	1.95 (3)	2.816 (2)	159 (2)
O6—H3W···O5A	0.91 (3)	2.55 (3)	3.172 (3)	126 (2)
O6—H3W···O5B	0.91 (3)	2.28 (3)	3.008 (4)	137 (2)
O6—H4W···O3^{ii}	0.99 (3)	1.87 (3)	2.833 (2)	163 (2)
O6—H4W···O5B^{ii}	0.99 (3)	2.51 (3)	3.210 (4)	127.0 (19)

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

influenced by the hydrogen bonds with the solvent molecules and the anion, and so the *E* isomers are observed. Figs. S1 and S2 in the supporting information present the extended supramolecular arrangements for (II) and (III).

The existence of hydrogen bonding involving the carbonyl O atom causes a slight elongation of the C═O bond. Compared to the distance in (I), which is 1.2173 (15) Å, in compounds (II)–(IV), the C═O distances are in the range 1.2232 (17)–1.2298 (14) Å (Table 2). In addition, the N—N bond length is somewhat shortened to 1.3447 (13)–1.3492 (15) Å compared to the value of 1.3615 (14) Å in (I).

Hydrated salts (III) and (IV) are soluble in pure ethanol. Salt (II) initially dissolves in ethanol; however, it precipitates again if water is not added. Compound (I) is soluble in ethanol and other common organic solvents, but insoluble in water.

The salts were characterized by the experimental IR spectra of the compounds (Fig. S3 in the supporting information) and by the calculated IR spectrum of the hydrated $[H_2BzPyS]^+$ cation, as shown in Table 6. The N—H stretching vibrations of the amide groups are found around 3330–3200 cm^{-1}. The O—H stretching vibrations in the range 3420–3373 cm^{-1} are due to the solvent water molecules. The ν(C═O) and ν(C═N) bands are found at approximately 1700 and 1617 cm^{-1}, respectively. N—H bending vibrations appear at 1558–1560 cm^{-1}. The NO and CN stretching vibration bands of the nitrate and thiocyanate anions are found at 1383 and 2056 cm^{-1}, respectively. The calculated spectrum (Fig. S4 in the supporting information) is in good agreement with the experimental results, showing normal modes of vibration

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.88	1.79	2.6531 (17)	166
N3—H3A···O3A	0.88	2.40	3.123 (5)	139
N3—H3A···O3B	0.88	2.04	2.809 (5)	146
N4—H4A···O3A	0.88	2.00	2.845 (4)	160
N4—H4A···O3B	0.88	1.88	2.718 (4)	160
O2—H1W···O1	0.82 (3)	1.94 (3)	2.7575 (15)	174 (2)
O2—H2W···S1A	0.83 (3)	2.40 (3)	3.225 (2)	168 (2)
O2—H2W···S1B	0.83 (3)	2.47 (3)	3.280 (3)	164 (2)
O3A—H3WA···S1A^{i}	0.86 (1)	2.69 (3)	3.319 (5)	131 (4)
O3B—H3WB···S1B^{i}	0.86 (1)	2.34 (2)	3.185 (5)	166 (5)

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

mostly due to the N—H stretching of 3329 cm^{-1} for the pyridinium group, and 3474 and 3552 cm^{-1} for the amide groups. The normal modes found in the range from 3892 to 3530 cm^{-1} can be assigned to the O—H stretching of solvent water molecules. The normal mode at 1733 cm^{-1} is due to the C═O stretching, and the normal modes found at 1585 and 1581 cm^{-1} correspond to the asymmetric and symmetric C═N stretching vibrations, respectively.

For the neutral compound, (I), the N—H stretching vibrations are observed as sharp bands at 3375 and 3341 cm^{-1}, while the ν(C═O) and ν(C═N) bands are found at 1698 and 1600 cm^{-1}, respectively, as has been observed previously (Kurup *et al.*, 2011). A band found at 1132 cm^{-1} is assigned to the ν(N—N) band of semicarbazide. The N—H bending vibration appears at 1535 cm^{-1}, which differs from that found in the salts since the main difference is the absence of

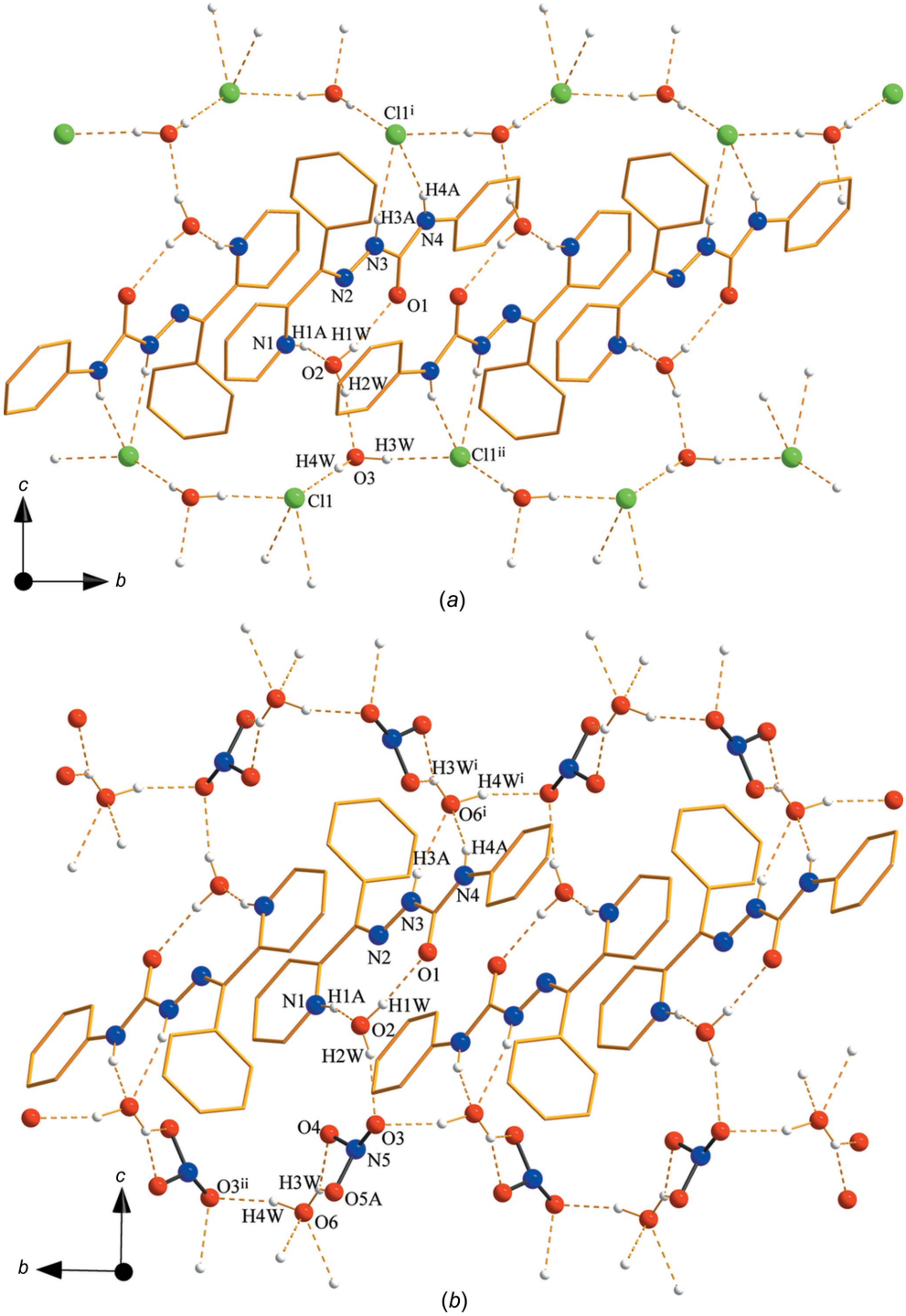


Figure 3
A view of the hydrogen bonds in (*a*) (II) and (*b*) (III), showing the formation of a two-dimensional supramolecular arrangement. Aromatic H atoms have been omitted for clarity. [Symmetry codes for (II): (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; symmetry codes for (III): (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.]

Table 6
Selected normal modes of vibration calculated for the hydrated $[H_2BzPyS]^+$ cation.

Normal vibrations	Frequency (cm^{-1})	Normal vibrations	Frequency (cm^{-1})
$\nu_2(O_2-H)$	3892.64	$\nu_1(N_3-H)$	3474.86
$\nu_1(O_2-H)$	3530.41	$\nu_1(N_1-H)$	3329.39
$\nu_2(O_3-H)$	3883.54	$\nu_1(C_{13}-O_1)$	1733.86
$\nu_1(O_3-H)$	3763.48	$\nu_2(C_{13}-N_4)$	1585.25
$\nu_1(N_4-H)$	3552.76	$\nu_1(C_{13}-N_4)$	1581.30

hydrogen bonds (Fig. S3 in the supporting information). In the solid state, all compounds are in the keto form, which has been proven by the crystal structures.

The NMR spectra of compounds (I) and (II) were recorded in the same deuterated solvent (DMSO-d_6). The signals for the amide-group H atoms appear as singlets at 9.26 and 8.92 ppm for (I), and at 10.08 and 9.71 ppm for (II). These differences in chemical shifts can be rationalized by differences in the strengths of the hydrogen bonds involving the N3—H and N4—H amidic H atoms, since (II) could interact preferentially with water molecules or chloride ions present in the sample, leading to stronger interactions. Also, it is worthy of note that the signals in the ^{1}H and ^{13}C NMR spectra are not duplicated, indicating the presence of only one configurational isomeric form for each compound in DMSO-d_6 solution.

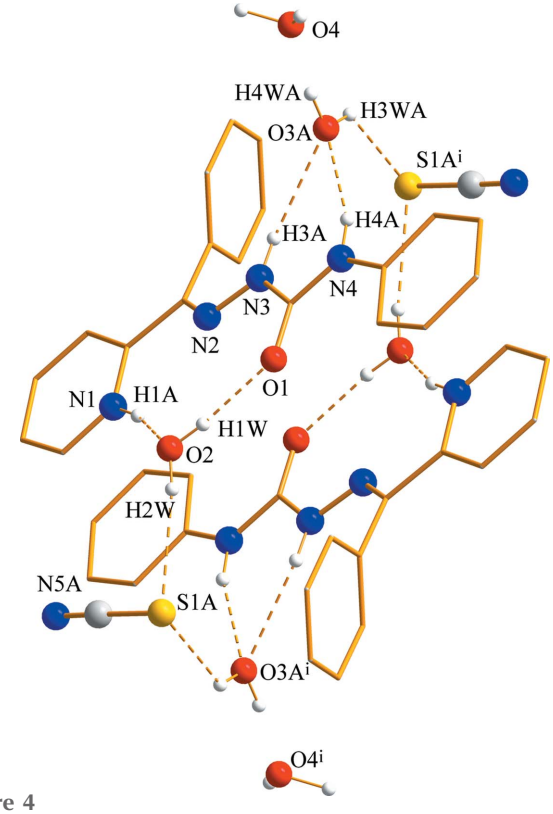


Figure 4
A view of the hydrogen bonds (dashed lines) in (IV). Only hydrogen bonds involving molecules with full occupancy were considered. Aromatic H atoms have been omitted for clarity. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

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supporting information

Acta Cryst. (2019). C**75** [https://doi.org/10.1107/S2053229618016467]

Neutral 4-phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazide and its salt forms with inorganic anions

Vinicius Oliveira Araujo, Bárbara Tirloni, Lívia Streit and Vânia Denise Schwade

Computing details

For all structures, data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

4-Phenyl-1-[phenyl(pyridin-2-yl)methylidene]semicarbazide (I)

Crystal data

$C_{19}H_{16}N_4O$
$M_r = 316.36$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 5.6126$ (3) Å
$b = 10.0683$ (4) Å
$c = 27.2349$ (12) Å
$\beta = 90.095$ (2)°
$V = 1539.02$ (12) Å^3
$Z = 4$
$F(000) = 664$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9971 reflections
$\theta = 2.5$–30.5°
$\mu = 0.09$ mm^{-1}
$T = 100$ K
Block, colourless
0.31 × 0.13 × 0.07 mm

Data collection

Bruker D8 Venture Photon 100 diffractometer
Radiation source: microfocus X ray tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
$T_{min} = 0.715$, $T_{max} = 0.746$
37458 measured reflections
4693 independent reflections
3813 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 30.5°$, $\theta_{min} = 3.0°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -38 \rightarrow 38$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.130$
$S = 1.02$
4693 reflections
217 parameters
0 restraints
0 constraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.7078P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ 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}
O1	1.05213 (17)	0.05900 (9)	0.62708 (3)	0.0231 (2)
N1	0.09296 (18)	0.44896 (10)	0.55743 (4)	0.0173 (2)
N2	0.58312 (18)	0.28384 (10)	0.61287 (3)	0.0152 (2)
N3	0.73938 (19)	0.18385 (10)	0.60314 (4)	0.0182 (2)
H3A	0.7275	0.14	0.5753	0.022*
N4	0.91577 (18)	0.22644 (10)	0.67747 (4)	0.0173 (2)
H4A	0.7922	0.2792	0.6812	0.021*
C1	−0.0760 (2)	0.53746 (13)	0.56891 (4)	0.0199 (2)
H1	−0.1889	0.5609	0.5444	0.024*
C2	−0.0950 (2)	0.59682 (12)	0.61466 (4)	0.0196 (2)
H2	−0.2206	0.6573	0.6216	0.023*
C3	0.0740 (2)	0.56568 (12)	0.65015 (4)	0.0200 (2)
H3	0.0673	0.6056	0.6817	0.024*
C4	0.2517 (2)	0.47617 (12)	0.63895 (4)	0.0181 (2)
H4	0.3705	0.4545	0.6625	0.022*
C5	0.2540 (2)	0.41762 (11)	0.59223 (4)	0.0135 (2)
C6	0.4318 (2)	0.31515 (11)	0.57900 (4)	0.0136 (2)
C7	0.4285 (2)	0.25270 (11)	0.52920 (4)	0.0135 (2)
C8	0.2388 (2)	0.17334 (12)	0.51455 (4)	0.0185 (2)
H8	0.1083	0.1594	0.5361	0.022*
C9	0.2392 (2)	0.11422 (12)	0.46839 (5)	0.0204 (2)
H9	0.1087	0.0605	0.4585	0.024*
C10	0.4293 (2)	0.13349 (12)	0.43688 (4)	0.0191 (2)
H10	0.4298	0.0923	0.4055	0.023*
C11	0.6184 (2)	0.21273 (14)	0.45113 (4)	0.0215 (3)
H11	0.7484	0.2264	0.4294	0.026*
C12	0.6188 (2)	0.27252 (13)	0.49728 (4)	0.0189 (2)
H12	0.749	0.3269	0.507	0.023*
C13	0.9165 (2)	0.15002 (11)	0.63625 (4)	0.0158 (2)
C14	1.0893 (2)	0.23100 (12)	0.71477 (4)	0.0154 (2)
C15	1.2864 (2)	0.14683 (13)	0.71683 (4)	0.0183 (2)
H15	1.3078	0.0797	0.6927	0.022*
C16	1.4520 (2)	0.16245 (13)	0.75474 (4)	0.0213 (3)
H16	1.5862	0.1051	0.7563	0.026*
C17	1.4241 (2)	0.26024 (14)	0.79021 (4)	0.0227 (3)
H17	1.5396	0.271	0.8154	0.027*
C18	1.2252 (2)	0.34212 (13)	0.78834 (4)	0.0218 (3)
H18	1.2029	0.4082	0.8128	0.026*
C19	1.0589 (2)	0.32794 (12)	0.75103 (4)	0.0188 (2)

H19	0.9234	0.3844	0.7501	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0272 (5)	0.0230 (4)	0.0191 (4)	0.0077 (4)	−0.0042 (3)	−0.0028 (3)
N1	0.0197 (5)	0.0177 (5)	0.0144 (4)	−0.0005 (4)	−0.0046 (4)	−0.0013 (4)
N2	0.0171 (5)	0.0149 (4)	0.0137 (4)	−0.0004 (4)	−0.0020 (3)	0.0009 (3)
N3	0.0223 (5)	0.0183 (5)	0.0138 (4)	0.0031 (4)	−0.0044 (4)	−0.0035 (4)
N4	0.0169 (5)	0.0201 (5)	0.0149 (4)	0.0040 (4)	−0.0028 (4)	−0.0023 (4)
C1	0.0205 (6)	0.0214 (6)	0.0180 (5)	0.0009 (5)	−0.0049 (4)	−0.0012 (4)
C2	0.0211 (6)	0.0176 (5)	0.0199 (5)	0.0009 (4)	0.0003 (4)	−0.0016 (4)
C3	0.0257 (6)	0.0208 (6)	0.0135 (5)	−0.0007 (5)	−0.0006 (4)	−0.0028 (4)
C4	0.0214 (6)	0.0209 (5)	0.0120 (5)	−0.0014 (5)	−0.0036 (4)	−0.0003 (4)
C5	0.0155 (5)	0.0133 (5)	0.0118 (4)	−0.0034 (4)	−0.0018 (4)	0.0012 (4)
C6	0.0157 (5)	0.0133 (5)	0.0120 (4)	−0.0038 (4)	−0.0010 (4)	0.0009 (4)
C7	0.0158 (5)	0.0129 (5)	0.0118 (4)	−0.0003 (4)	−0.0021 (4)	0.0003 (4)
C8	0.0172 (5)	0.0197 (5)	0.0186 (5)	−0.0055 (4)	0.0019 (4)	−0.0029 (4)
C9	0.0207 (6)	0.0191 (5)	0.0213 (5)	−0.0056 (5)	−0.0016 (4)	−0.0048 (4)
C10	0.0254 (6)	0.0178 (5)	0.0142 (5)	−0.0014 (5)	−0.0015 (4)	−0.0023 (4)
C11	0.0211 (6)	0.0284 (6)	0.0150 (5)	−0.0046 (5)	0.0026 (4)	−0.0013 (5)
C12	0.0163 (5)	0.0243 (6)	0.0160 (5)	−0.0061 (5)	−0.0011 (4)	−0.0010 (4)
C13	0.0197 (5)	0.0155 (5)	0.0124 (5)	−0.0016 (4)	−0.0003 (4)	0.0016 (4)
C14	0.0161 (5)	0.0176 (5)	0.0124 (5)	−0.0008 (4)	−0.0013 (4)	0.0027 (4)
C15	0.0175 (5)	0.0221 (6)	0.0154 (5)	0.0023 (4)	−0.0001 (4)	0.0014 (4)
C16	0.0169 (5)	0.0286 (6)	0.0182 (5)	0.0035 (5)	−0.0014 (4)	0.0033 (5)
C17	0.0220 (6)	0.0304 (7)	0.0157 (5)	−0.0030 (5)	−0.0036 (4)	0.0012 (5)
C18	0.0272 (6)	0.0224 (6)	0.0159 (5)	−0.0020 (5)	−0.0018 (4)	−0.0019 (4)
C19	0.0211 (6)	0.0189 (5)	0.0164 (5)	0.0017 (4)	−0.0016 (4)	0.0005 (4)

Geometric parameters (Å, º)

O1—C13	1.2173 (15)	C7—C12	1.3926 (16)
N1—C1	1.3385 (16)	C8—C9	1.3911 (16)
N1—C5	1.3462 (14)	C8—H8	0.95
N2—C6	1.2919 (14)	C9—C10	1.3839 (18)
N2—N3	1.3615 (14)	C9—H9	0.95
N3—C13	1.3839 (15)	C10—C11	1.3829 (18)
N3—H3A	0.88	C10—H10	0.95
N4—C13	1.3610 (15)	C11—C12	1.3936 (16)
N4—C14	1.4066 (14)	C11—H11	0.95
N4—H4A	0.88	C12—H12	0.95
C1—C2	1.3864 (17)	C14—C15	1.3949 (16)
C1—H1	0.95	C14—C19	1.3990 (16)
C2—C3	1.3891 (17)	C15—C16	1.3968 (16)
C2—H2	0.95	C15—H15	0.95
C3—C4	1.3785 (18)	C16—C17	1.3883 (18)
C3—H3	0.95	C16—H16	0.95

C4—C5	1.4024 (15)	C17—C18	1.3888 (19)
C4—H4	0.95	C17—H17	0.95
C5—C6	1.4804 (16)	C18—C19	1.3858 (16)
C6—C7	1.4949 (15)	C18—H18	0.95
C7—C8	1.3894 (16)	C19—H19	0.95

C1—N1—C5	117.81 (10)	C10—C9—H9	119.9
C6—N2—N3	117.67 (9)	C8—C9—H9	119.9
N2—N3—C13	121.17 (9)	C11—C10—C9	119.92 (11)
N2—N3—H3A	119.4	C11—C10—H10	120
C13—N3—H3A	119.4	C9—C10—H10	120
C13—N4—C14	127.66 (10)	C10—C11—C12	120.16 (11)
C13—N4—H4A	116.2	C10—C11—H11	119.9
C14—N4—H4A	116.2	C12—C11—H11	119.9
N1—C1—C2	123.55 (11)	C7—C12—C11	120.07 (11)
N1—C1—H1	118.2	C7—C12—H12	120
C2—C1—H1	118.2	C11—C12—H12	120
C1—C2—C3	118.32 (11)	O1—C13—N4	126.70 (11)
C1—C2—H2	120.8	O1—C13—N3	120.02 (10)
C3—C2—H2	120.8	N4—C13—N3	113.28 (10)
C4—C3—C2	119.15 (11)	C15—C14—C19	119.53 (11)
C4—C3—H3	120.4	C15—C14—N4	123.87 (10)
C2—C3—H3	120.4	C19—C14—N4	116.59 (10)
C3—C4—C5	118.90 (10)	C14—C15—C16	119.22 (11)
C3—C4—H4	120.5	C14—C15—H15	120.4
C5—C4—H4	120.5	C16—C15—H15	120.4
N1—C5—C4	122.21 (11)	C17—C16—C15	121.23 (12)
N1—C5—C6	116.36 (10)	C17—C16—H16	119.4
C4—C5—C6	121.41 (10)	C15—C16—H16	119.4
N2—C6—C5	116.03 (10)	C16—C17—C18	119.14 (11)
N2—C6—C7	123.52 (10)	C16—C17—H17	120.4
C5—C6—C7	120.45 (9)	C18—C17—H17	120.4
C8—C7—C12	119.43 (10)	C19—C18—C17	120.40 (12)
C8—C7—C6	120.71 (10)	C19—C18—H18	119.8
C12—C7—C6	119.86 (10)	C17—C18—H18	119.8
C7—C8—C9	120.21 (11)	C18—C19—C14	120.45 (11)
C7—C8—H8	119.9	C18—C19—H19	119.8
C9—C8—H8	119.9	C14—C19—H19	119.8
C10—C9—C8	120.20 (11)		

C6—N2—N3—C13	175.88 (11)	C7—C8—C9—C10	0.36 (19)
C5—N1—C1—C2	−0.80 (19)	C8—C9—C10—C11	−0.59 (19)
N1—C1—C2—C3	1.8 (2)	C9—C10—C11—C12	0.42 (19)
C1—C2—C3—C4	−0.86 (19)	C8—C7—C12—C11	−0.19 (18)
C2—C3—C4—C5	−0.99 (18)	C6—C7—C12—C11	178.94 (11)
C1—N1—C5—C4	−1.21 (17)	C10—C11—C12—C7	−0.03 (19)
C1—N1—C5—C6	177.43 (10)	C14—N4—C13—O1	10.2 (2)
C3—C4—C5—N1	2.11 (18)	C14—N4—C13—N3	−170.32 (11)

C3—C4—C5—C6	−176.45 (11)	N2—N3—C13—O1	178.95 (11)
N3—N2—C6—C5	175.80 (10)	N2—N3—C13—N4	−0.52 (16)
N3—N2—C6—C7	−3.42 (16)	C13—N4—C14—C15	−5.38 (19)
N1—C5—C6—N2	−178.80 (10)	C13—N4—C14—C19	173.74 (11)
C4—C5—C6—N2	−0.15 (16)	C19—C14—C15—C16	−0.99 (18)
N1—C5—C6—C7	0.45 (15)	N4—C14—C15—C16	178.09 (11)
C4—C5—C6—C7	179.09 (10)	C14—C15—C16—C17	−0.18 (19)
N2—C6—C7—C8	113.46 (13)	C15—C16—C17—C18	1.3 (2)
C5—C6—C7—C8	−65.72 (15)	C16—C17—C18—C19	−1.2 (2)
N2—C6—C7—C12	−65.65 (15)	C17—C18—C19—C14	0.00 (19)
C5—C6—C7—C12	115.16 (12)	C15—C14—C19—C18	1.09 (18)
C12—C7—C8—C9	0.03 (18)	N4—C14—C19—C18	−178.07 (11)
C6—C7—C8—C9	−179.09 (11)		

2-[Phenyl({[(phenylcarbamoyl)amino]imino})methyl]pyridinium chloride dihydrate (II)

Crystal data

$C_{19}H_{17}N_4O^+·Cl^-·2H_2O$
M_r = 388.85
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.4452 (19) Å
b = 9.5489 (19) Å
c = 21.039 (4) Å
β = 95.26 (3)°
V = 1889.5 (7) Å^3
Z = 4
$F(000)$ = 816
D_x = 1.367 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9932 reflections
θ = 2.9–30.5°
μ = 0.23 mm^{-1}
T = 100 K
Block, yellow
0.28 × 0.23 × 0.13 mm

Data collection

Bruker D8 Venture Photon 100 diffractometer
Radiation source: microfocus X ray tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.724, T_{max} = 0.745
66072 measured reflections
5794 independent reflections
4889 reflections with $I > 2\sigma(I)$
R_{int} = 0.119
θ_{max} = 30.6°, θ_{min} = 2.3°
h = −13→13
k = −13→13
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.112
S = 1.04
5794 reflections
256 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.9098P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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	0.06783 (3)	0.09797 (4)	0.22145 (2)	0.02280 (9)
O1	−0.17520 (9)	0.40910 (9)	0.50096 (4)	0.01606 (18)
N1	0.10125 (10)	0.07050 (10)	0.43270 (4)	0.01254 (18)
H1A	0.0284	0.1283	0.4307	0.015*
N2	0.05449 (10)	0.24698 (10)	0.52436 (4)	0.01189 (18)
N3	0.01723 (10)	0.33890 (10)	0.56830 (4)	0.01274 (19)
H3A	0.0691	0.3502	0.6049	0.015*
N4	−0.13882 (10)	0.49480 (11)	0.60335 (5)	0.01421 (19)
H4A	−0.081	0.4876	0.6384	0.017*
C1	0.11352 (13)	−0.01729 (13)	0.38390 (5)	0.0155 (2)
H1	0.0446	−0.0152	0.3481	0.019*
C2	0.22502 (13)	−0.11075 (13)	0.38504 (6)	0.0164 (2)
H2	0.2337	−0.1734	0.3505	0.02*
C3	0.32428 (13)	−0.11085 (13)	0.43795 (6)	0.0169 (2)
H3	0.4021	−0.1742	0.44	0.02*
C4	0.30990 (12)	−0.01824 (13)	0.48798 (5)	0.0153 (2)
H4	0.378	−0.0184	0.5241	0.018*
C5	0.19622 (12)	0.07440 (12)	0.48516 (5)	0.0116 (2)
C6	0.17085 (12)	0.17684 (12)	0.53552 (5)	0.0116 (2)
C7	0.27603 (12)	0.19470 (12)	0.59235 (5)	0.0125 (2)
C8	0.30414 (13)	0.08615 (13)	0.63600 (6)	0.0165 (2)
H8	0.2542	0	0.6305	0.02*
C9	0.40567 (14)	0.10438 (14)	0.68769 (6)	0.0204 (3)
H9	0.4248	0.0305	0.7175	0.024*
C10	0.47906 (13)	0.22994 (15)	0.69591 (6)	0.0201 (3)
H10	0.5501	0.2408	0.7305	0.024*
C11	0.44861 (13)	0.33944 (14)	0.65360 (6)	0.0191 (2)
H11	0.4973	0.4261	0.6598	0.023*
C12	0.34667 (12)	0.32249 (13)	0.60189 (5)	0.0153 (2)
H12	0.3253	0.3979	0.5732	0.018*
C13	−0.10673 (12)	0.41545 (12)	0.55349 (5)	0.0118 (2)
C14	−0.25407 (12)	0.58765 (12)	0.60569 (5)	0.0115 (2)
C15	−0.24406 (12)	0.68459 (12)	0.65562 (5)	0.0139 (2)
H15	−0.161	0.6875	0.6847	0.017*
C16	−0.35501 (13)	0.77650 (12)	0.66282 (5)	0.0154 (2)
H16	−0.3471	0.8433	0.6964	0.018*
C17	−0.47787 (13)	0.77128 (13)	0.62103 (6)	0.0169 (2)
H17	−0.5545	0.8333	0.6264	0.02*
C18	−0.48763 (13)	0.67484 (13)	0.57150 (6)	0.0168 (2)

H18	−0.5714	0.6714	0.5429	0.02*
C19	−0.37619 (12)	0.58294 (12)	0.56314 (5)	0.0140 (2)
H19	−0.3834	0.5178	0.5289	0.017*
O2	−0.13582 (10)	0.21563 (10)	0.40474 (4)	0.01835 (18)
H1W	−0.144 (2)	0.278 (2)	0.4289 (9)	0.028*
H2W	−0.154 (2)	0.2521 (19)	0.3676 (10)	0.028*
O3	−0.17336 (12)	0.28318 (13)	0.27789 (5)	0.0287 (2)
H3W	−0.152 (2)	0.377 (2)	0.2752 (10)	0.043*
H4W	−0.110 (2)	0.232 (2)	0.2630 (11)	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02539 (17)	0.02989 (17)	0.01209 (14)	−0.00797 (12)	−0.00386 (11)	−0.00191 (11)
O1	0.0156 (4)	0.0207 (4)	0.0110 (4)	0.0054 (3)	−0.0033 (3)	−0.0029 (3)
N1	0.0126 (4)	0.0153 (4)	0.0097 (4)	0.0016 (3)	0.0009 (3)	0.0000 (3)
N2	0.0118 (4)	0.0132 (4)	0.0107 (4)	0.0017 (3)	0.0013 (3)	−0.0013 (3)
N3	0.0120 (4)	0.0165 (5)	0.0093 (4)	0.0041 (3)	−0.0016 (3)	−0.0029 (3)
N4	0.0124 (4)	0.0190 (5)	0.0104 (4)	0.0058 (4)	−0.0033 (3)	−0.0034 (3)
C1	0.0179 (5)	0.0188 (5)	0.0098 (5)	−0.0007 (4)	0.0007 (4)	−0.0010 (4)
C2	0.0186 (6)	0.0188 (6)	0.0123 (5)	0.0001 (4)	0.0036 (4)	−0.0028 (4)
C3	0.0158 (5)	0.0192 (6)	0.0161 (5)	0.0041 (4)	0.0032 (4)	−0.0026 (4)
C4	0.0133 (5)	0.0201 (6)	0.0125 (5)	0.0030 (4)	0.0005 (4)	−0.0027 (4)
C5	0.0115 (5)	0.0143 (5)	0.0092 (4)	−0.0004 (4)	0.0015 (4)	−0.0003 (4)
C6	0.0112 (5)	0.0137 (5)	0.0097 (4)	0.0013 (4)	0.0008 (4)	−0.0003 (4)
C7	0.0093 (5)	0.0175 (5)	0.0106 (5)	0.0034 (4)	0.0005 (4)	−0.0027 (4)
C8	0.0183 (5)	0.0169 (5)	0.0139 (5)	0.0052 (4)	−0.0005 (4)	−0.0020 (4)
C9	0.0235 (6)	0.0235 (6)	0.0133 (5)	0.0101 (5)	−0.0029 (4)	−0.0015 (4)
C10	0.0149 (5)	0.0319 (7)	0.0127 (5)	0.0060 (5)	−0.0024 (4)	−0.0074 (5)
C11	0.0144 (5)	0.0277 (6)	0.0153 (5)	−0.0027 (5)	0.0017 (4)	−0.0068 (5)
C12	0.0136 (5)	0.0202 (6)	0.0123 (5)	−0.0001 (4)	0.0015 (4)	−0.0015 (4)
C13	0.0110 (5)	0.0127 (5)	0.0118 (5)	0.0015 (4)	0.0007 (4)	−0.0002 (4)
C14	0.0112 (5)	0.0132 (5)	0.0100 (4)	0.0022 (4)	0.0009 (4)	0.0001 (4)
C15	0.0128 (5)	0.0177 (5)	0.0109 (5)	−0.0002 (4)	−0.0003 (4)	−0.0025 (4)
C16	0.0175 (5)	0.0160 (5)	0.0130 (5)	0.0010 (4)	0.0032 (4)	−0.0042 (4)
C17	0.0162 (5)	0.0166 (5)	0.0178 (5)	0.0057 (4)	0.0015 (4)	−0.0019 (4)
C18	0.0145 (5)	0.0190 (6)	0.0160 (5)	0.0049 (4)	−0.0035 (4)	−0.0020 (4)
C19	0.0141 (5)	0.0154 (5)	0.0119 (5)	0.0029 (4)	−0.0023 (4)	−0.0026 (4)
O2	0.0207 (4)	0.0202 (4)	0.0132 (4)	0.0053 (3)	−0.0034 (3)	−0.0023 (3)
O3	0.0287 (5)	0.0355 (6)	0.0213 (5)	0.0013 (5)	−0.0020 (4)	0.0026 (4)

Geometric parameters (Å, º)

O1—C13	1.2298 (14)	C8—H8	0.95
N1—C1	1.3387 (15)	C9—C10	1.388 (2)
N1—C5	1.3575 (15)	C9—H9	0.95
N1—H1A	0.88	C10—C11	1.3863 (19)
N2—C6	1.2901 (14)	C10—H10	0.95

N2—N3	1.3448 (13)	C11—C12	1.3946 (17)
N3—C13	1.3912 (14)	C11—H11	0.95
N3—H3A	0.88	C12—H12	0.95
N4—C13	1.3507 (14)	C14—C19	1.3946 (16)
N4—C14	1.4083 (14)	C14—C15	1.3968 (15)
N4—H4A	0.88	C15—C16	1.3858 (16)
C1—C2	1.3790 (17)	C15—H15	0.95
C1—H1	0.95	C16—C17	1.3911 (17)
C2—C3	1.3881 (17)	C16—H16	0.95
C2—H2	0.95	C17—C18	1.3874 (17)
C3—C4	1.3910 (16)	C17—H17	0.95
C3—H3	0.95	C18—C19	1.3939 (16)
C4—C5	1.3883 (16)	C18—H18	0.95
C4—H4	0.95	C19—H19	0.95
C5—C6	1.4777 (15)	O2—H1W	0.79 (2)
C6—C7	1.4926 (16)	O2—H2W	0.86 (2)
C7—C8	1.3942 (16)	O3—H3W	0.92 (2)
C7—C12	1.3963 (17)	O3—H4W	0.85 (2)
C8—C9	1.3935 (17)		

C1—N1—C5	122.92 (10)	C10—C9—H9	119.8
C1—N1—H1A	118.5	C8—C9—H9	119.8
C5—N1—H1A	118.5	C11—C10—C9	119.99 (11)
C6—N2—N3	119.08 (10)	C11—C10—H10	120
N2—N3—C13	117.18 (9)	C9—C10—H10	120
N2—N3—H3A	121.4	C10—C11—C12	120.08 (12)
C13—N3—H3A	121.4	C10—C11—H11	120
C13—N4—C14	127.56 (10)	C12—C11—H11	120
C13—N4—H4A	116.2	C11—C12—C7	120.02 (11)
C14—N4—H4A	116.2	C11—C12—H12	120
N1—C1—C2	120.77 (11)	C7—C12—H12	120
N1—C1—H1	119.6	O1—C13—N4	126.06 (10)
C2—C1—H1	119.6	O1—C13—N3	122.54 (10)
C1—C2—C3	118.23 (11)	N4—C13—N3	111.40 (10)
C1—C2—H2	120.9	C19—C14—C15	119.95 (10)
C3—C2—H2	120.9	C19—C14—N4	123.62 (10)
C2—C3—C4	120.06 (11)	C15—C14—N4	116.38 (10)
C2—C3—H3	120	C16—C15—C14	120.14 (11)
C4—C3—H3	120	C16—C15—H15	119.9
C5—C4—C3	120.10 (11)	C14—C15—H15	119.9
C5—C4—H4	120	C15—C16—C17	120.24 (11)
C3—C4—H4	120	C15—C16—H16	119.9
N1—C5—C4	117.92 (10)	C17—C16—H16	119.9
N1—C5—C6	117.56 (10)	C18—C17—C16	119.52 (11)
C4—C5—C6	124.52 (10)	C18—C17—H17	120.2
N2—C6—C5	113.87 (10)	C16—C17—H17	120.2
N2—C6—C7	125.44 (10)	C17—C18—C19	120.91 (11)
C5—C6—C7	120.68 (10)	C17—C18—H18	119.5

C8—C7—C12	119.69 (11)	C19—C18—H18	119.5
C8—C7—C6	121.02 (11)	C18—C19—C14	119.24 (10)
C12—C7—C6	119.29 (10)	C18—C19—H19	120.4
C9—C8—C7	119.81 (12)	C14—C19—H19	120.4
C9—C8—H8	120.1	H1W—O2—H2W	104.9 (18)
C7—C8—H8	120.1	H3W—O3—H4W	111 (2)
C10—C9—C8	120.35 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*W*···O1	0.79 (2)	2.01 (2)	2.7906 (13)	169.6 (19)
N3—H3*A*···Cl1^{i}	0.88	2.5	3.2698 (12)	146
O3—H3*W*···Cl1^{ii}	0.92 (2)	2.25 (2)	3.1665 (14)	171.1 (19)
N1—H1*A*···O2	0.88	1.8	2.6531 (14)	162
N4—H4*A*···Cl1^{i}	0.88	2.29	3.1432 (13)	163
O3—H4*W*···Cl1	0.85 (2)	2.35 (2)	3.1973 (14)	178 (2)
O2—H2*W*···O3	0.86 (2)	1.90 (2)	2.7370 (15)	163.8 (18)

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

2-[Phenyl({[(phenylcarbamoyl)amino]imino})methyl]pyridinium nitrate dihydrate (III)

Crystal data

$C_{19}H_{17}N_4O^+·NO_3^-·2H_2O$
M_r = 415.41
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.5556 (4) Å
b = 9.3050 (4) Å
c = 22.2715 (10) Å
β = 96.048 (2)°
V = 1969.24 (15) Å^3
Z = 4
$F(000)$ = 872
D_x = 1.401 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8565 reflections
θ = 2.7–27.9°
μ = 0.11 mm^{-1}
T = 100 K
Block, colourless
0.21 × 0.10 × 0.08 mm

Data collection

Bruker D8 Venture Photon 100 diffractometer
Radiation source: microfocus X ray tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.683, T_{max} = 0.746
42340 measured reflections
6023 independent reflections
3810 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 30.6°, θ_{min} = 2.4°
h = −10→13
k = −11→13
l = −31→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.140
S = 1.02
6023 reflections
293 parameters
0 restraints
0 constraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.9729P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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	0.32424 (12)	0.59204 (13)	0.50656 (5)	0.0272 (3)	
N1	0.61087 (14)	0.92847 (15)	0.44107 (6)	0.0235 (3)	
H1A	0.538	0.8701	0.438	0.028*	
N2	0.55957 (14)	0.74698 (14)	0.52725 (6)	0.0222 (3)	
N3	0.52299 (14)	0.65225 (15)	0.56847 (6)	0.0231 (3)	
H3A	0.5761	0.6381	0.6027	0.028*	
N4	0.36940 (14)	0.49149 (15)	0.60069 (6)	0.0257 (3)	
H4A	0.434	0.4888	0.6319	0.031*	
C1	0.62604 (18)	1.01918 (19)	0.39554 (8)	0.0276 (4)	
H1	0.5586	1.0192	0.361	0.033*	
C2	0.73808 (19)	1.11222 (19)	0.39826 (8)	0.0287 (4)	
H2	0.7494	1.1762	0.3659	0.034*	
C3	0.83374 (18)	1.11048 (19)	0.44915 (8)	0.0298 (4)	
H3	0.9118	1.1742	0.4522	0.036*	
C4	0.81631 (17)	1.01591 (19)	0.49601 (8)	0.0278 (4)	
H4	0.8822	1.0152	0.5311	0.033*	
C5	0.70294 (16)	0.92278 (17)	0.49155 (7)	0.0220 (3)	
C6	0.67558 (16)	0.81803 (17)	0.53874 (7)	0.0222 (3)	
C7	0.77787 (16)	0.80131 (18)	0.59359 (7)	0.0232 (3)	
C8	0.79217 (19)	0.90835 (19)	0.63769 (8)	0.0283 (4)	
H8	0.7356	0.9924	0.6332	0.034*	
C9	0.8892 (2)	0.8918 (2)	0.68806 (8)	0.0341 (4)	
H9	0.898	0.9643	0.7183	0.041*	
C10	0.97306 (19)	0.7707 (2)	0.69468 (8)	0.0323 (4)	
H10	1.0416	0.7615	0.7286	0.039*	
C11	0.95692 (18)	0.6625 (2)	0.65172 (8)	0.0313 (4)	
H11	1.013	0.5782	0.6567	0.038*	
C12	0.85883 (18)	0.6771 (2)	0.60138 (8)	0.0281 (4)	
H12	0.8471	0.6023	0.5723	0.034*	
C13	0.39750 (17)	0.57767 (17)	0.55469 (7)	0.0228 (3)	
C14	0.24971 (17)	0.40541 (17)	0.60497 (7)	0.0240 (3)	
C15	0.25362 (19)	0.31422 (19)	0.65482 (8)	0.0304 (4)	
H15	0.3352	0.311	0.6831	0.036*	
C16	0.1394 (2)	0.2286 (2)	0.66323 (9)	0.0344 (4)	
H16	0.1436	0.1656	0.6969	0.041*	
C17	0.0190 (2)	0.2338 (2)	0.62299 (9)	0.0353 (4)	
H17	−0.0598	0.1755	0.6292	0.042*	

C18	0.0146 (2)	0.32443 (19)	0.57376 (8)	0.0337 (4)	
H18	−0.068	0.3281	0.5461	0.04*	
C19	0.12930 (18)	0.41061 (18)	0.56400 (8)	0.0277 (4)	
H19	0.1254	0.4721	0.5298	0.033*	
N5	0.35984 (18)	0.7937 (2)	0.26526 (7)	0.0420 (4)	
O3	0.27741 (16)	0.73306 (18)	0.29534 (6)	0.0475 (4)	
O4	0.4492 (2)	0.8758 (3)	0.28338 (8)	0.0799 (7)	
O5A	0.3005 (3)	0.8518 (4)	0.21244 (13)	0.0435 (11)	0.448 (4)
O5B	0.4115 (4)	0.7187 (4)	0.22044 (14)	0.0774 (15)	0.552 (4)
O2	0.36998 (14)	0.78603 (15)	0.41599 (6)	0.0318 (3)	
H1W	0.359 (2)	0.721 (3)	0.4424 (11)	0.048*	
H2W	0.342 (2)	0.755 (3)	0.3815 (12)	0.048*	
O6	0.60636 (15)	0.95394 (19)	0.18834 (6)	0.0431 (4)	
H3W	0.563 (3)	0.907 (3)	0.2169 (12)	0.065*	
H4W	0.656 (3)	1.044 (3)	0.2014 (12)	0.065*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0320 (6)	0.0274 (6)	0.0225 (6)	−0.0074 (5)	0.0041 (5)	0.0012 (5)
N1	0.0258 (7)	0.0223 (7)	0.0234 (7)	−0.0013 (6)	0.0079 (5)	−0.0009 (5)
N2	0.0244 (7)	0.0218 (7)	0.0217 (6)	0.0005 (6)	0.0084 (5)	0.0006 (5)
N3	0.0235 (7)	0.0262 (7)	0.0201 (6)	−0.0013 (6)	0.0047 (5)	0.0039 (5)
N4	0.0228 (7)	0.0290 (7)	0.0259 (7)	−0.0008 (6)	0.0055 (5)	0.0053 (6)
C1	0.0330 (9)	0.0281 (9)	0.0230 (8)	0.0029 (7)	0.0091 (7)	0.0030 (7)
C2	0.0355 (9)	0.0257 (8)	0.0278 (8)	0.0033 (7)	0.0162 (7)	0.0043 (7)
C3	0.0290 (9)	0.0285 (9)	0.0341 (9)	−0.0042 (7)	0.0136 (7)	0.0009 (7)
C4	0.0247 (8)	0.0320 (9)	0.0276 (8)	−0.0027 (7)	0.0075 (7)	0.0005 (7)
C5	0.0235 (8)	0.0231 (8)	0.0209 (7)	0.0018 (6)	0.0086 (6)	−0.0016 (6)
C6	0.0223 (8)	0.0241 (8)	0.0214 (7)	0.0024 (6)	0.0079 (6)	−0.0007 (6)
C7	0.0211 (7)	0.0272 (8)	0.0227 (8)	−0.0025 (7)	0.0084 (6)	0.0020 (6)
C8	0.0330 (9)	0.0245 (8)	0.0279 (8)	−0.0027 (7)	0.0055 (7)	0.0019 (7)
C9	0.0424 (11)	0.0338 (10)	0.0261 (9)	−0.0081 (8)	0.0026 (8)	−0.0011 (7)
C10	0.0272 (9)	0.0462 (11)	0.0239 (8)	−0.0064 (8)	0.0044 (7)	0.0073 (8)
C11	0.0272 (8)	0.0415 (10)	0.0265 (9)	0.0067 (8)	0.0087 (7)	0.0058 (8)
C12	0.0277 (8)	0.0340 (9)	0.0238 (8)	0.0035 (7)	0.0082 (7)	−0.0011 (7)
C13	0.0261 (8)	0.0200 (8)	0.0237 (8)	0.0010 (6)	0.0084 (6)	−0.0015 (6)
C14	0.0283 (8)	0.0191 (7)	0.0267 (8)	0.0006 (6)	0.0134 (7)	−0.0015 (6)
C15	0.0315 (9)	0.0308 (9)	0.0308 (9)	0.0049 (8)	0.0126 (7)	0.0065 (7)
C16	0.0429 (11)	0.0273 (9)	0.0367 (10)	0.0009 (8)	0.0208 (8)	0.0051 (8)
C17	0.0423 (11)	0.0262 (9)	0.0399 (10)	−0.0122 (8)	0.0166 (9)	−0.0042 (8)
C18	0.0398 (10)	0.0280 (9)	0.0336 (10)	−0.0127 (8)	0.0056 (8)	−0.0054 (7)
C19	0.0360 (9)	0.0221 (8)	0.0259 (8)	−0.0072 (7)	0.0073 (7)	−0.0038 (7)
N5	0.0413 (9)	0.0690 (12)	0.0153 (7)	−0.0250 (9)	0.0002 (6)	−0.0117 (7)
O3	0.0451 (8)	0.0632 (10)	0.0341 (7)	−0.0108 (7)	0.0034 (6)	0.0024 (7)
O4	0.0730 (12)	0.1290 (18)	0.0398 (9)	−0.0472 (13)	0.0160 (8)	−0.0220 (11)
O5A	0.0423 (19)	0.060 (2)	0.0261 (16)	−0.0135 (16)	−0.0057 (13)	0.0111 (14)
O5B	0.109 (3)	0.082 (3)	0.0463 (19)	−0.036 (2)	0.0351 (19)	−0.0313 (17)

O2	0.0369 (7)	0.0350 (7)	0.0232 (6)	−0.0070 (6)	0.0023 (5)	0.0055 (5)
O6	0.0371 (8)	0.0598 (10)	0.0333 (8)	−0.0059 (7)	0.0082 (6)	−0.0129 (7)

Geometric parameters (Å, º)

O1—C13	1.224 (2)	C9—H9	0.95
N1—C1	1.339 (2)	C10—C11	1.386 (3)
N1—C5	1.354 (2)	C10—H10	0.95
N1—H1A	0.88	C11—C12	1.390 (2)
N2—C6	1.293 (2)	C11—H11	0.95
N2—N3	1.3451 (18)	C12—H12	0.95
N3—C13	1.391 (2)	C14—C19	1.392 (2)
N3—H3A	0.88	C14—C15	1.395 (2)
N4—C13	1.350 (2)	C15—C16	1.380 (3)
N4—C14	1.408 (2)	C15—H15	0.95
N4—H4A	0.88	C16—C17	1.383 (3)
C1—C2	1.373 (2)	C16—H16	0.95
C1—H1	0.95	C17—C18	1.381 (3)
C2—C3	1.379 (3)	C17—H17	0.95
C2—H2	0.95	C18—C19	1.393 (2)
C3—C4	1.389 (2)	C18—H18	0.95
C3—H3	0.95	C19—H19	0.95
C4—C5	1.383 (2)	N5—O4	1.185 (2)
C4—H4	0.95	N5—O3	1.224 (2)
C5—C6	1.477 (2)	N5—O5B	1.353 (3)
C6—C7	1.490 (2)	N5—O5A	1.363 (3)
C7—C12	1.391 (2)	O2—H1W	0.86 (3)
C7—C8	1.395 (2)	O2—H2W	0.84 (3)
C8—C9	1.386 (2)	O6—H3W	0.91 (3)
C8—H8	0.95	O6—H4W	0.99 (3)
C9—C10	1.382 (3)		

C1—N1—C5	122.74 (15)	C9—C10—C11	119.83 (17)
C1—N1—H1A	118.6	C9—C10—H10	120.1
C5—N1—H1A	118.6	C11—C10—H10	120.1
C6—N2—N3	118.62 (14)	C10—C11—C12	120.15 (17)
N2—N3—C13	117.15 (13)	C10—C11—H11	119.9
N2—N3—H3A	121.4	C12—C11—H11	119.9
C13—N3—H3A	121.4	C11—C12—C7	120.04 (17)
C13—N4—C14	128.13 (14)	C11—C12—H12	120
C13—N4—H4A	115.9	C7—C12—H12	120
C14—N4—H4A	115.9	O1—C13—N4	126.03 (15)
N1—C1—C2	120.68 (16)	O1—C13—N3	122.58 (14)
N1—C1—H1	119.7	N4—C13—N3	111.39 (14)
C2—C1—H1	119.7	C19—C14—C15	119.60 (16)
C1—C2—C3	118.35 (16)	C19—C14—N4	123.86 (15)
C1—C2—H2	120.8	C15—C14—N4	116.51 (15)
C3—C2—H2	120.8	C16—C15—C14	120.28 (17)

C2—C3—C4	120.23 (16)	C16—C15—H15	119.9
C2—C3—H3	119.9	C14—C15—H15	119.9
C4—C3—H3	119.9	C15—C16—C17	120.53 (17)
C5—C4—C3	119.88 (16)	C15—C16—H16	119.7
C5—C4—H4	120.1	C17—C16—H16	119.7
C3—C4—H4	120.1	C18—C17—C16	119.32 (17)
N1—C5—C4	118.10 (15)	C18—C17—H17	120.3
N1—C5—C6	117.94 (14)	C16—C17—H17	120.3
C4—C5—C6	123.96 (15)	C17—C18—C19	121.13 (18)
N2—C6—C5	114.14 (14)	C17—C18—H18	119.4
N2—C6—C7	125.70 (14)	C19—C18—H18	119.4
C5—C6—C7	120.16 (14)	C14—C19—C18	119.15 (16)
C12—C7—C8	119.55 (16)	C14—C19—H19	120.4
C12—C7—C6	119.81 (15)	C18—C19—H19	120.4
C8—C7—C6	120.64 (15)	O4—N5—O3	126.39 (16)
C9—C8—C7	119.86 (17)	O4—N5—O5B	106.1 (2)
C9—C8—H8	120.1	O3—N5—O5B	118.2 (2)
C7—C8—H8	120.1	O4—N5—O5A	104.9 (2)
C10—C9—C8	120.50 (17)	O3—N5—O5A	114.96 (19)
C10—C9—H9	119.7	H1W—O2—H2W	109 (2)
C8—C9—H9	119.7	H3W—O6—H4W	116 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2	0.88	1.81	2.6639 (19)	164
N3—H3*A*···O6^{i}	0.88	2.08	2.8794 (19)	150
N4—H4*A*···O6^{i}	0.88	2.03	2.875 (2)	159
O2—H1*W*···O1	0.86 (3)	1.92 (3)	2.7756 (17)	174 (2)
O2—H2*W*···O3	0.84 (3)	1.96 (3)	2.783 (2)	165 (2)
O6—H3*W*···O4	0.91 (3)	1.95 (3)	2.816 (2)	159 (2)
O6—H3*W*···O5*A*	0.91 (3)	2.55 (3)	3.172 (3)	126 (2)
O6—H3*W*···O5*B*	0.91 (3)	2.28 (3)	3.008 (4)	137 (2)
O6—H4*W*···O3^{ii}	0.99 (3)	1.87 (3)	2.833 (2)	163 (2)
O6—H4*W*···O5*B*^{ii}	0.99 (3)	2.51 (3)	3.210 (4)	127.0 (19)

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

2-[Phenyl({[(phenylcarbamoyl)amino]imino})methyl]pyridinium thiocyanate 2.5-hydrate (IV)

Crystal data

$C_{19}H_{17}N_4O^+·NCS^-·2.5H_2O$
M_r = 420.48
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 13.0053 (4) Å
b = 7.7965 (2) Å
c = 20.8703 (7) Å
β = 107.887 (1)°
V = 2013.87 (11) Å^3
Z = 4
F(000) = 884
D_x = 1.387 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9596 reflections
θ = 2.8–30.4°
μ = 0.20 mm^{-1}

T = 100 K
Block, colourless

0.24 × 0.10 × 0.05 mm

Data collection

Bruker D8 Venture Photon 100 diffractometer
Radiation source: microfocus X ray tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.707, T_{max} = 0.746
31447 measured reflections

6146 independent reflections
4590 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 30.6°, θ_{min} = 2.8°
h = −18→18
k = −9→11
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.131
S = 1.02
6146 reflections
326 parameters
6 restraints
0 constraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 1.2977P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.4 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 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	0.47184 (8)	0.41475 (14)	0.59764 (5)	0.0210 (2)	
N1	0.61991 (9)	0.14483 (15)	0.45619 (6)	0.0149 (2)	
H1A	0.6215	0.203	0.4926	0.018*	
N2	0.44095 (9)	0.23927 (15)	0.48298 (6)	0.0152 (2)	
N3	0.35678 (9)	0.30584 (16)	0.49958 (6)	0.0177 (2)	
H3A	0.29	0.2947	0.4729	0.021*	
N4	0.28807 (9)	0.44702 (15)	0.57257 (6)	0.0174 (2)	
H4A	0.2267	0.42	0.5421	0.021*	
C1	0.71372 (11)	0.09103 (18)	0.44878 (7)	0.0180 (3)	
H1	0.7798	0.1174	0.4824	0.022*	
C2	0.71496 (11)	−0.00216 (19)	0.39290 (7)	0.0197 (3)	
H2	0.7811	−0.0414	0.3877	0.024*	
C3	0.61693 (12)	−0.03710 (19)	0.34444 (8)	0.0209 (3)	
H3	0.6155	−0.1005	0.3053	0.025*	
C4	0.52099 (11)	0.02051 (18)	0.35314 (7)	0.0182 (3)	
H4	0.454	−0.0039	0.32	0.022*	
C5	0.52304 (10)	0.11323 (17)	0.40989 (7)	0.0141 (3)	
C6	0.42486 (10)	0.17971 (17)	0.42306 (7)	0.0143 (2)	
C7	0.32143 (10)	0.17993 (17)	0.36716 (7)	0.0149 (3)	

C8	0.31493 (11)	0.27020 (19)	0.30834 (7)	0.0197 (3)	
H8	0.376	0.3318	0.3048	0.024*	
C9	0.21989 (12)	0.2705 (2)	0.25502 (8)	0.0219 (3)	
H9	0.2161	0.3321	0.2151	0.026*	
C10	0.13050 (12)	0.18130 (19)	0.25987 (8)	0.0209 (3)	
H10	0.0656	0.1813	0.2232	0.025*	
C11	0.13570 (11)	0.09185 (19)	0.31826 (8)	0.0209 (3)	
H11	0.0741	0.0316	0.3216	0.025*	
C12	0.23077 (11)	0.09030 (18)	0.37174 (7)	0.0179 (3)	
H12	0.2343	0.0282	0.4115	0.022*	
C13	0.37967 (11)	0.39275 (17)	0.56052 (7)	0.0162 (3)	
C14	0.28004 (11)	0.54163 (17)	0.62831 (7)	0.0163 (3)	
C15	0.17552 (12)	0.5914 (2)	0.62653 (8)	0.0218 (3)	
H15	0.1152	0.5589	0.5896	0.026*	
C16	0.16016 (13)	0.6876 (2)	0.67847 (8)	0.0252 (3)	
H16	0.0892	0.7209	0.677	0.03*	
C17	0.24754 (13)	0.7358 (2)	0.73280 (8)	0.0243 (3)	
H17	0.2369	0.8039	0.768	0.029*	
C18	0.35041 (13)	0.68370 (19)	0.73511 (8)	0.0231 (3)	
H18	0.4103	0.7143	0.7727	0.028*	
C19	0.36737 (11)	0.58715 (18)	0.68315 (7)	0.0188 (3)	
H19	0.4384	0.5526	0.6852	0.023*	
S1A	0.89347 (17)	0.4590 (5)	0.6458 (2)	0.0352 (6)	0.571 (10)
C20A	0.9293 (4)	0.3324 (9)	0.5930 (3)	0.0380 (13)	0.571 (10)
N5A	0.9541 (3)	0.2489 (9)	0.5538 (3)	0.0572 (18)	0.571 (10)
O3A	0.1094 (3)	0.2788 (8)	0.4800 (2)	0.0432 (12)	0.571 (10)
H3WA	0.068 (3)	0.319 (6)	0.4430 (14)	0.065*	0.571 (10)
H4WA	0.077 (3)	0.204 (5)	0.496 (2)	0.065*	0.571 (10)
S1B	0.9023 (2)	0.4113 (5)	0.6645 (2)	0.0313 (5)	0.429 (10)
C20B	0.9362 (5)	0.2778 (9)	0.6152 (4)	0.0328 (13)	0.429 (10)
N5B	0.9595 (5)	0.1776 (7)	0.5811 (3)	0.0436 (13)	0.429 (10)
O3B	0.1309 (4)	0.3389 (7)	0.4610 (3)	0.0346 (11)	0.429 (10)
H3WB	0.110 (4)	0.407 (5)	0.4269 (17)	0.052*	0.429 (10)
H4WB	0.098 (5)	0.243 (4)	0.453 (3)	0.052*	0.429 (10)
O2	0.65756 (10)	0.29775 (19)	0.57474 (6)	0.0339 (3)	
H1W	0.604 (2)	0.340 (3)	0.5815 (12)	0.051*	
H2W	0.714 (2)	0.346 (3)	0.5973 (13)	0.051*	
O4	−0.0067 (3)	0.0865 (5)	0.46176 (17)	0.0568 (8)	0.5
H5W	−0.0156	0.0898	0.5085	0.085*	0.5
H6W	0.0065	−0.036	0.4523	0.085*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0158 (5)	0.0269 (5)	0.0219 (5)	0.0016 (4)	0.0084 (4)	−0.0045 (4)
N1	0.0160 (5)	0.0168 (5)	0.0135 (5)	0.0018 (4)	0.0068 (4)	0.0022 (4)
N2	0.0157 (5)	0.0156 (5)	0.0172 (6)	0.0024 (4)	0.0092 (4)	0.0026 (4)
N3	0.0139 (5)	0.0215 (6)	0.0195 (6)	0.0027 (4)	0.0080 (4)	−0.0014 (5)

N4	0.0146 (5)	0.0208 (6)	0.0185 (6)	0.0025 (4)	0.0078 (4)	−0.0007 (5)
C1	0.0149 (6)	0.0207 (7)	0.0195 (7)	0.0034 (5)	0.0071 (5)	0.0073 (5)
C2	0.0191 (6)	0.0208 (7)	0.0229 (7)	0.0054 (5)	0.0122 (6)	0.0063 (6)
C3	0.0252 (7)	0.0202 (7)	0.0219 (7)	0.0026 (5)	0.0139 (6)	−0.0008 (6)
C4	0.0185 (6)	0.0187 (6)	0.0189 (7)	0.0002 (5)	0.0080 (5)	−0.0005 (5)
C5	0.0150 (6)	0.0131 (6)	0.0158 (6)	0.0012 (5)	0.0069 (5)	0.0036 (5)
C6	0.0138 (6)	0.0140 (6)	0.0167 (6)	0.0006 (5)	0.0068 (5)	0.0031 (5)
C7	0.0145 (6)	0.0148 (6)	0.0163 (6)	0.0014 (5)	0.0063 (5)	−0.0002 (5)
C8	0.0163 (6)	0.0220 (7)	0.0219 (7)	0.0007 (5)	0.0073 (5)	0.0053 (6)
C9	0.0220 (7)	0.0238 (7)	0.0192 (7)	0.0037 (6)	0.0052 (6)	0.0065 (6)
C10	0.0186 (6)	0.0199 (7)	0.0211 (7)	0.0024 (5)	0.0017 (5)	−0.0004 (5)
C11	0.0178 (6)	0.0194 (7)	0.0260 (8)	−0.0030 (5)	0.0076 (6)	−0.0019 (6)
C12	0.0193 (6)	0.0177 (6)	0.0183 (7)	−0.0006 (5)	0.0080 (5)	0.0012 (5)
C13	0.0185 (6)	0.0153 (6)	0.0179 (7)	0.0018 (5)	0.0102 (5)	0.0020 (5)
C14	0.0201 (6)	0.0144 (6)	0.0184 (7)	0.0022 (5)	0.0119 (5)	0.0032 (5)
C15	0.0185 (6)	0.0259 (7)	0.0243 (8)	0.0026 (6)	0.0114 (6)	0.0020 (6)
C16	0.0242 (7)	0.0273 (8)	0.0314 (8)	0.0043 (6)	0.0195 (6)	0.0019 (6)
C17	0.0327 (8)	0.0204 (7)	0.0279 (8)	−0.0004 (6)	0.0214 (7)	−0.0014 (6)
C18	0.0274 (7)	0.0204 (7)	0.0249 (8)	−0.0022 (6)	0.0132 (6)	−0.0019 (6)
C19	0.0202 (6)	0.0166 (6)	0.0228 (7)	0.0014 (5)	0.0111 (6)	0.0015 (5)
S1A	0.0246 (5)	0.0454 (12)	0.0383 (11)	−0.0050 (6)	0.0136 (6)	−0.0152 (8)
C20A	0.0224 (16)	0.054 (3)	0.039 (3)	−0.0089 (19)	0.0109 (18)	−0.016 (2)
N5A	0.0403 (19)	0.076 (4)	0.058 (3)	−0.007 (2)	0.0193 (19)	−0.033 (3)
O3A	0.0255 (14)	0.064 (3)	0.033 (2)	0.0072 (15)	−0.0012 (12)	−0.0149 (17)
S1B	0.0217 (6)	0.0371 (11)	0.0338 (11)	−0.0032 (6)	0.0068 (7)	−0.0009 (8)
C20B	0.036 (3)	0.032 (3)	0.031 (3)	−0.009 (2)	0.012 (2)	0.006 (2)
N5B	0.063 (3)	0.036 (3)	0.038 (3)	−0.004 (2)	0.025 (2)	0.009 (2)
O3B	0.0267 (19)	0.044 (3)	0.031 (2)	0.0023 (16)	0.0051 (15)	−0.0012 (17)
O2	0.0160 (5)	0.0557 (8)	0.0280 (6)	0.0060 (5)	0.0041 (5)	−0.0176 (6)
O4	0.066 (2)	0.055 (2)	0.055 (2)	−0.0040 (17)	0.0280 (17)	−0.0048 (16)

Geometric parameters (Å, º)

O1—C13	1.2232 (17)	C10—H10	0.95
N1—C1	1.3431 (17)	C11—C12	1.388 (2)
N1—C5	1.3542 (17)	C11—H11	0.95
N1—H1A	0.88	C12—H12	0.95
N2—C6	1.2895 (18)	C14—C19	1.388 (2)
N2—N3	1.3492 (15)	C14—C15	1.4030 (19)
N3—C13	1.3902 (18)	C15—C16	1.382 (2)
N3—H3A	0.88	C15—H15	0.95
N4—C13	1.3585 (17)	C16—C17	1.388 (2)
N4—C14	1.4081 (18)	C16—H16	0.95
N4—H4A	0.88	C17—C18	1.385 (2)
C1—C2	1.378 (2)	C17—H17	0.95
C1—H1	0.95	C18—C19	1.392 (2)
C2—C3	1.389 (2)	C18—H18	0.95
C2—H2	0.95	C19—H19	0.95

C3—C4	1.3894 (19)	S1A—C20A	1.650 (5)
C3—H3	0.95	C20A—N5A	1.166 (6)
C4—C5	1.3809 (19)	O3A—H3WA	0.855 (10)
C4—H4	0.95	O3A—H4WA	0.850 (10)
C5—C6	1.4798 (18)	S1B—C20B	1.616 (8)
C6—C7	1.4855 (18)	C20B—N5B	1.159 (8)
C7—C8	1.3950 (19)	O3B—H3WB	0.863 (10)
C7—C12	1.3988 (19)	O3B—H4WB	0.856 (10)
C8—C9	1.386 (2)	O2—H1W	0.82 (3)
C8—H8	0.95	O2—H2W	0.83 (3)
C9—C10	1.385 (2)	O4—H5W	1.016
C9—H9	0.95	O4—H6W	1.0012
C10—C11	1.388 (2)		

C1—N1—C5	122.68 (12)	C9—C10—C11	120.07 (13)
C1—N1—H1A	118.7	C9—C10—H10	120
C5—N1—H1A	118.7	C11—C10—H10	120
C6—N2—N3	119.00 (12)	C10—C11—C12	120.10 (13)
N2—N3—C13	117.37 (11)	C10—C11—H11	119.9
N2—N3—H3A	121.3	C12—C11—H11	119.9
C13—N3—H3A	121.3	C11—C12—C7	120.14 (13)
C13—N4—C14	127.43 (12)	C11—C12—H12	119.9
C13—N4—H4A	116.3	C7—C12—H12	119.9
C14—N4—H4A	116.3	O1—C13—N4	125.70 (13)
N1—C1—C2	120.60 (13)	O1—C13—N3	122.73 (12)
N1—C1—H1	119.7	N4—C13—N3	111.57 (12)
C2—C1—H1	119.7	C19—C14—C15	119.45 (13)
C1—C2—C3	118.20 (13)	C19—C14—N4	124.44 (12)
C1—C2—H2	120.9	C15—C14—N4	116.10 (13)
C3—C2—H2	120.9	C16—C15—C14	120.10 (14)
C2—C3—C4	120.11 (13)	C16—C15—H15	119.9
C2—C3—H3	119.9	C14—C15—H15	119.9
C4—C3—H3	119.9	C15—C16—C17	120.55 (14)
C5—C4—C3	119.98 (13)	C15—C16—H16	119.7
C5—C4—H4	120	C17—C16—H16	119.7
C3—C4—H4	120	C18—C17—C16	119.26 (14)
N1—C5—C4	118.41 (12)	C18—C17—H17	120.4
N1—C5—C6	118.07 (12)	C16—C17—H17	120.4
C4—C5—C6	123.52 (12)	C17—C18—C19	120.93 (15)
N2—C6—C5	114.46 (12)	C17—C18—H18	119.5
N2—C6—C7	126.82 (12)	C19—C18—H18	119.5
C5—C6—C7	118.65 (12)	C14—C19—C18	119.68 (13)
C8—C7—C12	119.19 (13)	C14—C19—H19	120.2
C8—C7—C6	119.16 (12)	C18—C19—H19	120.2
C12—C7—C6	121.65 (12)	N5A—C20A—S1A	177.1 (5)
C9—C8—C7	120.36 (13)	H3WA—O3A—H4WA	111 (3)
C9—C8—H8	119.8	N5B—C20B—S1B	177.7 (5)
C7—C8—H8	119.8	H3WB—O3B—H4WB	111 (3)

C10—C9—C8	120.14 (14)	H1W—O2—H2W	112 (2)
C10—C9—H9	119.9	H5W—O4—H6W	106.9
C8—C9—H9	119.9		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2	0.88	1.79	2.6531 (17)	166
N3—H3*A*···O3*A*	0.88	2.4	3.123 (5)	139
N3—H3*A*···O3*B*	0.88	2.04	2.809 (5)	146
N4—H4*A*···O3*A*	0.88	2	2.845 (4)	160
N4—H4*A*···O3*B*	0.88	1.88	2.718 (4)	160
O2—H1*W*···O1	0.82 (3)	1.94 (3)	2.7575 (15)	174 (2)
O2—H2*W*···S1*A*	0.83 (3)	2.40 (3)	3.225 (2)	168 (2)
O2—H2*W*···S1*B*	0.83 (3)	2.47 (3)	3.280 (3)	164 (2)
O3*A*—H3*WA*···S1*A*^{i}	0.86 (1)	2.69 (3)	3.319 (5)	131 (4)
O3*B*—H3*WB*···S1*B*^{i}	0.86 (1)	2.34 (2)	3.185 (5)	166 (5)

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